



University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
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Engineering Chemistry-1 (BS109)

Atomic Structure

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PaperCode: BS109	Paper: Engineering Chemistry - I	L	T/P	C								
PaperID: 99109		3	-	3								
Marking Scheme:												
1. Teachers Continuous Evaluation: 25 marks												
2. Term end Theory Examinations: /5 marks												
Instruction for paper setter:												
1. There should be 9 questions in the term-end examinations question paper.												
2. The first unit will be compulsory and cover the entire syllabus. This question will have Five sub-parts, and the students will be required to answer any THREE parts of 5 marks each. This unit will have a total weightage of 15 marks.												
3. Apart from unit 1 which is compulsory, the rest of the paper shall consist of 4 units as per the syllabus. Every unit shall have two questions covering the corresponding unit of the syllabus. However, the student shall be asked to attempt only one of the two questions in the unit. Individual questions may contain up to 5 sub-parts / sub-questions. Each Unit shall have a marks weightage of 15.												
4. The questions are to be framed keeping in view the learning outcomes of the course/paper. The standard / level of the questions to be asked should be at the level of the prescribed textbook.												
5. The requirement of (scientific) calculators / log-tables / data - tables may be specified if required.												
Course Objectives:												
1:	To impart knowledge about understanding and modeling atomic structure and chemical bonding.											
2:	To impart knowledge about understanding and modeling Thermochemistry and Reaction Kinetics.											
3:	To impart knowledge about understanding and modeling organic compound structure and reactions.											
4:	To impart knowledge about understanding and modeling Stereochemistry.											
Course Outcomes (CO):												
CO1:	Ability to understand and model atomic structure and chemical bonding.											
CO2:	Ability to understand and model Thermochemistry and Reaction Kinetics.											
CO3:	Ability to understand and model organic compound structure and reactions.											
CO4:	Ability to understand and model Stereochemistry.											
Course Outcomes (CO to Programme Outcomes (PO) Mapping (scale 1: low, 2: Medium, 3: High)												
CO/P O	PO1	PO2	PO3	PO4	PO5	PO6	PO7	PO8	PO9	PO10	PO11	PO12
CO1	2	2	3	3	2	-	-	-	1	1	-	1
CO2	2	2	3	3	2	-	-	-	1	1	-	1
CO3	2	2	3	3	2	-	-	-	1	1	-	1
CO4	2	2	3	3	2	-	-	-	1	1	-	1



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Unit I

Atomic Structure: Introduction to wave mechanics, the Schrödinger equation as applied to hydrogen atom, origin of quantum numbers, Long form of periodic table on the basis of Electronic configuration s, p, d, f block elements periodic trends, Ionization potential, atomic and ionic radii electron affinity & electro-negativity. Chemical Bonding: Ionic bond, energy changes, lattice energy Born Haber Cycle, Covalent bond-energy changes, Potential energy curve for H₂ molecule, characteristics of covalent compound, co-ordinate bond-Werner's Theory, effective atomic numbers, A hybridization and resonance, Valence Shell Electron Repulsion theory (VSEPR), Discussion of structures of H₂O, NH₃, BrF₃, SiF₄, Molecular orbital theory, Linear combination of atomic orbitals (LCAO) method. Structure of simple homo nuclear diatomic molecule like H₂, N₂, O₂, F₂.

[12Hrs]

Unit II

Thermochemistry: Hess's Law, heat of reaction, effect of temperature on heat of reaction at constant pressure (Kirchhoff's Equation) heat of dilution, heat of hydration, heat of neutralization and heat of combustion, Flame temperature. Reaction Kinetics: Significance of rate law and rate equations, order and molecularity, Determinations of order of simple reactions-experimental method, Equilibrium constant and reaction rates -Lindemann, collision and activated complex theories, complex reactions of 1st order characteristics of consecutive, reversible and parallel reactions-Steady state and non-steady state approach.

[10 Hrs]

Unit III

Basic concepts of Organics: Inductive, electromeric, mesomeric and hyperconjugative effects. Stability of reaction intermediates. Electrophiles and nucleophiles, concepts of acids and bases. Arrhenius, Lowry-Bronsted and Lewis theory of acids and bases (HSAB), Carbon acids (active methylene groups), super acids. Bonds weaker than covalent bond: Hydrogen bonding - nature, types, stability and effects. IUPAC Nomenclature.[8Hrs]

Unit IV

Stereochemistry: Classification of stereoisomers, diastereomers, Separation of enantiomers. Absolute configuration (R and S), Projection formulae. Stereochemistry of compounds containing two asymmetric C-atoms. Elements of symmetry - center, plane and axis of symmetry, Conformations: Conformations around a C-C bond in acyclic and cyclic compounds.

[10Hrs]

Textbooks / References:

1. Engineering Chemistry (16th Edition) Jain, Jain, Dhanpat Rai Publishing Company, 2013.
2. Textbook of Engineering Chemistry by Jaya Shree Anireddy, Wiley, 2017
3. Engineering Chemistry by E.R. Nagarajan and S. Ramalingam, Wiley, 2017.



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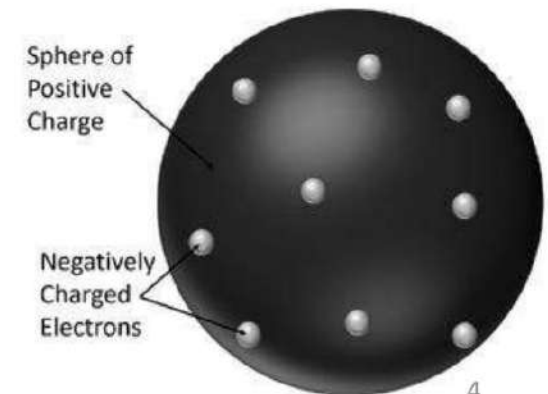


Atom:

- John Dalton said matter to be composed of indivisible particles called atoms.
- According to modern research, atoms are the smallest indivisible particles which cannot be further subdivided into smaller particles.
- However, it has been broken into smaller fragments like electrons, protons and neutrons. And in present “Quarks” represent the smallest known subatomic particles.
- Dalton was not able to explain the formation of chemical bond.
- Then, various model were discussed

Thomson Atomic Model or Plum Pudding Model:

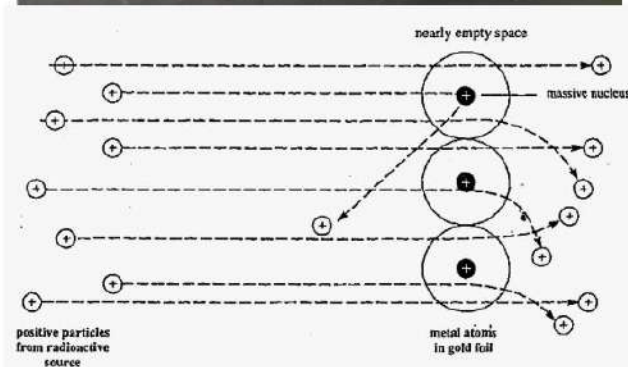
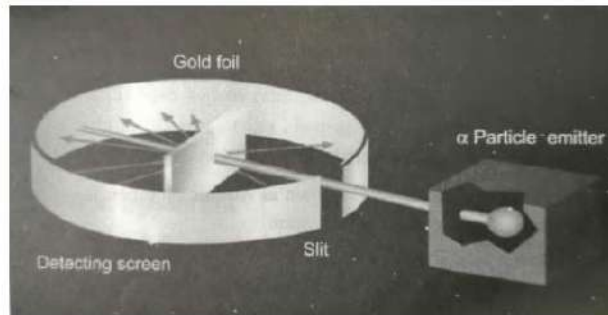
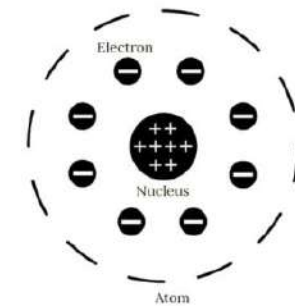
- In 1906, Thomson proposed atom is composed of the negative charge which is surrounded by a cloud of the positive charge so as to balance the negative charges.
- It appear as if the negatively charge of plums are surrounded by the positively charged pudding.
- Drawback: did not have any experimental evidence in its support.





Rutherford Atomic Model:

- In 1909, Rutherford gave the first successful model of the arrangement of electrons, protons and neutrons based on alpha-ray scattering experiment.
- The model described the atom as a tiny, dense, positively charged core called a *nucleus*, in which nearly all the mass is concentrated around which light, negatively charged constituents, called *electrons*, circulate at some distance.



Rutherford Experiment:

- a thin gold foil was placed in the path of the beam.
- Expectation as per Thomson model was that alpha particles would go undeflected.
- But found that
 - some particles are deflected by small angles,
 - some deflected at fairly large angles,
 - few particles are rebounded back along their path at 180°.



Conclusion of Rutherford experiment:

- The α -particle which is deflected largely is meeting a center of very high mass within the atom.
- The center of high mass is also positively charged, is very small, and extremely dense region which is called atomic nucleus.
- Most of the α -radiations pass through the metal foil unreflected in straight lines. This shows that there is a lot of empty space around the nucleus.
- This is extra nuclear part, where electrons revolve in high speed in fixed part called orbit.

From Rutherford's experiment it becomes clear

- ✓ that the entire mass of an atom is concentrated in a small region. Hence all the protons and neutrons which account for the mass of an atom, must be present in this region.
- ✓ Consequently this region is positively charged. This portion of the atom is known as the nucleus.
- ✓ The number of protons in the nucleus tells the number of positive charges on the nucleus. This number is called Atomic number of the element.
- ✓ the total number of protons (P) and neutrons (N) present in the nucleus is called the mass number of the element. The mass number thus, can be calculated as $= N + P$.
- ✓ atom as a whole is electrically neutral, so obviously, it is necessary that the number of electrons present in an atom must be equal to the number of protons present in its nucleus.

Drawbacks of the Rutherford model: as electron is revolving around the nucleus with a high speed, therefore must loses energy and its speed is decreased and electron should fall into the nucleus, thus making atom unstable. But this is not the case, and Rutherford model *could not explain the stability of an atom.*



Bohr Model of an Atom

- To overcome the drawbacks of the Rutherford's model and production of spectrum of H and hydrogen like species (eg. He^+ , Li^{2+}) in 1913 utilized the concept of quantization and proposed a new model of an atom.
- Postulates of the model are
 - An electron revolves around the nucleus in a certain fixed energy level, it does not radiate any energy.
 - An electron does not emit energy continuously but it does so only when it jumps from a higher energy level to a lower energy level. This energy loss is in terms of discrete units of energy called quantum. So these energy levels were also named as the **principal quantum numbers** later on.
 - The electron can only move in those circular orbits where the angular momentum (mvr) is a whole number multiple of $h/2\pi$ or it is quantized. This is called the Principle of Quantization of Angular Momentum.

$$mvr = \frac{nh}{2\pi}$$

Where, m is mass of electron; v is velocity of electron; r is radius of the orbit in which electron is moving; n is principle quantum number and h is Planck's constant.



- Based on these principles, *explained the emission spectrum of hydrogen* (Lyman series, Balmer series, Paschen series, Brackett series and Pfund series).

Limitations of Bohr's Postulates

- Explain the spectra of species having only one electron
- No explanation for Zeeman and Stark effect : effect of electric and magnetic fields on the spectral atoms.
(When a magnetic field is applied on an atom, its usually observed spectral lines split. This effect is known as Zeeman's effect)
(Spectral lines also get split in the presence of electric field. This effect is known as Stark effect.)
- Bohr's theory predicts the origin of only one spectral line from an electron between any two given energy states. But under spectroscopy of strong resolution, a single line was found to split in a number of very close related lines. Therefore, Bohr could not explain this multiple or fine structure of spectral lines. These multiple lines indicated the energy level of similar energy for each Principal quantum number, n . **Due to this concept of quantum numbers came into existence.**



Dual Nature of Electron-Particles and Wave

To overcome the inadequacies of Bohr's model, the modern structure of atom was developed in the light of observation by de-Broglie and Heisenberg Uncertainty Principle.

In 1924, the French physicist, Louis de Broglie suggested that if light has electron, behaves both as a material particle and as a wave.

This presented a new wave mechanical theory of matter. According to this theory, small particles like electrons when in motion possess wave properties.

According to de-Broglie, the wavelength associated with a particle of mass m , moving with velocity v is given by the relation

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

where h = Planck's constant.

Derivation of de-Broglie's equation

Energy of photon $E = hv = \frac{hc}{\lambda}$ (Planck's equation)

According to Einstein equation, $E = mc^2$

So, from both equations, $\frac{hc}{\lambda} = mc^2$ so, $\frac{h}{\lambda} = mc$ Therefore, $\lambda = \frac{h}{mc}$



According to wave mechanical model of the atom, an electron behaves as a standing wave which goes around the nucleus in a circular orbit. The only condition need to be followed is that the length of the orbit should be a whole number multiple of the wavelength of electron

If r is the radius of the orbit,

$$2\pi r = n\lambda$$

Now,

$$\lambda = h/mv$$

$$2\pi r = nh/mv$$

$$mvr = nh/2\pi$$

Where, $n = 1, 2, 3, \text{ etc.}$

Since, ' mvr ' is the angular momentum of electron. (This seen in Bohr's postulate)

Wave nature of electron experimentally verified by Davisson and Germer

Davisson and Germer designed and built a vacuum apparatus for the purpose of measuring the energy of electrons scattered from a metal surface. Electrons from a heated filament were accelerated by a voltage, and allowed to strike the surface of nickel metal.

The electrons were scattered and were obtained on the photographic plate on which electron produced the diffraction rings suggesting that electrons have the wave character.

Significance of the de-Broglie equation:



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Significance of the de-Broglie equation

- The wave character is only significant in case of small particles like atoms, electrons, protons etc., having small masses. The wave nature is of no significance in case of large microscopic objects.

$$\lambda \propto 1/m$$

Heisenberg Uncertainty Principle

- In 1926, Wernel Heisenberg, suggested that *simultaneous measurement of the position and momentum of sub-atomic particle like electron with complete accuracy is not possible.*
- In other words, the product of uncertainty in momentum (Δp) and that in position (Δx) almost remains constant.

Mathematically, principle can be expressed as

$$\Delta x \cdot \Delta p \geq h/4\pi$$

Also, can be written as

$$\Delta x \cdot m \Delta v \geq h/4\pi$$

This limitation is not due to lacking in experimental techniques but due to nature of sub-atomic particle itself.

- ❑ On the bases of this principle, Bohr's model of atoms no longer stand. The best way is to predict the probability of finding an electron with probable velocity with definite energy in a given region of space in given time. Thus, the uncertainty principle which gave the wave nature of the electron only provides probability of finding an electron in a given space. Thus, atomic model has been replaced by probability approach.



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Postulates of the wave mechanical model

- Electron wave is compared to a stationary or standing wave.
- Energy values of an electron are quantized.
- The wave length of electron is associated with a wave given by de-Broglie relation.
- The term probability distribution or mathematical wave function is used to describe the motion of an electron.



Quantum Numbers

- In general “address of the electron is given by the quantum number”
- **The set of four integers required to define the state of electron in an atom are called quantum numbers.** OR “A group of numerical values which provide solutions that are acceptable by the Schrodinger wave equation for hydrogen atoms.”
- The set of quantum numbers are:
 1. Principal Quantum number (n): proposed by *Bohr*, determines the main energy level, the average distance of electron from the nucleus, the magnitude of energy of the electron, and describes the size of orbital. $n = 1, 2, 3, \dots$

The maximum number of electrons in any principal shell is given by $2n^2$.

2. Azimuthal Quantum number (l): proposed by Sommerfeld, also known as orbital or angular momentum number. It describes the shape of the orbital.

Orbitals have shapes that are best described as **spherical** ($l=0$), **dumb-bell** ($l=1$), or double dumb-bell ($l=2$). More complex shapes at higher angular momentum quantum number.



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The l value depends upon value of n , the value of the azimuthal quantum number ranges between 0 and $(n-1)$.

Eg. $n = 3$, so l can be either 0,1 or 2.

The maximum number of orbitals in a sub-shell is given by $(2l+1)$ and the number of orbitals in n^{th} shell = n^2 .

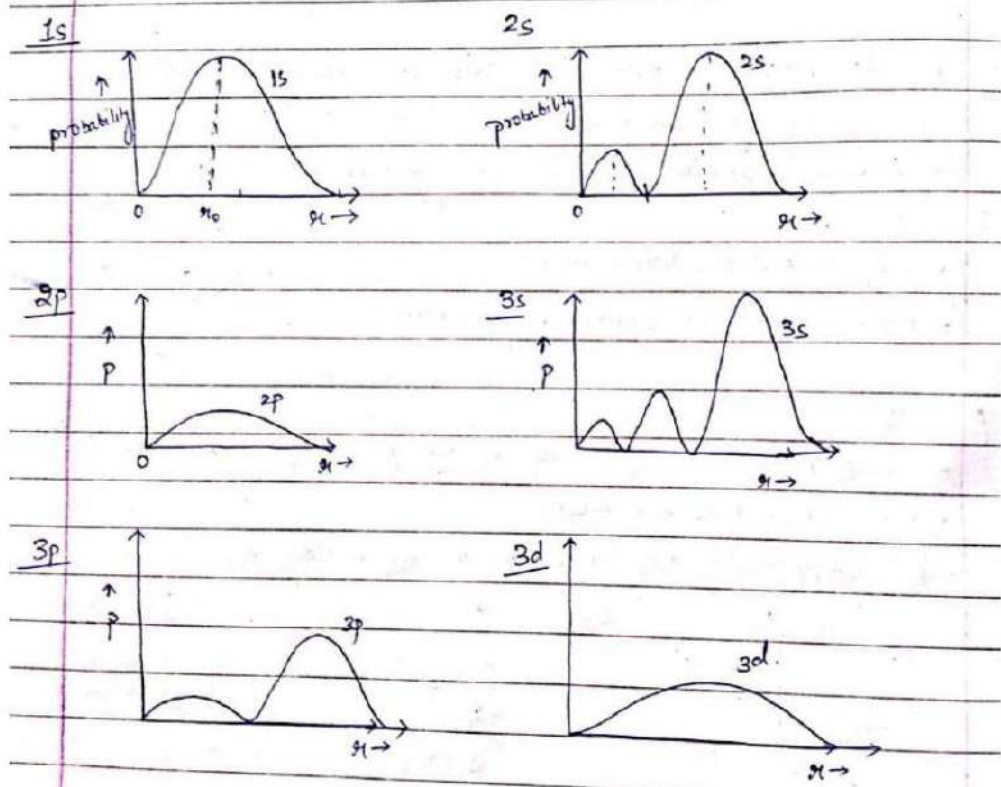
3. Magnetic Quantum number (m): proposed by Lande, describes the orientation of these orbitals.

For a given value of l , there can be $2l+1$ values for m . eg. For $l = 0$, $m=0$; $l=1$, $m= +1,0,-1$.

4. Spin Quantum number (s): proposed by Uhlenbeck and Goudsmith. This gives an idea about the electron spinning on its axis. Each spinning electron can have two values of spin quantum number i.e. $+1/2$ (clockwise spin) and $-1/2$ (anticlockwise spin).



- Radial probability distribution → probable distance to find electron from nucleus.
- at nucleus, probability is zero.
- larger value of principal quantum number, further is electron.





1. Calculate and compare the energies of two radiations, having wavelength of 400\AA and other with 800\AA .

Ans $\rightarrow E = h\nu = \frac{hc}{\lambda}$

$$E_{400} = \frac{6.62 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ m/s}}{400 \times 10^{-10} \text{ m}} = 4.965 \times 10^{-18} \text{ J}$$

$$E_{800} = \frac{6.62 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ m/s}}{800 \times 10^{-10} \text{ m}} = 2.482 \times 10^{-18} \text{ J}$$

$$\text{Hence, } \frac{E_{400}}{E_{800}} = \frac{4.965 \times 10^{-18} \text{ J}}{2.482 \times 10^{-18} \text{ J}} = 2$$

$$\text{Therefore, } E_{400} = 2 E_{800}.$$



2. Calculate the wavelength of 1000 kg rocket moving with a velocity of 300 km/h.

Ans → Mass of rocket = 1000 kg
Velocity = 300 km/h = $\frac{300 \times 1000}{60 \times 60} = 83.33 \text{ m/s}$.

From, de-Broglie equation

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34} \text{ Js}}{1000 \text{ kg} \times 83.33 \text{ m/s}} \quad (\text{J} = \text{kg m}^2/\text{s}^2)$$
$$= 7.95 \times 10^{-39} \text{ m}$$

3. A dust particle having mass equal to 10^{-11} kg and velocity $10^{-4} \text{ cm sec}^{-1}$. The error in the measurement of velocity is 0.1%. Calculate the uncertainty in its position.

Ans → velocity, $v = 10^{-4} \text{ cm/sec}$
 $\Delta v = 0.1\% \times 10^{-4} = 1 \times 10^{-7} \text{ cm/sec}$

$$\Delta x \cdot m \Delta v = \frac{h}{4\pi}$$

$$\Delta v \Delta x = \frac{h}{4\pi m}$$

$$\Delta x = \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times 10^{-11} \times 10^{-7}} = 0.527 \times 10^9 \text{ cm}$$



4. Consider a ball of mass $1g$ moving with a speed $1cm/s$ in one dimensional box of edge length equal to $10cm$.

(i) calculate its kinetic energy and number n corresponding to this kinetic energy.

(ii) if ball is promoted to next higher quantum level, then how much energy is required?

Ans. (i) K.E of ball $\Rightarrow E_n = \frac{1}{2}mv^2 = \frac{1}{2} \times (10^{-3}kg)(10^{-2}m/s)^2$
 $= 0.5 \times 10^{-7}J$

Since, $E_n = \frac{n^2 h^2}{8ml^2}$,

$\therefore n^2 = \frac{E_n \times 8ml^2}{h^2} = \frac{(0.5 \times 10^{-7}J)(8 \times 10^{-3}kg)(10^{-1}m)^2}{(6.626 \times 10^{-34}Js)^2}$
 $= 9.11 \times 10^{54}$

or $n \approx 3.02 \times 10^{27}$

(ii) Now, $\Delta E = E_{n+1} - E_n = (2n+1) \left(\frac{h^2}{8ml^2} \right)$

$= (2 \times 3.02 \times 10^{27} + 1) \left(\frac{(6.626 \times 10^{-34}Js)^2}{8 \times (10^{-3}kg)(10^{-1}m)^2} \right)$

$= 3.32 \times 10^{-35}J$



5. An electron is confined to a molecule of length of 1nm. (i) what is its minimum energy? (ii) what is the minimum excitation energy from this state.

Ans- (i) $E_1 = \frac{h^2}{8ml^2} = \frac{(6.626 \times 10^{-34} \text{ Js})^2}{8 \times (10^{-9} \text{ m})^2 (9.109 \times 10^{-31} \text{ Kg})}$
 $= 6.025 \times 10^{-20} \text{ J}$

(ii) Now, $E_2 = \frac{4h^2}{8ml^2} = 4(E_1) = 24.1 \times 10^{-20} \text{ J}$

$$\Delta E = E_2 - E_1 = 4E_1 - E_1 = 3E_1 = 18.075 \times 10^{-20} \text{ J}$$

6. What will happen if the walls of 1-D box are suddenly removed?

Ans. if walls are removed, particles become free to move without any restriction on the value of potential energy (P.E.). Thus energy value are not quantised, and it will have continuous energy spectrum.



7. What is the zero point energy of a particle in a one-dimensional box of infinite height? Is the occurrence of zero point energy in accordance with the Heisenberg Uncertainty principle?

Ans → Since, $E = \frac{n^2 h^2}{8mL^2}$

$$\therefore E_1 = \frac{h^2}{8mL^2} \Rightarrow \text{zero point energy (Z.P.E)}$$

Since, Z.P.E is finite (and not equal to zero) it means that the particle inside the box is not at rest even at 0K. This being so, the position of particle cannot be precisely known. Again, since only expectation value of $KE = \frac{1}{2}mv^2$ is known the linear momentum of particle is also not precisely known. Thus, occurrence of Z.P.E implies uncertainty in the position, Δx and also uncertainty in x -component of linear momentum Δp_x .

This means, Z.P.E is keeping accordance with Heisenberg Uncertainty Principle.



• Introduction to wave mechanics:

In view of shortcomings of Bohr model of atom, a new model was developed based on two concepts:

Quantum
or
wave
mechanical
model
of
atom

- (i). de Broglie concept of dual nature of matter.
- (ii). Heisenberg uncertainty principle.

(i). de Broglie's concept of dual nature of matter:

All material particles such as electrons, protons, atoms, a piece of stone (ie. microscopic as well as macroscopic objects) also possessed dual character.

This concept is also based on Planck's quantum theory (wave character) and on Einstein's equation (particle character)

$$\rightarrow E = h\nu \quad (\text{Planck's theory})$$

ν = freq. of wave, h = Planck's const.

$$\rightarrow E = mc^2 \quad (\text{Einstein theory})$$

m = mass of material, c = vel. of light

Based on above eqⁿs,

$$h\nu = mc^2$$

$$h \frac{c}{\lambda} = mc^2 \quad (\because \nu = \frac{c}{\lambda})$$

$$\Rightarrow \boxed{\lambda = \frac{h}{mc}}$$



or, $\lambda = \frac{h}{mv}$ or, $\lambda = \frac{h}{p}$ de Broglie's equation

where, $v =$ vel. of material particle
 $p =$ momentum of the particle

$\lambda =$ de Broglie's wavelength

Significance: It relates the particle character with the wave character of matter.

Heisenberg's Uncertainty Principle:

"It is impossible to measure simultaneously the position and momentum of a small particle with absolute accuracy or certainty."

$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$ or, $\Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$

where, $\Delta x =$ uncertainty in position
 $m =$ mass of the particle
 $\Delta v =$ uncertainty in velocity

The concept of an electron following a definite orbit, where its position and velocity are known exactly, must therefore be replaced by the probability of finding an electron in a particular position. The Schrodinger wave equation provides a satisfactory description of an atom in these terms. Solutions to the wave equations are called wave functions (ψ) and the probability of finding an e^- at a point in space whose coordinates are x, y, z is $\psi^2(x, y, z)$.



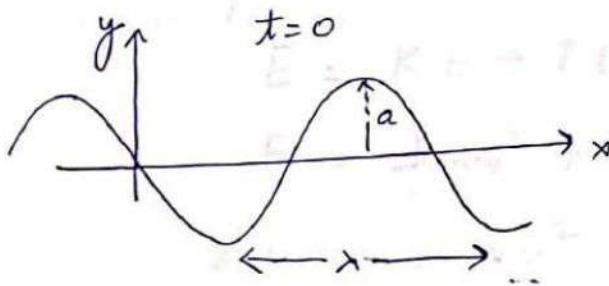
The SCHRÖDINGER WAVE EQUATION :

"Mathematical expression describing the energy and position of the electron in space and time, taking into account the matter wave nature of the electron inside an atom."

It is based on three considerations :

- (i). Classical plane wave equation
- (ii). Conservation of energy
- (iii). de Broglie's hypothesis of matter wave

Derivation :



Acc. to classical plane wave equation :

$$y = a \sin 2\pi \left(ft - \frac{x}{\lambda} \right) \quad - \textcircled{1}$$

where, y = displacement at time t and at distance x from origin

a = maximum displacement from mean posⁿ

λ = wavelength

f = frequency of vibration

When differentiated twice w.r.t. x ,

$$\frac{d^2 y}{dx^2} + \frac{4\pi^2}{\lambda^2} y = 0 \quad \text{--- (2)}$$

$$\text{or, } \frac{d^2 y}{dx^2} + k^2 y = 0 \quad \text{--- (3)}$$

The above eqⁿ involves only distance as the independent variable.

Now, according to the conservation of energy, the total energy 'E' of an electron is partly kinetic and partly potential.

$$E = K.E. + P.E.$$

$$E = \frac{1}{2} mv^2 + V$$

$$2(E - V) = mv^2$$

$$2m(E - V) = m^2 v^2 \quad (\text{on multiplying both sides by 'm'})$$

$$mv = \sqrt{2m(E - V)}$$

Acc. to de Broglie eqⁿ,

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m(E - V)}}$$

Substituting this value in eqⁿ (2), we get

$$\frac{d^2 y}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) y = 0$$

Replacing 'y' by wave fⁿ ψ , we get

$$\left\langle \frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \right\rangle \quad \text{--- (4)}$$

Time-independent
Schrödinger eqⁿ in
one dimension



For 3-D motion of an electron, the eqⁿ becomes:

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m}{h^2} (E-V)\psi = 0$$

or,
$$\nabla^2\psi + \frac{8\pi^2m}{h^2} (E-V)\psi = 0$$

where, $\nabla^2 =$ Laplacian's ~~factor~~ operator

Also, from eqⁿs (3) & (4)

$$k^2 = \frac{8\pi^2m}{h^2} (E-V)$$

Schrödinger eqⁿ is also governed by boundary conditions.

Physical significance of ψ & ψ^2 :

- (1). ψ is a mathematical fⁿ, known as eigen fⁿ or wave fⁿ.
↳ it is generally a complex value.

$$\psi = a + ib \quad \text{and its conjugate, } \psi^* = a - ib$$

$$\psi \cdot \psi^* = (a + ib)(a - ib) = a^2 + b^2 \Rightarrow \text{real.}$$

- (2). ψ denotes the amplitude of a 3-D stationary electron wave.

- (3). ψ^2 at any point gives the probability of finding the e⁻ at that point, i.e. electron density at that point.

↓
in a definite volume of space around the nucleus.

$$\int_{-\infty}^{+\infty} \psi^2 dV = 1$$

where, $dV = dx \cdot dy \cdot dz$

This is known as the condition of normalization.



For Schrödinger eqⁿ to be physically possible :

1. ψ must be continuous.
2. ψ must be finite
3. ψ must be single valued.
4. The probability of finding the e^- over all the space must be equal to 1.

This region around the nucleus which represents e^- density at diff. posⁿs is called an orbital.

Important features of the quantum mechanical model of atom :

- (1). The e^- in an atom have only quantised values of energy
- (2). These quantised values of energy are obtained from the Schrödinger wave eqⁿ. (and also the corresponding value of wave fn ψ)
- (3). Wave fn ψ is simply a fn of coordinates of the e^- and expressed as $\psi(x, y, z)$ & has no physical significance as such. ψ^2 , on the other hand, gives the probability of finding the e^- at the point i.e. e^- density at that pt.
- (4). Atomic orbital is the 3-D space around the nucleus within which the probability of finding the e^- is max. (upto 90%)
 ψ is therefore, called orbital wave function or atomic orbital.
- (5). Since an e^- can have many wave fn's, therefore, there are many atomic orbitals in an atom.
- (6). The orbital wave fn ψ contains all the information about an e^- in an atom.

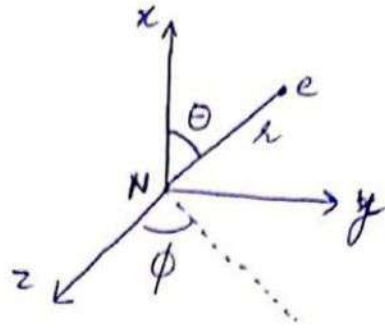
- Conversion of cartesian coordinates to polar coordinates:

Based on

$$x = r \cos \theta$$

$$y = r \sin \theta \sin \phi$$

$$z = r \sin \theta \cos \phi$$



SE converts to :

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right)$$

$$+ 8\pi^2 \mu (E - V) = 0$$

where, r , θ & ϕ are the polar coordinates of the e^- w.r.t. the nucleus (N) as origin

The permitted solution of the above eqⁿ can be expressed as :

$$\psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$$

where, $R(r)$ is a fⁿ that depends on the distance from the nucleus & is called radial wave fn. It depends on quantum nos. ' n ' & ' l '
principal azimuthal

Angular wave fn $\left[\begin{array}{l} \Theta(\theta) \text{ is a f}^n \text{ of } \theta \text{ that depends on 'l' \& 'm'} \\ \Phi(\phi) \text{ is a f}^n \text{ of } \phi \text{ that depends on 'm'}. \end{array} \right.$
magnetic

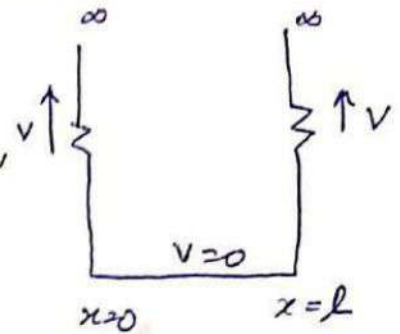
Total wave fn $\psi(r, \theta, \phi) \rightarrow$ total probability of finding an e^- & is called atomic orbital





• Application of Schrödinger Eqⁿ: Particle in a 1-D box

Let us consider a particle of mass 'm', moving freely in a 1-D box of length 'l'



The pot. energy 'V' of e⁻ at the bottom of the box is constant, V=0 (inside the box)
 ⇒ particle can't move outside the box
 for x < 0 and x > l, V = ∞

There is one further restriction that, the boundary condition for the particle in the box is that ψ must be 0 when x=0 and x=l

⇒ Particle is confined to the box and can't exist outside

Now, the S.E. for particle in 1-D box where V=0:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} E\psi = 0$$

$$\text{or, } \frac{d^2\psi}{dx^2} = -\frac{8\pi^2m}{h^2} E\psi = -k^2\psi \quad \left(k^2 = \frac{8\pi^2mE}{h^2}\right) \quad \text{--- (1)}$$

The general solⁿ of the above eqⁿ is:

$$\psi = a \sin kx + b \cos kx$$

where, a & b are integration constants

• on applying boundary cond^s:

(i) $\psi(x) = 0$ at $x = 0$
 $0 = a \sin 0 + b \cos 0$
 $\Rightarrow \boxed{b = 0}$

(ii) $\psi(x) = 0$ at $x = l$
 $\Rightarrow a \sin kl + b \cos kl = 0$



(ii). $\psi(x) = 0$ at $x = l$

$$0 = a \sin kl + b \cos kl$$

$$\Rightarrow a \sin kl = 0 \quad (\because b = 0)$$

this is possible only if

$$kl = n\pi, \text{ where } n \neq 0$$
$$k = n\pi/l, \quad n = 1, 2, 3, \dots$$

on substituting the value of k^2 in eqⁿ ①

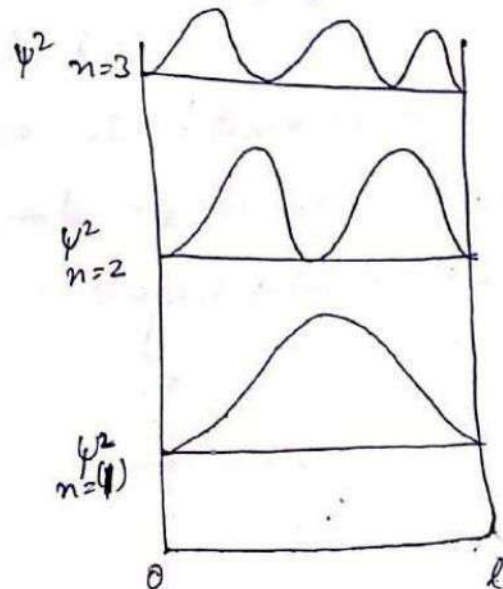
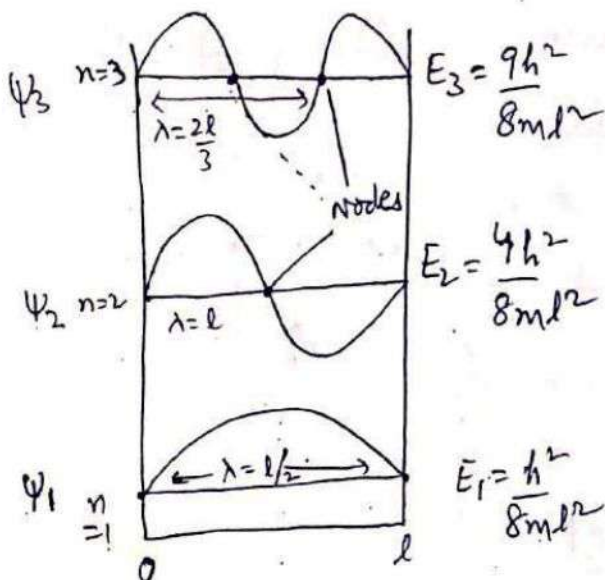
$$\frac{n^2 \pi^2}{l^2} = \frac{8\pi^2 m E}{h^2}$$

$$\Rightarrow \boxed{E_n = \frac{n^2 h^2}{8ml^2}}, \text{ where } n = \text{quantum number} = 1, 2, 3, \dots \infty$$

\Rightarrow Tot. energy, E of $e^- = \text{K.E. of } e^-$

\Rightarrow Particle in a box possesses discrete set of energy values, i.e. energy is quantized

So, for $n=1$, $E_1 = \frac{h^2}{8ml^2}$; $n=2$, $E_2 = \frac{4h^2}{8ml^2}$; $E_3 = \frac{9h^2}{8ml^2}$





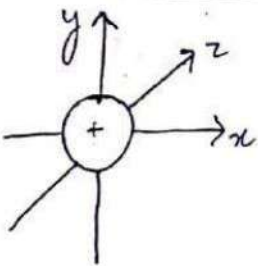
• Probability distribution :

The directional properties of an e^- in an atomic orbital depends on :

- (i). angular probability distribution (θ, ϕ)
- (ii). radial probability distribution (r)

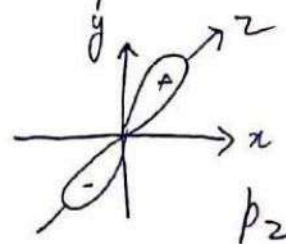
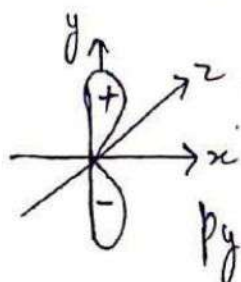
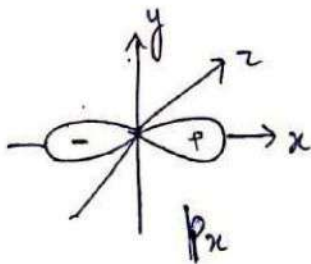
(i) angular prob. distribution : It tells how the angular posⁿ ϕ/θ varies from the nucleus w.r.t. a fixed axis. It describes the shapes or boundaries surfaces of orbitals giving the prob. of finding an e^- in a particular dirⁿ.

(a). For s-orbitals : angular wave funⁿ $A(\theta, \phi)$ is independent of the angles θ & ϕ and is of a const. value
 \Rightarrow s-orbitals are spherically symmetric about the nucleus. i.e. equal chance of finding electron in any direction.



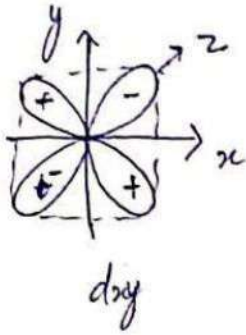
(b). For p-orbitals : • accommodate $6 e^-$

- triply degenerate (three orbitals: p_x, p_y, p_z)
- the 3 orbitals are at right angles to each other
- dumb-bell shaped orbitals along x, y, z.



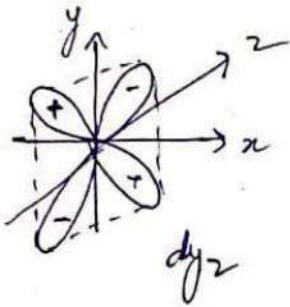
(c). d-orbitals :

- accommodate $10 e^-$
- five-fold degenerate (d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$, d_{z^2})



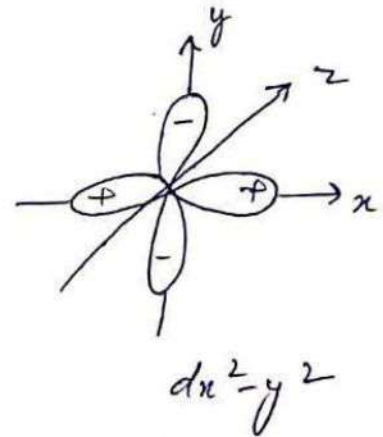
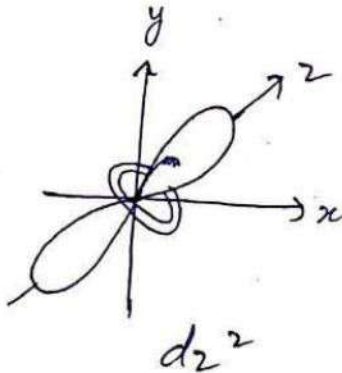
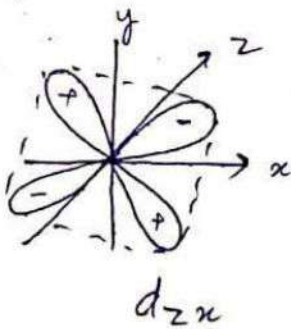
- trig set : d_{xy} , d_{yz} , d_{zx}

lobes lying symmetrically
 in between coordinate axes



- eg set : $d_{x^2-y^2}$, d_{z^2}

lobes lying along x & y axes;
 and z-axis lobe.





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Engineering Chemistry-1 (BS109)

Periodicity in Properties of Elements in the Periodic Table

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Assistant Professor

USAR, GGSIPU



Long Form of Periodic Table

1 IA		2 IIA		3-10										11-17					18 VIIIA
1 H Hydrogen 1.008		3 Li Lithium 6.94	4 Be Beryllium 9.012	5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180	11 Na Sodium 22.990	12 Mg Magnesium 24.305	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948		
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.63	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798		
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.6	53 I Iodine 126.905	54 Xe Xenon 131.29		
55 Cs Cesium 132.905	56 Ba Barium 137.33	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium 209	85 At Astatine 210	86 Rn Radon 222		
87 Fr Francium 223	88 Ra Radium 226	89-103 Actinides	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 263	107 Bh Bohrium 264	108 Hs Hassium 265	109 Mt Meitnerium 266	110 Ds Darmstadtium 267	111 Rg Roentgenium 268	112 Cn Copernicium 269	113 Nh Nihonium 270	114 Fl Flerovium 271	115 Mc Moscovium 272	116 Lv Livermorium 273	117 Ts Tennessine 274	118 Og Oganesson 276		
57 La Lanthanum 138.905	58 Ce Cerium 140.12	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 145	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.5	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.967					
89 Ac Actinium 227	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244	95 Am Americium 243	96 Cm Curium 247	97 Bk Berkelium 247	98 Cf Californium 251	99 Es Einsteinium 252	100 Fm Fermium 257	101 Md Mendelevium 258	102 No Nobelium 259	103 Lr Lawrencium 260					

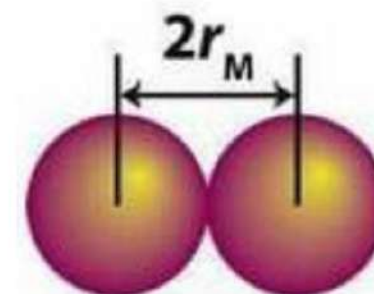
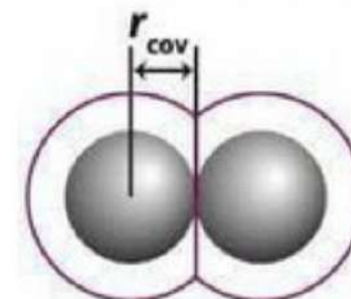
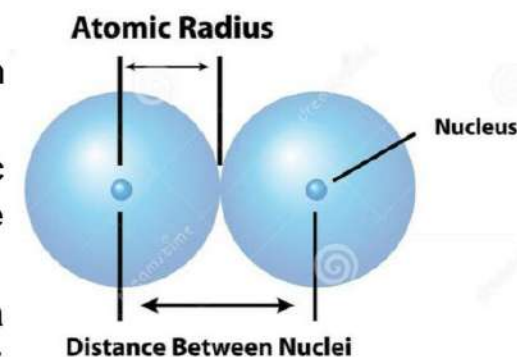


Long form of Periodic Table:

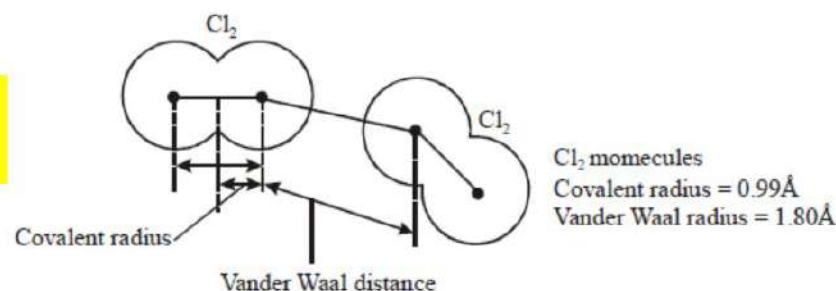
- Based on modern periodic law, according to which the physical and chemical properties of the elements are the periodic functions of their atomic number. Therefore elements are arranged in increasing order of their atomic numbers from left to right across each row.
- It consists of **18 vertical columns** and **7 horizontal rows**.
- **Vertical columns are known as Groups** in the Periodic Table
 1. There are **18 groups** in the periodic table.
 2. They are numbered from 1 to 18.
 3. Each group consists of elements having the same outer shell electronic configuration.
- **Horizontal rows are known as Periods** in the Periodic Table
 1. There are **7 periods** in the periodic table.
 2. They are numbered as 1, 2, 3, 4, 5, 6 and 7 from top to bottom.
 3. The 1st period consists of only two elements i.e. hydrogen and helium.
 4. 2nd and 3rd period consist of 8 elements each, 4th and 5th period consist of 18 elements each, 6th and 7th period consists of 32 elements.
 5. Also, the long form of the periodic table consists of a separate panel at the bottom. It consists of 14 elements of the 6th period 14 elements in the 7th period.
 6. Each period represents the number of shells or energy levels present in an atom of an element i.e. highest principal quantum number (n) of the elements in the period
 7. The cause of periodicity in properties is the repetition of similar outer electronic configuration after certain regular intervals.



- **(1) Atomic Radius** : distance from the nucleus to the outermost electron.
- Most of the time atoms are not in atomic state, so radius is measured as covalent radius, van der Waals radius and metallic radius.
- **Covalent radius**: one half of the internuclear distance in the homonuclear diatomic molecule. This is generally used for non-metals. The bond distance in the chlorine molecule (Cl_2) is 198 pm and half this distance (99 pm), is taken as the atomic radius of chlorine.
- **Metallic radius**: half of the internuclear distance separating two adjacent metal atoms in a metallic lattice. Distance between two adjacent copper atoms in solid copper is 256 pm; hence the metallic radius of copper is assigned a value of 128 pm.
- **van der Waals radius**: half the closest distance between two immediately adjacent atoms (either of same or different elements) in the structure of the solid compound in which they are not bonded to each other. It is always greater than the covalent radii as (i) the latter is formed by the overlap of two half-filled atomic orbitals, (ii) van der Waals forces of attraction are weak, internuclear distances between atoms held by these forces are is much large.



van der Waals radius > metallic radius > covalent radius



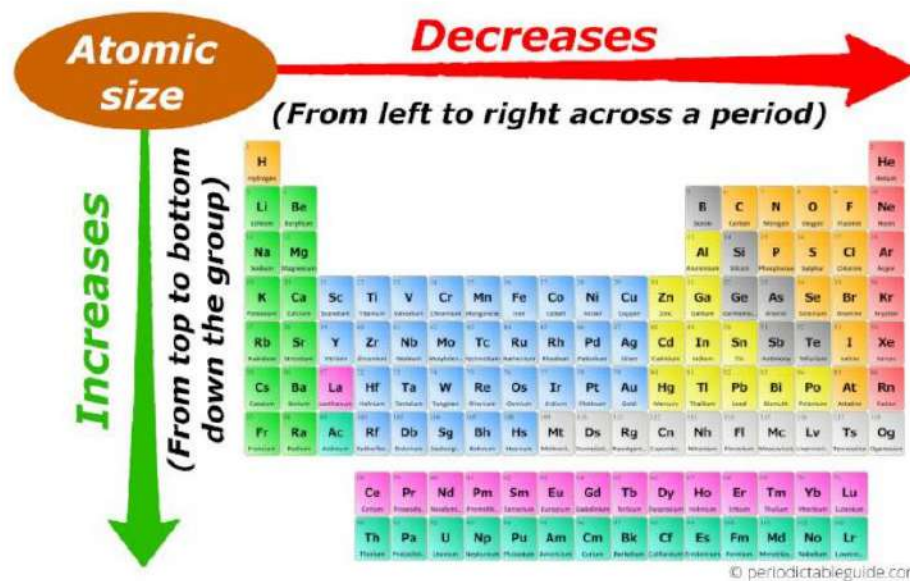


Variation in a period:

- In s- and p- block elements, atomic radius decreases with increase in atomic number in a period because the effective nuclear charge (Z_{eff}) increases across the period.
- The size of atoms of inert gases are larger than those of the preceding halogens owing to their completely filled orbitals resulting in maximum inter-electronic repulsions
- For d-block elements, atomic radius initially decreases, then remains constant and finally increase again.

Variation in a group:

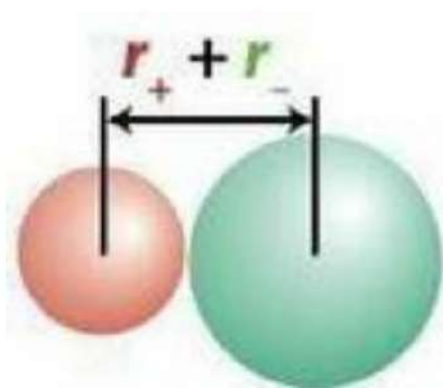
- For s- and p- block elements, the atomic radii increases down the group due to the addition of a new energy shell.
- For d-block elements, the trend in atomic radii is: $r_{3d \text{ series}} < r_{4d \text{ series}} < r_{5d \text{ series}}$. This is because the radius increases as the shell number increases.
- The radius of elements of 4d- series is about the same as elements of 5d series. This is due to the lanthanoid contraction that causes increase in Z_{eff} value due to poor shielding of f electrons.
- For f-block elements, in lanthanoids, the effective nuclear charge increases along the period so the atomic radius for the elements decreases. For actinoids, there is also a decrease in atomic radius from Th to Lr.





(2) **Ionic radius** : the effective distance from the center of the nucleus of the ion upto which it exerts its influence on its electronic cloud, i.e. distance between the nuclei of neighboring cations and anions.

- When a positive ion (cation) is formed, effective nuclear charge is increased resulting in strong attraction of electrons by the nucleus. Also, there is a decrease in the number of shells. Thus a **positive ion is always smaller than the corresponding atom** and more the electrons removed smaller is the ion.
- When a negative ion (anion) is formed, one or more electrons are added to an atom which results in reduced effective nuclear charge causing inter-electronic repulsions. As a result, electron cloud expands and the **size of anion is more than that of the atom**.

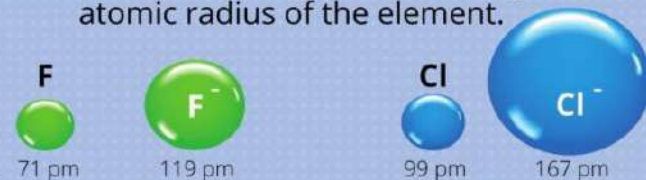


Atomic Radius vs Ionic Radius

The ionic radius of a positive ion is smaller than atomic radius of the element.

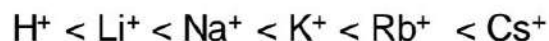
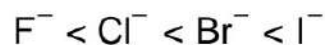


The ionic radius of a negative ion is larger than atomic radius of the element.

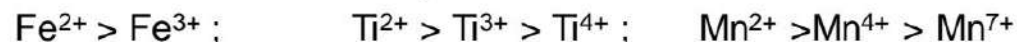




- Ionic radius depends upon following factors:
 - Ionic radius increases down the group due to an increase in the number of shells



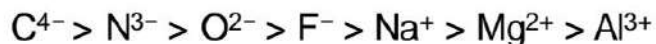
- (a) If the charge of cation increases, the ionic radius decreases owing to increased effective nuclear charge.



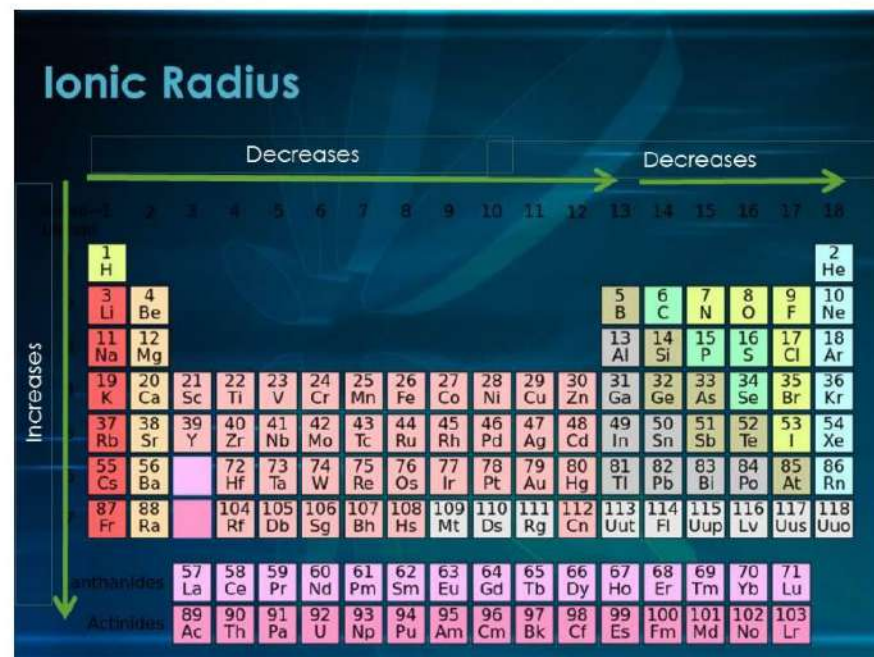
- (b) If the charge of anion increases, the ionic radius increases owing to decrease in the effective nuclear charge



- For isoelectronic species, as the number of protons increases the radius of ion decreases. Ionic radii decrease with increase in the magnitude of the nuclear charge.



- The ionic radii decreases moving from left to right across any period due to the increased effective nuclear charge





(3) Ionization energy:

- Ionization energy (IE) is the energy required by an isolated gaseous atom to remove an electron in its ground state.



- It is measured in eV atom⁻¹ or kJ mol⁻¹.
- Whenever an electron is removed from an atom, a specific amount of energy is required to remove it, hence the ionization enthalpies of chemical elements are always positive.
- Successive ionization energy always increases because the e/p ratio gradually decreases i.e. effective nuclear charge increases, electrons will be tightly held and more potential will be required to take off the valence electron.

$$IE_1 < IE_2 < IE_3$$

- Ionization energy depends upon the following factors:

1. **Atomic Size:** IE decreases when shell number or the radius increases. $Li > Na > K > Rb > Cs$

2. **Nuclear Charge:** IE increases when nuclear charge increases. $Li < Be > B < C < N > O < F < Ne$

3. **Screening effect of inner electrons:** IE decreases when σ (shielding constant) increases.

4. **Effect of arrangement of electrons:** IE is more for half-filled and fully-filled electronic configurations (more stable configs)

5. **Penetration effect of the electrons:** IE also depends upon the orbitals from which the electron is removed. If the principal quantum number is the same, then the energy required for removal of electrons from different orbitals shows the following order:

$s > p > d > f$. $\Rightarrow IE_1 Al < IE_1 Be$



General periodic trends:

In a group, while moving from top to bottom it decreases.
It increases from left to right across a period.

1. Trends in ionization enthalpy **in a group**:

The first ionization enthalpy of elements **decreases** as we move down in a group. While moving down in a group, the atomic number increases and the number of shells also increases. Outermost electrons are far away from the nucleus and thus can be removed easily. The second factor that decreases the ionization energy is the shielding effect due to an increasing number of shells as we move down a group.

2. Trends in ionization enthalpy **across a period**:

As we move from left to right across a period, the ionization energy of elements **increases**. This is due to the decrease in the size of atoms across a period. The valence electrons get closer to the nucleus of an atom as we move from left to right due to increased nuclear charge. The force of attraction between the nucleus and the electrons increases and hence more energy is required to remove an electron from the valence shell.





Periodic variations in ionization energy (IE)

(s and p block)

Along period: the Z_{eff} increases in a period, hence IE increases.

Irregular trend

$$\left\{ \begin{array}{l} \text{Li} < \text{B} < \text{Be} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne} \\ \text{Na} < \text{Al} < \text{Mg} < \text{Si} < \text{S} < \text{P} < \text{Cl} < \text{Ar} \\ \text{K} < \text{Ga} < \text{Ca} < \text{Ge} < \text{Se} < \text{As} < \text{Br} < \text{Kr} \end{array} \right.$$

Regular trend

$$\left\{ \begin{array}{l} \text{Rb} < \text{Sr} < \text{In} < \text{Sn} < \text{Sb} < \text{Te} < \text{I} < \text{Xe} \\ \text{Cs} < \text{Ba} < \text{Tl} < \text{Pb} < \text{Bi} < \text{Po} < \text{At} < \text{Rn} \end{array} \right.$$

Exceptions to trends are

(i) $\text{Be} > \text{B}$ $\text{Mg} > \text{Al}$ $\text{Ca} > \text{Ga}$

Be, Mg and Ca have fully filled ns^2 , but B, Al & Ga attain fully filled ns^2 after losing one electron.

(ii) $\text{N} > \text{O}$ $\text{P} > \text{S}$ $\text{As} > \text{Se}$

N, P, As have half filled np^3 , while O, S, Se obtain half filled np^3 on losing $1e^-$.

(iii) (a) IE_2 of group 1A $>$ IE_2 of group 2A elements.

(b) IE_3 of group 5A $>$ IE_3 of group 6A elements.



In a group: IE generally decreases down the group. Some exceptions are:

(i) Al (577 kJ/mol) \approx Ga (579 kJ/mol) [because poor shielding effect of 10 $d e^-$ in Ga]

(ii) In (558 kJ/mol) < Tl (589 kJ/mol) [due to lanthanoid contraction]

So, for Group 13, order is $B > Tl > Ga \geq Al > In$.

→ Sn (707 kJ/mol) < Pb (715 kJ/mol) [due to lanthanoid contraction in Pb]

So, for Group 14, order is $C > Si > Ge > Pb > Sn$

(d-block) Period: IE slightly increases due to increase in Z_{eff} . (But not prominent)

B'coz $Cu \rightarrow Zn$, $Ag \rightarrow Cd$ and $Au \rightarrow Hg$ there is sudden jump due to fully filled configuration.

Group: IE_1 of 3d series \approx IE_1 of 4d series < IE_1 of 5d series
should decrease but more due to lanthanide contraction.

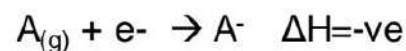
exception: $Sc (6.54 eV) > Y (6.38 eV) > La (5.57 eV)$

regular trend as La element has no lanthanide contraction.



Electron affinity:

- The electron affinity (EA) is the potential energy change of the atom when an electron is added to a neutral gaseous atom to form a negative ion. So the more negative the electron affinity the more favourable the electron addition process is.



- The electron gain enthalpy for **halogens is highly negative** because they can acquire the nearest stable noble gas configuration by accepting an extra electron.
- Noble gases have large positive** electron gain enthalpies because the extra electron has to be placed in the next higher principle quantum energy level thereby producing highly unstable electronic configuration.
- Successive electron gain enthalpies:** After the addition of one electron, the atom becomes negatively charged and the addition of second electron onto this negatively charged ion is opposed by inter-electronic repulsions and hence the energy has to be supplied resulting in positive second enthalpy.
- Factors affecting EA:
 - 1. Atomic size:** If the atomic size increases, then there will be smaller electron gain enthalpy (less negative) as the distance between the nucleus and the last shell (receiving the electron) increases resulting in decrease forces of attraction between them. While in small sized atoms, enthalpy gain is more (more negative) because the effective nuclear forces will be greater in the smaller atoms and the electrons will be held firmly.
 - 2. Nuclear charge:** The greater the nuclear charge more will be the value for electron gain enthalpy (more negative) because an increase in nuclear charge will increase the effective nuclear force on valence electrons.
 - 3. Electronic configuration:** Half-filled and fully-filled orbitals are very stable and will have large positive gain enthalpy values.



Electron Affinity variation in the periodic table

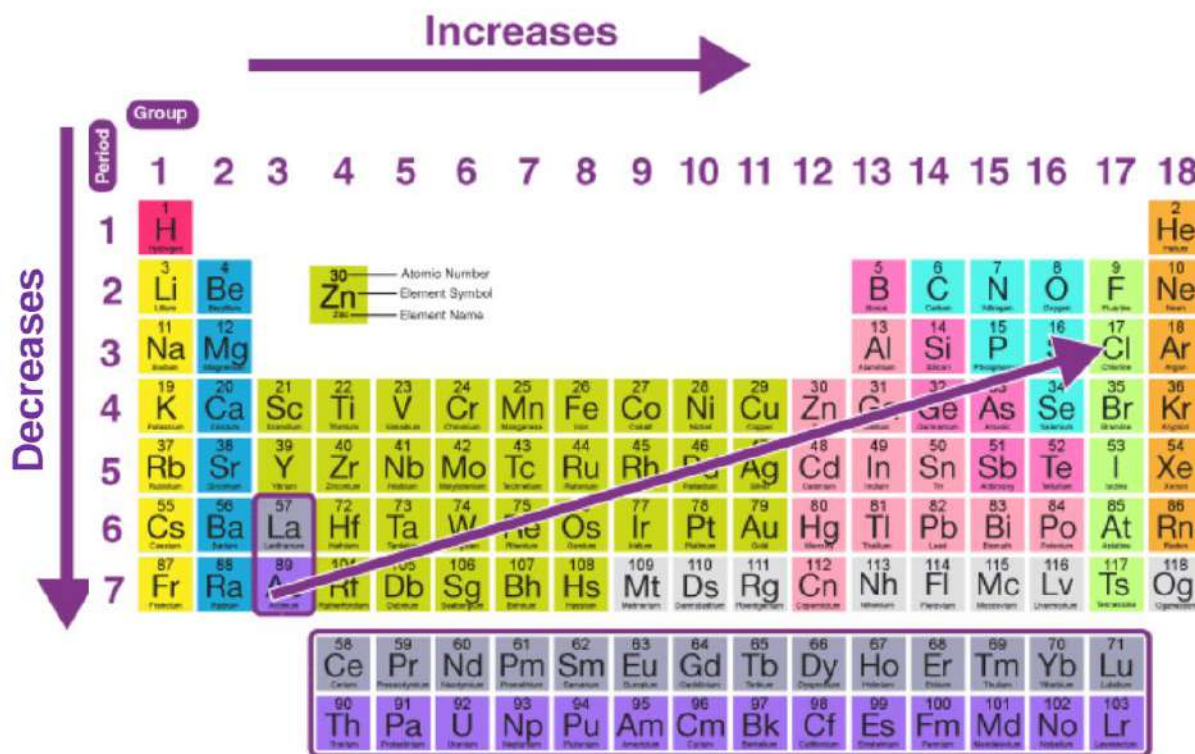
- Trends in ionization enthalpy **in a group**:
Going down the group the electron affinity should **decrease** since the electron is being added increasingly further away from the atom.

- Trends in ionization enthalpy **across a period**:
Electron affinity **increases** (more negative) going from left to right across a period. The overall trend across a period occurs because of increased nuclear attraction.

- EA of second period < EA of third period elements because of presence of vacant d orbitals
 $B < Al$; $C < Si$; $N < P$; $O < S$; $F < Cl$

Chlorine has the most negative electron gain enthalpy

- EA of alkali metals > alkaline metals as the former will attain the stable configuration
- EA of group 14 > group 15 because of half-filled configuration in the latter



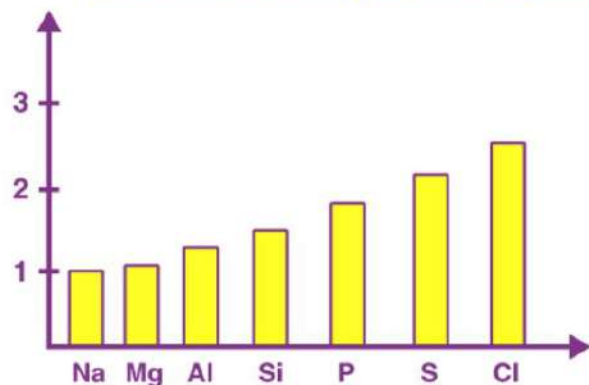


Electronegativity:

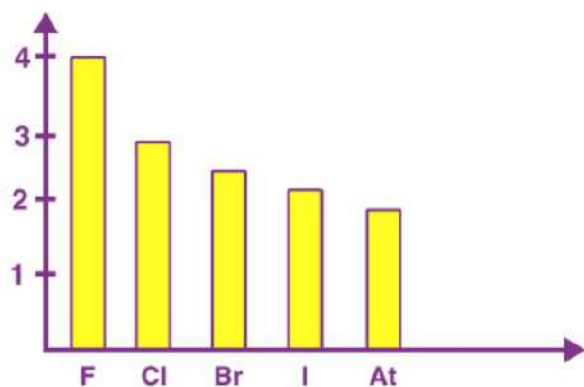
- The tendency of an atom in a molecule to attract the shared pair of electrons towards itself is known as electronegativity.
- It is a dimensionless property because it is only a tendency. It basically indicates the net result of the tendencies of atoms in different elements to attract the bond-forming electron pairs.
- It is measured on the Pauling scale. According to this scale, fluorine is the most electronegative element with a value of 4.0 and cesium is the least electronegative element with a value of 0.7.
- As we move across a period from left to right the nuclear charge increases and the atomic size decreases, therefore the value of **electronegativity increases across a period**.
- Electronegativity **decrease down the group**. The nuclear charge also increases but the effect of the increase in nuclear charge is overcome by the addition of one shell.
- Generally, **metals show a lower value of electronegativity as compared to the non-metals**. Therefore, metals are electropositive and non-metals are electronegative in nature.
- Factors affecting electronegativity:
 1. **Size of an atom:** A greater atomic size will result in less value of electronegativity, this happens because electrons being far away from the nucleus will experience a lesser force of attraction.
 2. **Nuclear charge:** A greater value of nuclear charge will result in a greater value of electronegativity. This happens because an increase in nuclear charge causes electron attraction with greater force.
 3. **Effect of substituent:** The difference in electronegativity of an atom caused by substituents results in different chemical behaviour of that atom.
 4. Larger is the s-character, more is the electronegativity: $sp > sp^2 > sp^3$



Electronegativity variation in the periodic table



Electronegativity Trend – Across the Period



Electronegativity Trend – Down the Group

Table 2.1: Electronegativity values (L. Pauling Scale)

Group → Period ↓	I (1)	II (2)	III (13)	IV (14)	V (15)	VI (16)	VII (17)
1	H 2.1						
2	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
3	Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
4	K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
5	Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
6	Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.9	Bi 2.0	Po 2.0	At 2.2
7	Fr 0.7	Ra 0.9					



s-block elements: outermost electronic shell configuration: ns^{1-2}

- Group 1 (alkali metals) and Group 2 (alkaline earth metals)
- Except H all elements of s-Block elements are active metals.
- They have +1/ +2 oxidation state.
- They form basic oxides
- They **impart characteristic colour to the flame** due to the heat generated from the flame which excites the valence electrons from one energy level to another energy level. This helps in the detection of alkali metals during the flame test.
- Generally they form ionic salts with nonmetals.
- They have **low ionization potentials**
- They have **very small electron gain enthalpies**.
- They are solids at room temperature (Cs is liquid at about at 35oC)
- Their hydroxides are basic in nature.
- The density of the alkali metals increases down the group. **Exception:** the density of potassium is less than the density of sodium.
- The alkali metals have a low melting and boiling point due to the weak metallic bonding.

(i) Atomic and Ionic Radii: Size of the alkali metals is larger compared to other elements in a particular period. As the atomic number increases the total number of electrons increases along with the addition of shells. $Na^+ > Mg^{2+}$

On moving down the group the atomic number increases. As a result, the atomic and ionic radius of the alkali metals increases. $H^+ < Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$



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(ii) Ionization potential: As we go down the group the size of the atoms increases due to which the attraction between the nucleus and the electrons in the outermost shell decreases. As a result, the **ionization enthalpy decreases**. The ionization enthalpy of the alkali metals is comparatively lesser than other elements.

(iii) Diagonal relationship:

Lithium and Beryllium differ much from the rest of their members but at the same time, they resemble more with the diagonal element present in the next column.

The anomaly of these S-block elements is due to:

Low atomic and ionic size

Greater charge density (charge/volume of the atom)

Greater polarization

Absence of d-orbitals.



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p-block elements: outermost electronic shell configuration: ns^2, np^{1-6}

- Most of p-Block elements are non-metals.
- They have variable oxidation states.
- They form acidic oxides
- They impart no characteristic colour to the flame
- Generally they form covalent compounds. Halogens form salts with alkali metals
- They have very large electron gain enthalpies.
- They are solids/liquids/gases at room temperature (Br is liquid)
- The aqueous solutions their oxides are acidic in nature.
- p- block elements consist of
 - Group 13 Elements: Boron family
 - Group 14 Elements: Carbon family
 - Group 15 Elements: Nitrogen family
 - Group 16 Elements: Oxygen family
 - Group 17 Elements: Fluorine family
 - Group 18 Elements: Neon family
- In the period from left to right, there is a regular increase in non-metallic character. However, non-metallic character decreases in the groups from top to bottom.
- Ionization energies increase from left to right in a period while decrease in a group from top to bottom. Group VA and zero group have exceptionally high values of ionization energies on account of half-filled and fully filled orbitals in the valency shell.
- The first member of the p block elements differs from other elements in two major respects:
 - First is the size and each and every property which depends upon the size.
 - The second difference applies only to the p-block element, which arises from the effects of d-orbitals in the valence shell of heavier elements.



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d-block elements: Elements having electrons (1 to 10) present in the d-orbital of the penultimate energy level and in the outermost 's' orbital (1-2) are **d block elements**.

- Electrons added to the 'd' sub-orbitals that lie between their (n+1) s and (n+1) p sub-orbitals.
- The general electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{0-2}$.
- There are four series in the d block corresponding to the filling up of 3d, 4d, 5d or 6d orbitals.
 - 3d- Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn
 - 4d- Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd
 - 5d- La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg
 - 6d- incomplete.
- d-block elements are called transition metals indicating their positioning and transition of properties between, s and p block elements.
- Anomalies do occur in all the series, which can be explained from the following considerations:
 - The energy gap between the ns and (n-1) d orbitals
 - Pairing energy for the electrons in s-orbital
 - Stability of half-filled orbitals to the partly filled orbitals.
- Unpaired electrons and the empty or partially filled d-orbitals form covalent bonding in addition to the metallic bonding by s-electrons. Because of such strong bonding, d-block elements have high melting and boiling points than s and p block elements. This trend goes till d⁵ configuration and then decreases as more electrons get paired in the d-orbital.
- **Mercury – the liquid metal:** Mercury is the only metal that exists in its liquid state at room temperature. 6s valence electrons of Mercury are more closely pulled by the nucleus (lanthanide contraction) such that outer s-electrons are less involved in metallic bonding.



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Atomic and ionic radii of elements of all three-transition series

- Decreases rapidly, from column 3 to 6
- Remains steady, from column 7 to 10 and
- Starts increasing from column 11 to 12.

For example, in the first transition series, atomic radii, the decrease is more from Sc to Cr (group 3 to 6), is almost the same for Mn, Fe, Co, Ni (group 7, 8, 9 & 10) and increase in Cu and Zn.

- The larger decrease in atomic radii, in column 3 to 6 elements is due to the increase in effective nuclear charge but poor shielding because of the smaller number of d-electrons.
- In elements of column 7 to 10 increasing effective nuclear charge is balanced by the repulsion between the shared d electrons so that radii remain the same.
- In the case of 11 and 12 columns elements, the d orbital is full with ten electrons and shield the electrons present in the higher s-orbital. So, groups 11 and 12 elements like Cu and Zn have bigger sizes than their earlier elements in the block.

Since electrons occupy a higher orbital, radii of the third series are to be more than the second series elements. But radii of both series are almost the same. In the third series of elements, 5d orbitals are filled only after the filling up of 4f orbitals, which increases the effective nuclear charge by 14 units.

This higher nuclear charge leads to the larger shrinkage of radii known as Lanthanide contraction. An increase in radii due to the higher orbital will be effectively neutralized by the increase in the nuclear effective charge. So, radii of second and third series elements have the same atomic radii. For example, Niobium and hafnium have almost the same atomic radii.



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Ionization Energy of the d block elements is larger than s-block and smaller than the p-block elements, between which, they are placed. In the first series, except chromium and copper first Ionization Energy involves removal from filled s-orbital. Among them, the ionization energy of d block elements increases with the increase in atomic number up to Fe.

In Co and Ni, increasing sharing of d-electrons compensate for the atomic number increase resulting in the decrease of Ionization Energy. Copper and zinc show increasing IE, as s-block elements. In the second series, elements from Niobium have single electrons in the s-orbital.

Hence, they show a gradual increase in IE with increasing atomic number. Palladium, on the other hand, has a completed d-shell and no electron in the s-shell. So, Pd shows the maximum IE. Because of lanthanide contraction, the attraction of electrons by the nuclear charge is much higher and hence IE of 5d elements are much larger than 4d and 3d. In 5d series, all elements except Pt and Au have filled s-shell.

Elements from Hafnium to rhenium have the same IE and after IE increases with the number of shared d-electrons such that Iridium and Gold have the maximum IE.



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f-block elements: Electronic configuration: $ns^2 (n-1)d^0-1(n-2)f^1-14$

- They are also called as inner transition elements. They are: Lanthanides and actinides.
- **Lanthanides. (58Ce- 71Lu):** last electron enters into **4f-orbital**
- All lanthanides closely resemble lanthanum
- Lanthanoids are chemically similar to each other
- Except for cerium (III and IV) and europium (III and II), the lanthanides occur as trivalent cations in nature. Most lanthanides are widely used in lasers
- These elements deflect UV and Infrared electromagnetic radiation and are commonly used in the production of sunglass lenses.
- The ionic radii of the lanthanoids decrease through the period — the so-called **lanthanide contraction**
- **Actinides(90Th– 103Lr):** last electron enters into **5f-orbital**
- All the actinides are radioactive
- These are highly electro-positive (show +3,+4,+5,+6 oxidation states)
- These metals tarnish in air
- They have number of isotopes.
- They react with boiling water or dilute acids to give H₂ gas.
- These directly combine with non-metals.

- **Similarities between Lanthanides and Actinides:**
 - Both lanthanides and Actinides show +3 oxidation states
 - Both are electropositive and very reactive
 - Both are paramagnetic



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Engineering Chemistry-I (BS-109)

Chemical Bonding

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How do atoms combine to form molecules?

Why do atoms form bonds?

A molecule will only be formed if it is more stable, and has a lower energy than the individual atoms. During chemical combination, the electron of the atoms rearrange to form a molecule.

Electrons in the outermost shell (valence electrons) are involved in the bond formation in order to achieve stable electronic configuration, which is achieved either by losing electrons or gaining electrons or sharing them.

Types of elements:

1. **Electropositive:** whose atoms give up one or more electrons such as alkali metals. (Cs is the most electropositive element)
2. **Electronegative:** acceptance of electrons. (F is the most electronegative element)
3. Elements which have little tendency to lose or gain electrons.

Types of bond formed based on the above character of element:

1. **Ionic bond:** Between an electropositive and an electronegative element
2. **Covalent bond:** Between two electronegative elements
3. **Metallic bond:** Between two electropositive elements



Types of valencies based on electronic theory of valency:

1. Ionic valency or electrovalency:

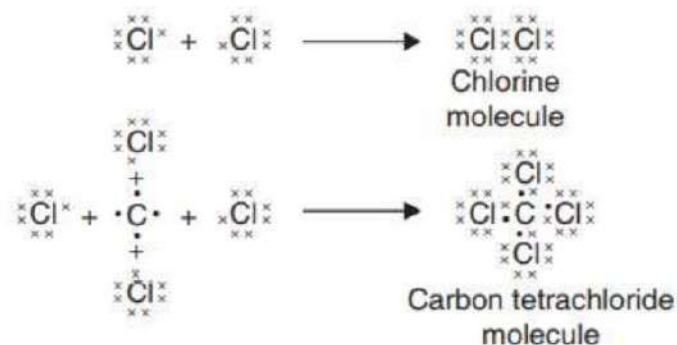
Electronic configuration of Na: $1s^2 2s^2 2p^6 3s^1$ → lose one electron from its outer shell to attain stable noble gas confgn

Electronic configuration of Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$ → gain one electron => it is electronegative

When Na and Cl react together, the outermost electrons of the Na is transferred to Cl atoms to produce Na^+ and Cl^- ions, which are held together in a crystal lattice through electrostatic attractions. This combination of two atoms by complete transfer of outermost electrons is known as electrovalency and this bond is known as ionic bond.

Electrovalency is seen in the case of atoms with a marked difference in their electronegativity values

2. Covalency: When atoms of similar electronegativity values combine to form molecules, they share their electrons to fill up their octets in the outermost shells. This combination is known as covalency and the bond formed is called covalent bond





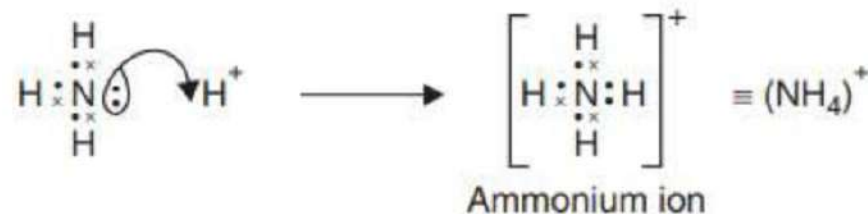
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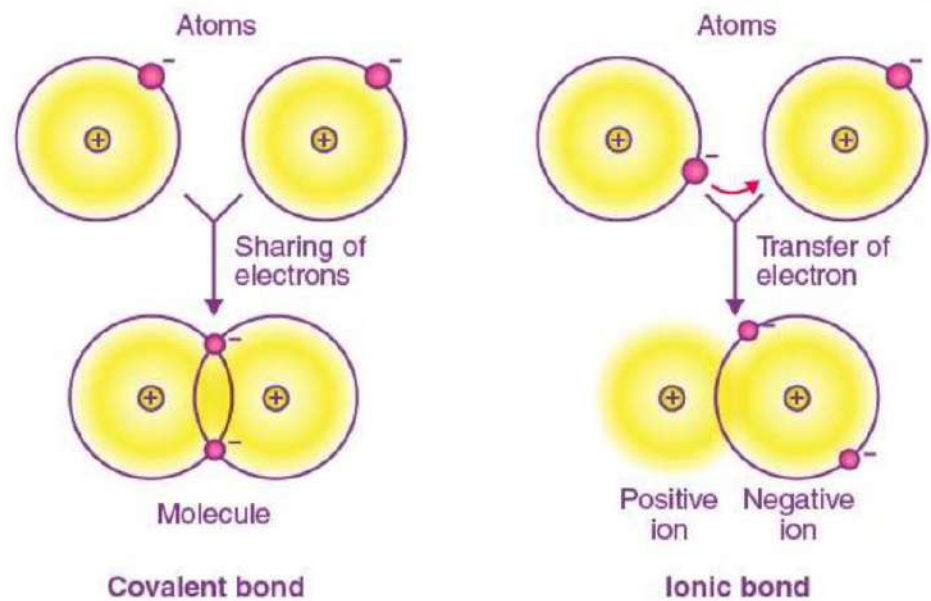


The main difference between valency and covalency is that valency is the number of electrons that an atom will lose or gain in order to stabilize itself whereas covalency is the maximum number of covalent bonds that an atom can form using its empty orbitals e.g. valency of N is 5 ($1s^2 2s^2 2p^3$) whereas its covalency is 3 i.e. it forms three covalent bonds

3. Co-ordinate valency: Unlike equal contribution from both atoms in case of covalency, here, a pair of electrons is being contributed by a single atom while other atom contribute no electron towards the bond formation. After combination, the bond acts as purely covalent. This combination of atoms is called co-ordinate covalency and the bond is called coordinate bond.

The atom which donates the pair of electrons is known as 'donor' atom (should have a lone pair of electrons) and the atom which accepts the electron is known as 'acceptor' atom. It is indicated by the sign ' \rightarrow '





<i>Electrovalent Compounds</i>	<i>Covalent Compounds</i>
<ul style="list-style-type: none"> (i) They are Non-directional. (ii) They cannot exhibit isomerism. (iii) m.p. and b.p. are high. (iv) They are conductors of electricity in solution or in their molten state. (v) They are soluble in polar solvents (H_2O) and insoluble in non-polar solvents (C_6H_6, CCl_4). (vi) They are polar in nature. 	<ul style="list-style-type: none"> (i) They are directional in nature. (ii) They can show isomerism. (iii) m.p. and b.p. are low. (iv) They are nonconductors of electricity in solution or in molten state. (v) They are soluble in organic solvents, generally insoluble in water. (vi) They are non-polar in nature.



- The attraction and repulsive tendencies of atoms in a covalent bond arising due to their electronegativity difference impart partial ionic character to the covalent bond.
 - Case I: When electronegative values (x) of atoms A and B are equal, $x_A = x_B$, the bond A-B is 100% covalent.
 - Case II: When $x_A \neq x_B$, the bond gains partial ionic character and the molecule AB becomes polar e.g. HCl.
- Greater the difference ($x_A - x_B$), greater is the ionic character of the bond.
- The relation is represented as:

$$\begin{aligned} \text{\% ionic character} &= 100 \left[1 - \exp \left\{ 1 - \frac{1}{4} (x_A - x_B)^2 \right\} \right] && \text{Pauling's equation} \\ &= 16(x_A - x_B) + 3.5 (x_A - x_B)^2 && \text{Hannay-Smith equation} \end{aligned}$$

Calculation of partial ionic character of HF molecule:

$$\begin{aligned} \text{\% ionic character in HF molecule} &= 16(4.0 - 2.1) + 3.5(4.0 - 2.1)^2 \\ &= 43\%. \end{aligned}$$

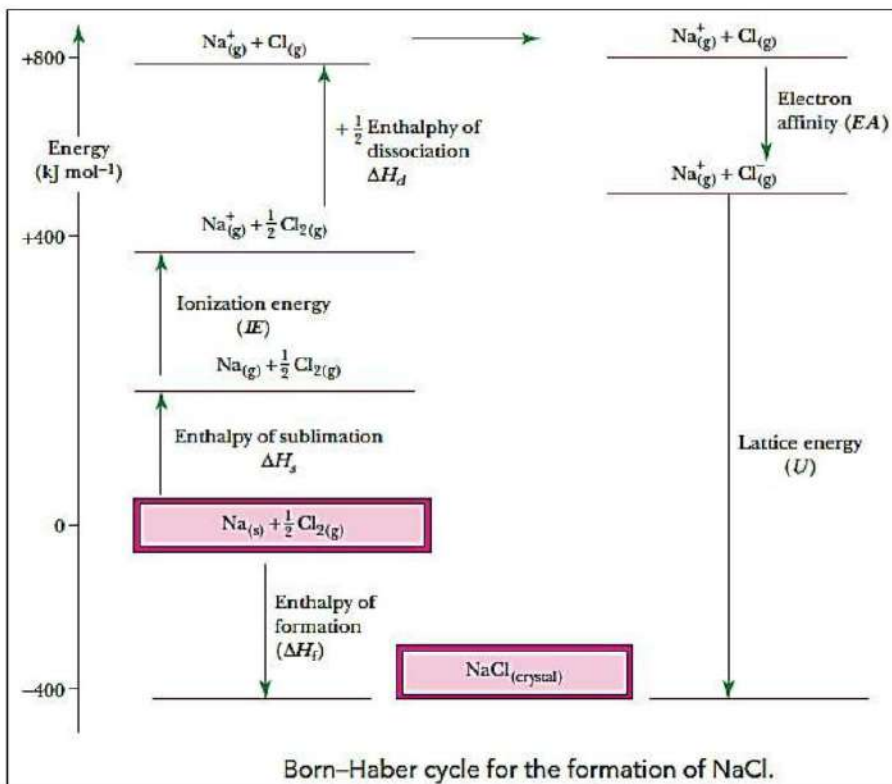
- **Lattice Energy (U):** It is a type of potential energy that may be defined in two ways:
 - (i) the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. (U is always positive)
 - (ii) The other definition says that lattice energy is the reverse process, meaning it is the energy released when gaseous ions bind to form an ionic solid. (U is always negative)
- It is a measure of the cohesive forces that bind ions i.e. it estimates the strength of the bonds in an ionic compound (units: kJ/mol) ($U_{\text{NaCl}} = -774$ kJ/mol)
- Greater the lattice energy, more is the stability. The crystalline structure allows each ion to interact with multiple oppositely charge ions, which causes a highly favorable change in the enthalpy of the system. A lot of energy is released as the oppositely charged ions interact. It is this that causes ionic solids to have such high melting and boiling points.



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- **Born-Haber cycle:** Given by Born and Haber in 1919. It is a thermochemical cycle that can be used to
 - (i) calculate the lattice energy
 - (ii) determine the electron affinity
 - (iii) determine whether the bonding in a compound is truly ionic
- It is an application of **Hess's law** (overall change in energy of a process can be determined by breaking the process down into steps, then adding the changes in energy of each step)
- It takes into account the **ionization energy, electron affinity, dissociation energy, sublimation energy, heat of formation**. The atoms in their standard state are first converted into gaseous atoms, then to ions and finally packed into crystal lattice
- **Ionization energy, sublimation energy and dissociation energy:** positive value (energy is required). **Dissociation energy** is the energy required to break apart a compound. **Sublimation energy** is the energy required to cause a change of phase from solid to gas, bypassing the liquid phase.
- **Electron affinity and lattice energy:** negative value (energy is released)
- The **heat of formation** is the change in energy when forming a compound from its elements. This may be positive or negative, depending on the atoms involved and how they interact.



Born-Haber cycle of NaCl:

- Step-1: Sublimation energy (ΔH_s) of metal. $\text{Na}(s) \rightarrow \text{Na}(g)$
- Step-2: Ionization enthalpy (IE) of metal $\text{Na}(g) \rightarrow \text{Na}^+(g) + e^-$
- Step-3: Dissociation energy (ΔH_d) of NON metal $\frac{1}{2}\text{Cl}_2(g) \rightarrow \text{Cl}(g)$
- Step-4: Electron Affinity (EA) of NON metal $\text{Cl}(g) + e^- \rightarrow \text{Cl}^-(g)$
- Step-5: Lattice Enthalpy (U) of NaCl $\text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}(s)$.

Hence, Enthalpy of formation (ΔH_f) = $\Delta H_s + \text{IE} + \frac{1}{2}\Delta H_d + \text{EA} + U$

As, except EA & U , all can be measured. Originally cycle was used to calculate electron affinity. By using known crystal structure, it was possible to calculate the lattice energy (U) & hence electron affinity (EA) was calculated.

Higher lattice energy then,

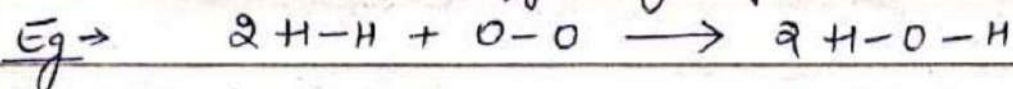
1. higher is stability of ionic solids.
2. higher melting & boiling points.
3. lesser is the solubility.



⇒ Covalent Bond - Energy changes:

- Bond energies can be used to estimate the energy change of a chemical reaction.
- When a bond is broken in the reactant, process is endothermic. ($\Delta H = +ve$)
- When a bond is formed in the products, process is exothermic. ($\Delta H = -ve$)

So, we combine the positive energy change with the negative energy change to estimate the overall energy change of the reaction.



Energy required to break

$$2 \text{H}-\text{H} = 2(+436 \text{ KJ/mol})$$

$$1 \text{O}-\text{O} = (+498 \text{ KJ/mol})$$

$$\text{Total} = +1,370 \text{ KJ/mol}$$

Energy required to form 4 O-H bonds.

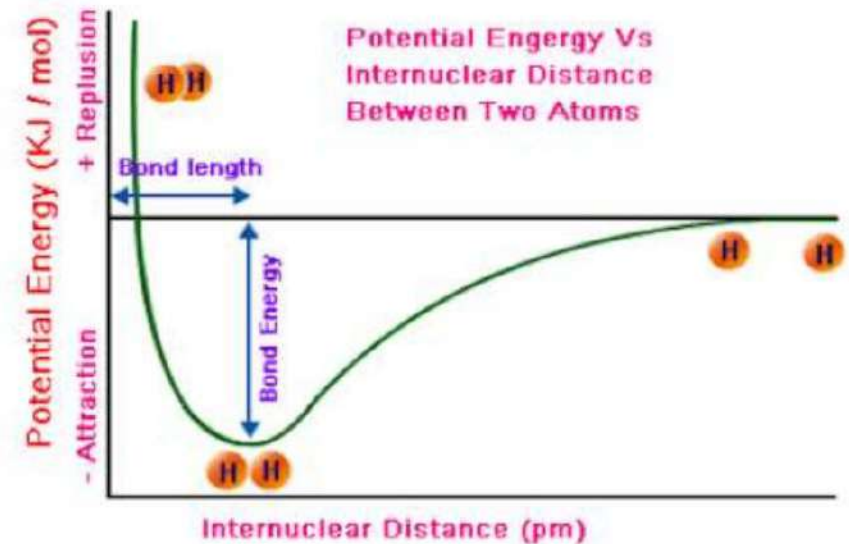
$$4(\text{O}-\text{H}) = 4(-463 \text{ KJ/mol})$$

$$\text{Total} = -1,852 \text{ KJ/mol}$$

$$\text{Net energy change} \Rightarrow (+1,370) + (-1,852) = -482 \text{ KJ/mol}$$



- **Potential energy curve for H₂ molecule:**
- When the H-atoms are separated by a large distance (infinity) we take this energy to be zero.
- Bringing the atoms closer to one another has an attractive potential and the bond has formed on reaching the lowest point on your curve. Lower the energy, more is the stability. At this point a covalent bond is formed and this distance is known as bond length. For H₂ molecule, the **bond length is 74 pm**.
- Moving the atoms closer together increases the potential energy because here we push electrons closer to one another and this energy increases rapidly with each small decrease in separation due to repulsion of similar charges.





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- **Properties of covalent bond:**

- (i) Covalent bonding does not result in the formation of new electrons. The bond only pairs them.
- (ii) They are very powerful chemical bonds that exist between atoms.
- (iii) Most compounds having covalent bonds exhibit relatively low melting points and boiling points.
- (iv) Compounds with covalent bonds usually have lower enthalpies of vaporization and fusion.
- (v) Compounds formed by covalent bonding don't conduct electricity due to the lack of free electrons.
- (vi) Covalent compounds are not soluble in water.

- **Bond parameters of covalent bond:**

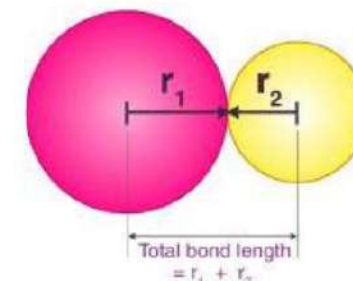
Covalent bonds can be characterized on the basis of several bond parameters such as **bond length, bond angle, bond order, and bond energy** (also known as bond enthalpy). These bond parameters offer insight into the stability of a chemical compound and the strength of the chemical bonds holding its atoms together.



- **Bond Order:** It is the total number of covalently bonded electron pairs between two atoms in a molecule.
 - Single bonds have a bond order of 1.
 - Double bonds have a bond order of 2.
 - Triple bonds have a bond order of 3.
- Examples:
 - (i) The bond order of the carbon-hydrogen bond in C₂H₂ (ethene) is 1 and that of the carbon-carbon bond is 2.
 $\text{H}_2\text{C}=\text{CH}_2$
 - (ii) The bond order of the oxygen-oxygen bond in an O₂ molecule is 2. $\text{O}=\text{O}$
 - (iii) In a carbon monoxide molecule, the carbon-oxygen bond has a bond order of 3. $\text{C}\equiv\text{O}$
- **Bond angle:** The angle formed between two covalent bonds that originate from the same atom. E.g. bond angle in a water molecule is 104.5°

- bond angle increases with increase in s character: sp^3 (109.28) < sp^2 (120 °) < sp (180 °)
- bond angle decreases with decrease in electronegativity (less repulsions in bond pairs)
 H_2O (104.5) > H_2S (92.2) > H_2Se (91) > H_2Te (89.5)

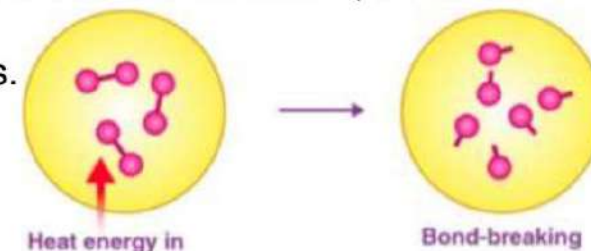


- **Bond length:** It is a measure of the distance between the nuclei of two chemically bonded atoms in a molecule. It is approximately equal to the sum of the covalent radii of the two bonded atoms.



- For covalent bonds, the **bond length is inversely proportional to the bond order** – higher bond orders result in stronger bonds, which are accompanied by stronger forces of attraction holding the atoms together. Short bonds are a consequence of these strong forces of attraction.
- For a given molecule, bond length increases with the size of the other bonded atom. $\text{H-I} > \text{H-Br} > \text{H-Cl} > \text{H-F}$
- Bond length decreases with increase in s-character. sp^3 (110 pm) > sp^2 (109 pm) > sp (108 pm)

- **Bond energy:** It is a measure of the strength of a chemical bond. It can be defined as the energy required to break all covalent bonds of a specific type in one mole of a chemical compound (which is in its gaseous state).
- The strength of a chemical bond is directly proportional to the amount of energy required to break it. Therefore, bond energy is:



- Inversely proportional to the bond length, i.e. longer bonds have lower bond energies.
- Directly proportional to the bond order, i.e. multiple bonds have high bond energies.
- Bond energy increases with increase in the electronegativity difference



- Bond energy decreases with increase in number of lone pairs on bonded atoms due to l.p.- l.p. repulsions





- **Werner's theory of coordination compounds:** Put forward in 1893 in order to explain the structures, formation and nature of bonding in coordination compounds. He was the first inorganic chemist to win Nobel Prize and is also known as **Father of coordination chemistry**.
- Major postulates are: The central metal atom/ ion in a coordination compound exhibits two types of valencies - **primary and secondary**.
 - **Primary valency:**
 - (i) It is the number of charges on the complex ion, which is matched (or neutralized) by the same number of charges from the negative ions) i.e. the **oxidation number** of the ion
 - (ii) It is written outside the coordination sphere.
 - (iii) These are non-directional and do not give any geometry to complex compound.
 - (iv) e.g. $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$, number of primary valencies 3, oxidation state +3
 - **Secondary valency:**
 - i. It is the number of ligand atoms coordinated to the metal i.e. the **coordination number** of the metal.
 - ii. They are satisfied by negative ion or by neutral molecules.
 - iii. It is written inside the coordination sphere.
 - iv. e.g. $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$, coordination number of Co is 6
 - v. They are always directed towards fixed position in space and this cause definite geometry of the coordinate compound. For Example: If a metal ion has six secondary valencies, these are arranged octahedrally around the central metal ion. If the metal ion has four secondary valencies, these are arranged in either tetrahedral or square planar arrangement around the central metal ion. The secondary valency thus determines the stereochemistry of the complex ion.

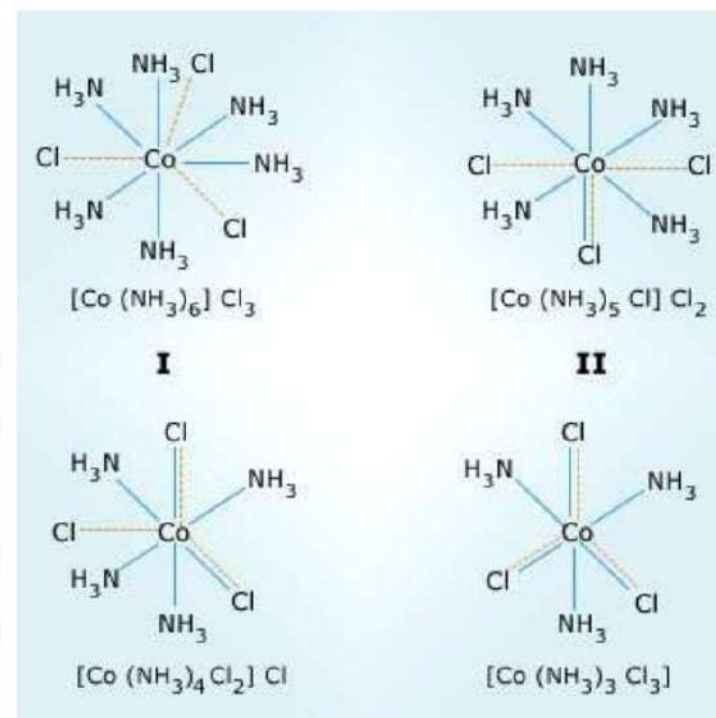


- **Explanation of the structures of four complexes of Co (III) chloride with ammonia:** Werner treated a series of coordinate complexes with an excess of AgNO_3 , and weighed the AgCl precipitated.

- $\text{CoCl}_3 \cdot 6\text{NH}_3 + \text{Excess Ag}^+ \rightarrow 3\text{AgCl} \Rightarrow (3\text{Cl}^- \text{ ion get precipitated})$
- $\text{CoCl}_3 \cdot 5\text{NH}_3 + \text{Excess Ag}^+ \rightarrow 2\text{AgCl} \Rightarrow (2\text{Cl}^- \text{ ion get precipitated})$
- $\text{CoCl}_3 \cdot 4\text{NH}_3 + \text{Excess Ag}^+ \rightarrow \text{AgCl} \Rightarrow (1\text{Cl}^- \text{ ion get precipitated})$
- $\text{CoCl}_3 \cdot 3\text{NH}_3 + \text{Excess Ag}^+ \rightarrow \text{no ppt} \Rightarrow (0\text{Cl}^- \text{ ion get precipitated})$

- **Conclusions:**

- In $\text{CoCl}_3 \cdot 6\text{NH}_3$, 3Cl^- ions react with 3 silver ion form 3 silver chloride precipitates which act as primary valency and 6NH_3 molecules act as secondary valency. Thus the compound is written as $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$.
- Similarly, for $\text{CoCl}_3 \cdot 5\text{NH}_3$, 2Cl^- ions act as primary valency, the remaining 1Cl^- and 5NH_3 ions act as secondary valency. So the compound is $[\text{Co}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_2$
- For $\text{CoCl}_3 \cdot 4\text{NH}_3$, 1Cl^- is primary valency, 2Cl^- and 4NH_3 is secondary valency. So the compound is $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl}$
- For $\text{CoCl}_3 \cdot 3\text{NH}_3$, all 3Cl^- and 3NH_3 ion act as secondary valency So the compound is $[\text{Co}(\text{NH}_3)_3 \text{Cl}_3]$

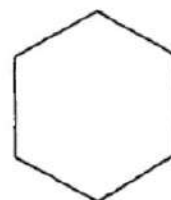


Dotted line represents the primary valency. Normal line represents the secondary valency.

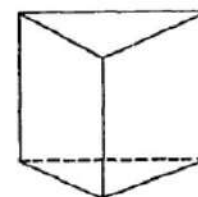


Table 7.2 Number of isomers predicted and actually found

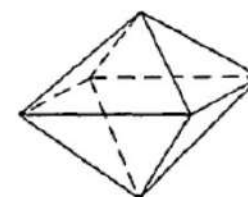
Complex	Observed	Predicted		
		Octahedral	Planar hexagon	Trigonal prism
$[MX_6]$	1	1	1	1
$[MX_5Y]$	1	1	1	1
$[MX_4Y_2]$	2	2	3	3
$[MX_3Y_3]$	2	2	3	3



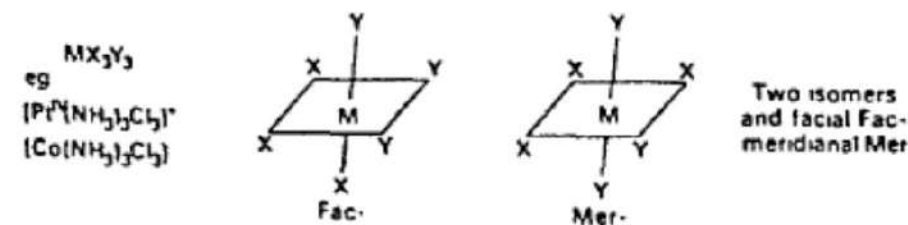
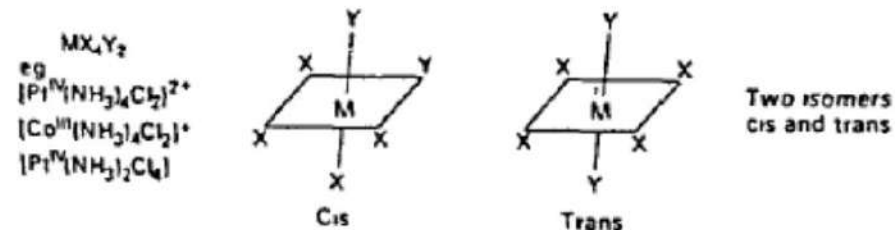
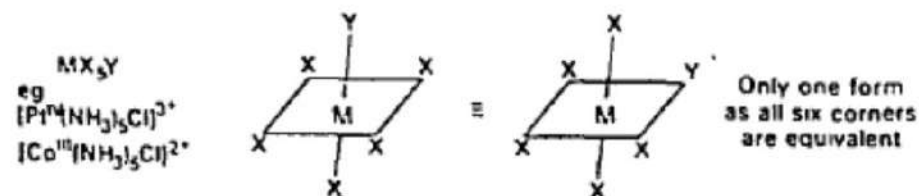
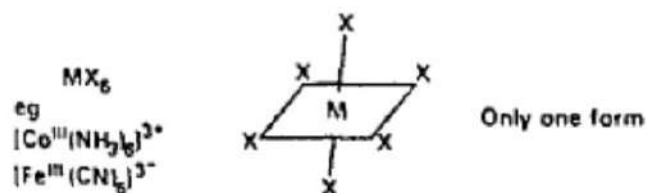
Planar hexagon



Trigonal prism

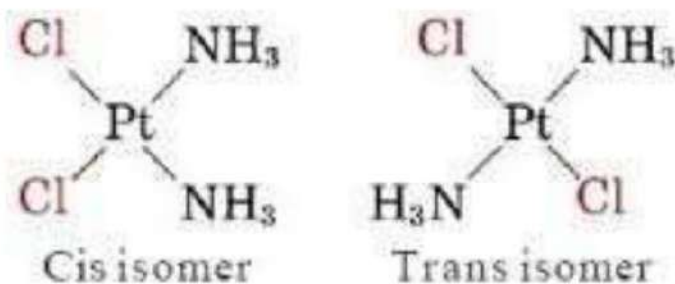


Octahedron





- He also studied the geometry of the complexes in which the **coordination number of the central metal atom is 4**. He proposed that there are two possible structure: Square Planar and Tetrahedral.
- $[\text{PtCl}_2(\text{NH}_3)_2]$ complex: In this complex the coordination number of the metal is 4, Werner found that it existed in two isomeric forms, cis and trans. This shows that all the four ligands lie in the same plane. Therefore the structure should be a square planar or tetrahedral.



Isomerism in square planar complexes



- **Effective Atomic Number (EAN):** It represents the total number of electrons surrounding the nucleus of a metal atom in a metal complex. It is composed of the metal atom's electrons and the bonding electrons from the surrounding electron-donating atoms and molecules. This rule was given by English chemist Nevil V. Sidgwick
- In a number of metal complexes the metal atom tends to surround itself with sufficient ligands that the resulting effective atomic number is numerically equal to the atomic number of the noble-gas element found in the same period in which the metal is situated.
- EAN of the cobalt atom in the complex $[\text{Co}(\text{NH}_3)_6]^{3+}$ is 36, the sum of the number of electrons in the trivalent cobalt ion (24) and the number of bonding electrons from six surrounding ammonia molecules, each of which contributes an electron pair ($2 \times 6 = 12$).
- EAN of the iron atom in the complex $\text{K}_4[\text{Fe}(\text{CN})_6]$ is 36, the sum of the number of electrons in the divalent iron ion (24) and the number of bonding electrons from six surrounding cyanide molecules, each of which contributes an electron pair ($2 \times 6 = 12$).
- **$\text{EAN} = \text{Atomic number (Z)} - \text{Oxidation number (x)} + 2 \times \text{Coordination number}$**
or, **$\text{EAN} = Z - x + 2nL$** , where $n = \text{Number of the ligands}$; $L = \text{Number of co-ordinate bonds formed by ligand}$
- e.g. $[\text{Cu}(\text{NH}_3)_4]^{2+}$: $\text{EAN} = 29 - 2 + 2(4) = 35$ (exception to the EAN rule due to presence of odd number of electrons)
 $[\text{Ni}(\text{CO})_4]$: $\text{EAN} = 28 - 0 + 2(4) = 36$



Effective atomic numbers of some metals in complexes

Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by coordination	EAN
Cr	24	$[\text{Cr}(\text{CO})_6]$	0	12	36
Fe	26	$[\text{Fe}(\text{CN})_6]^{4-}$	2	12	36
Fe	26	$[\text{Fe}(\text{CO})_5]$	0	10	36
Co	27	$[\text{Co}(\text{NH}_3)_6]^{3+}$	3	12	36
Ni	28	$[\text{Ni}(\text{CO})_4]$	0	8	36
Cu	29	$[\text{Cu}(\text{CN})_4]^{3-}$	1	8	36
Pd	46	$[\text{Pd}(\text{NH}_3)_6]^{4+}$	4	12	54
Pt	78	$[\text{PtCl}_6]^{2-}$	4	12	86
Fe	26	$[\text{Fe}(\text{CN})_6]^{3-}$	3	12	35
Ni	28	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	2	12	38
Pd	46	$[\text{PdCl}_4]^{2-}$	2	8	52
Pt	78	$[\text{Pt}(\text{NH}_3)_4]^{2+}$	2	8	84



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Engineering Chemistry-I (BS-109)

Chemical Bonding-2

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Assistant Professor

USAR, GGSIPU



Valence Shell Electron Pair (VSEPR) Theory: Given by Gillespie-Nyholm in 1957

“Whenever there is a repulsion between the pairs of valence electrons in all atoms, the atoms will rearrange themselves in a geometric shape so as to minimize the electron pair repulsion.” (molecule must have minimum energy and maximum stability). This arrangement of the atom determines the geometry of the resulting molecule.

Postulates of VSEPR Theory:

- In polyatomic molecules (i.e. molecules made up of three or more atoms), one of the constituent atoms is identified as the central atom to which all other atoms belonging to the molecule are linked.
- The total number of valence shell electron pairs decides the shape of the molecule.
- The electron pairs have a tendency to orient themselves in a way that minimizes the electron-electron repulsion between them and maximizes the distance between them.
- If the central atom of the molecule is surrounded by bond pairs of electrons, then, the asymmetrically shaped molecule can be expected and if the central atom is surrounded by both lone pairs and bond pairs of electrons, the molecule would tend to have a distorted shape.
- The VSEPR theory can be applied to each resonance structure of a molecule.
- The strength of the repulsion is strongest in two lone pairs and weakest in two bond pairs.
 $l.p.-l.p > l.p.-b.p. > b.p.-b.p.$
- If electron pairs around the central atom are closer to each other, they will repel each other. This results in an increase in the energy of the molecules. If the electron pairs lie far from each other, the repulsions between them will be less and eventually, the energy of the molecule will be low.
- The magnitude of repulsions between b.p. of electrons depends on the electronegativity difference between the central atom and other atoms.
- **Triple bond > double bond > single bond** : order of repulsion



Number of
valence electrons

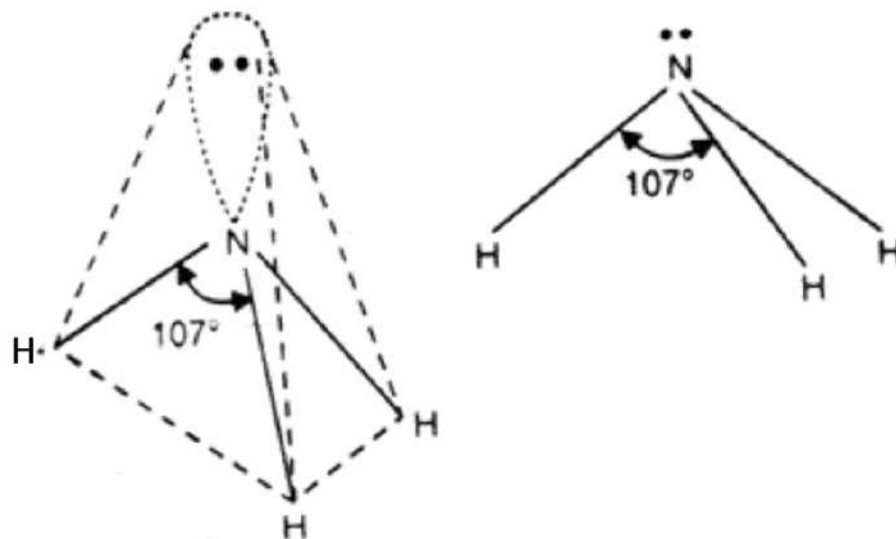
VSEPR Geometries					
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal Pyramid	 Bent or Angular		
5	 Trigonal Bipyramid	 Sawhorse or Seesaw	 T-shape	 Linear	
6	 Octahedral	 Square Pyramid	 Square Planar	 T-shape	 Linear

Number of electron pairs in outer shell	Shape of molecule	Bond angles
2	linear	180°
3	plane triangle	120°
4	tetrahedron	109°28'
5	trigonal bipyramid	120° and 90°
6	octahedron	90°
7	pentagonal bipyramid	72° and 90°



- **Structure of NH₃:**

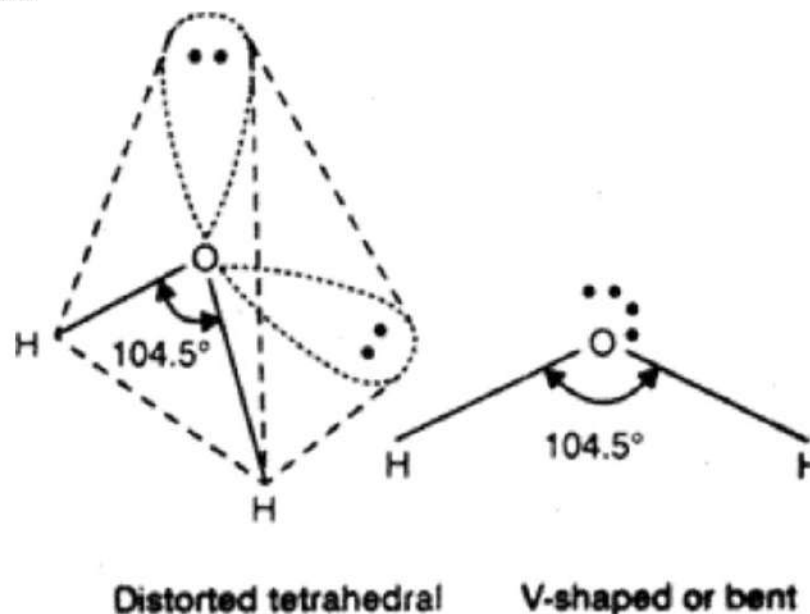
- N is the central atom having electronic configuration of $1s^2 2s^2 2p^3$ (**5** electrons in its valence shell)
- Three electrons participate in the bond formation with H while 2 electrons do not bond => **3 b.p. and 1 l.p.**
- Thus NH₃ has 4 valence electron pairs, expected geometry: tetrahedral
- Presence of l.p. on N will repel the b.p. more than b.p.-b.p. repulsions. This leads to decrease in H-N-H bond angle from $109^\circ 28'$ to $107^\circ 48'$
- Final geometry: **Pyramidal**





- **Structure of H₂O:**

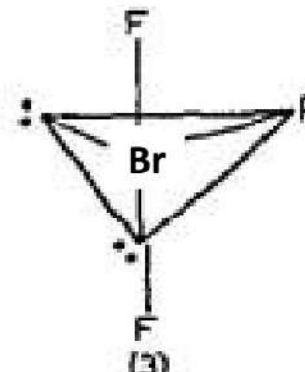
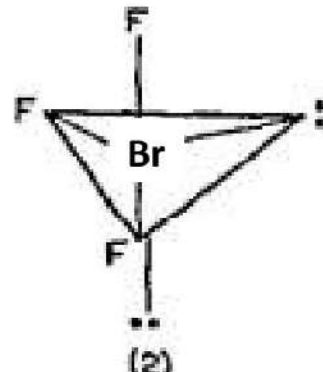
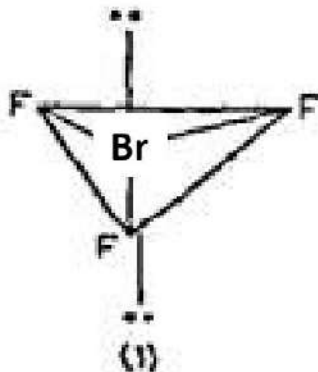
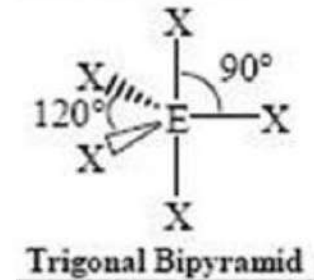
- O is the central atom having electronic configuration of $1s^2 2s^2 2p^4$ (6 electrons in its valence shell)
- Two electrons participate in the bond formation with H while 4 electrons do not bond => **2 b.p. and 2 l.p.**
- Thus H₂O has 4 valence electrons pairs, expected geometry: tetrahedral
- Due to the presence of two l.p. on O, the repulsion will occur between both the l.p.'s, l.p.-b.p and both the b.p.'s. Since the extent of repulsions between two l.p.'s is more, the water molecule is more deviated from the symmetrical tetrahedral geometry resulting in bent shape for the water molecule where the H-O-H angle is 104.5 °.
- Final geometry: **Bent or angular or V-shaped**





• Structure of BrF₃:

- Br is the central atom, which belongs to halogen group (17) having electronic configuration of 1s² 2s² 2p⁶ 3s² 3p⁶ 4s² 3d¹⁰ 4p⁵ (7 electrons in its valence shell)
- Three electrons participate in the bond formation with F while 4 electrons do not bond => **3 b.p. and 2 l.p.**
- Thus BrF₃ has 5 electrons pairs resulting into **trigonal bipyramidal geometry** (5 corners)
- TBP is not a regular shape since all the bond angles are not same (atoms at equatorial positions are at 120° while axial corners are at 90° with the equatorial atoms)
- Possible structures:



- Most symmetrical, but six 90° repulsions between l.p.-b.p
- No l.p.-l.p at 90°

- Three 90° repulsions between l.p.-b.p
- 1 l.p.-l.p. at 90°

- Four 90° repulsions between l.p.-b.p
- No l.p.-l.p. at 90°

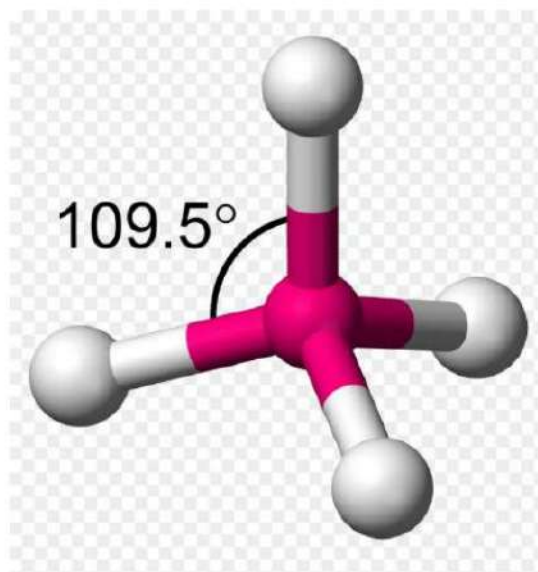
In tbp geometry the l.p. will be located at equatorial position rather than at apical position as this minimizes the repulsive forces

Structure 3 is most probable and the observed bond angles are 87° 40' (slight distortion to 90° is due to 2 l.p.)



- **Structure of SiF_4 :**

- Si is the central atom having valence electronic configuration of $3s^2 3p^2$ (4 electrons in its valence shell)
- All the four electrons participate in the bond formation with F \Rightarrow **4 b.p. and 0 l.p.**
- Thus SiF_4 has 4 valence electrons pairs.
- Geometry: **Tetrahedral**





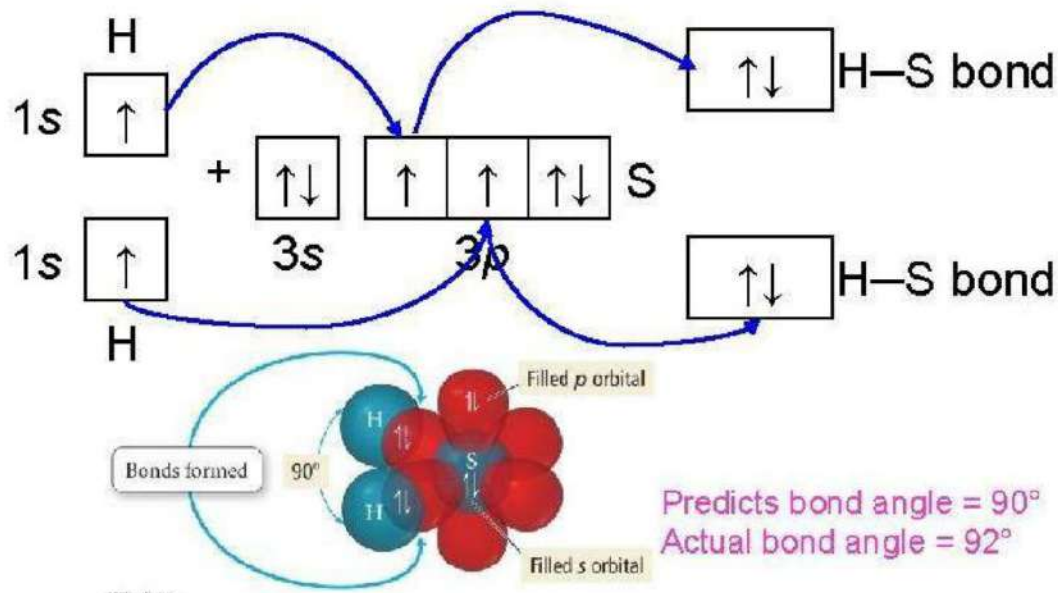
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- **Valence Bond Theory (VBT):** describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms.
- According to valence bond theory, a covalent bond results when two conditions are met:
 1. an orbital on one atom overlaps an orbital on a second atom and
 2. the single electrons in each orbital combine to form an electron pair.
- Salient features:
 - Covalent bonds are formed when two valence orbitals (half-filled) belonging to two different atoms overlap on each other. The electron density in the area between the two bonding atoms increases as a result of this overlapping, thereby increasing the stability of the resulting molecule
 - The presence of many unpaired electrons in the valence shell of an atom enables it to form multiple bonds with other atoms. The paired electrons present in the valence shell do not take part in the formation of chemical bonds as per the valence bond theory.
 - Covalent chemical bonds are directional and are also parallel to the region corresponding to the atomic orbitals that are overlapping.
 - the difference in the length and strength of the chemical bonds in H₂ and F₂ molecules can be explained by the difference in the overlapping orbitals in these molecules.
 - The covalent bond in an HF molecule is formed from the overlap of the 1s orbital of the hydrogen atom and a 2p orbital belonging to the fluorine atom, which is explained by the valence bond theory.



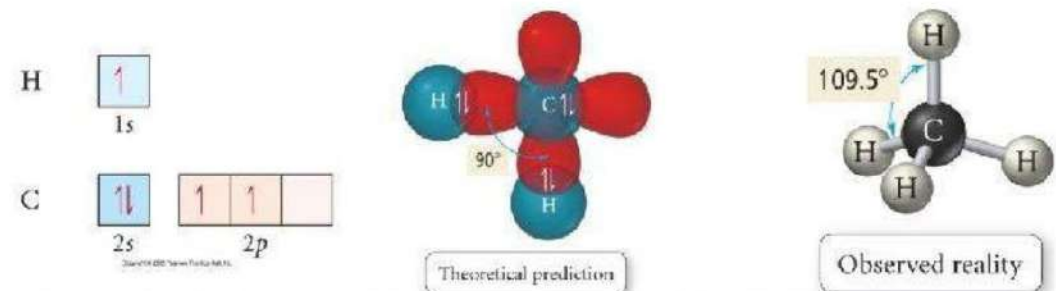
Atomic Orbital in the Bonding of H₂S



Limitation of VBT

Many molecules such as methane (tetrahedral, bond angle = 109.5°) can not be explained by half-filled atomic orbitals

$\checkmark C = 2s^2 2p_x^1 2p_y^1 2p_z^0$ would predict two or three bonds that are 90° apart





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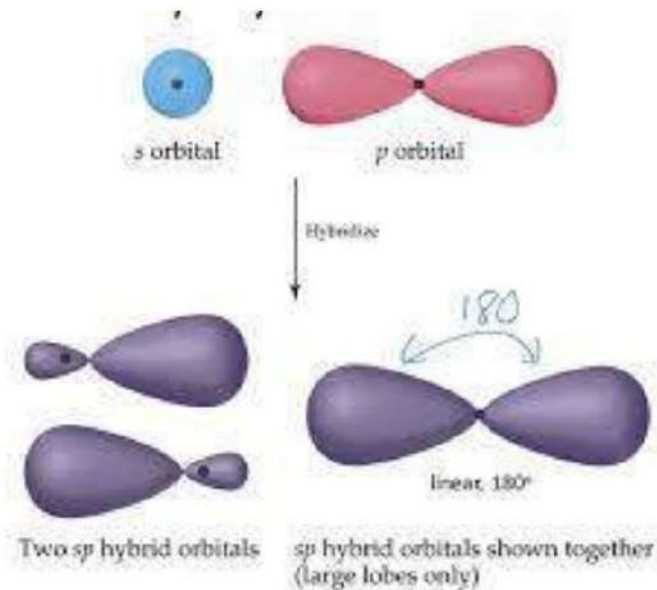
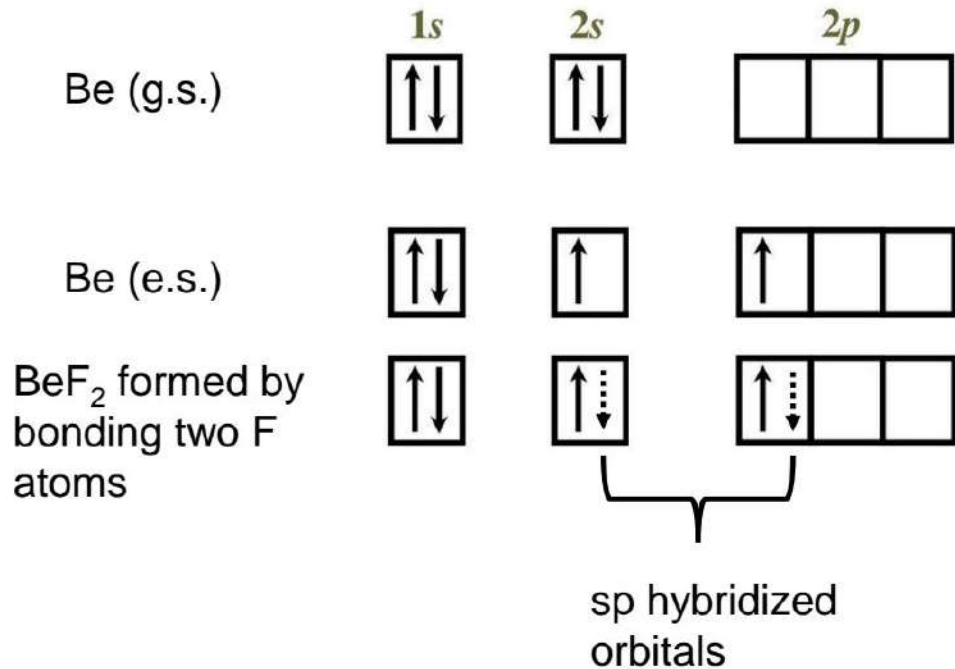
- **Hybridization:** Concept of mixing two atomic orbitals to give rise to a new type of hybridized orbitals. This intermixing usually results in the formation of hybrid orbitals having entirely different energies, shapes, etc.
- Redistribution of the energy of orbitals of individual atoms to give orbitals of equivalent energy happens when two atomic orbitals combine to form a hybrid orbital in a molecule. This process is called hybridization.
- Salient features:
 - Atomic orbitals of comparable energies are mixed together and mostly involves the merging of two 's' orbitals or two 'p' orbitals or mixing of an 's' orbital with a 'p' orbital as well as 's' orbital with a 'd' orbital. The new orbitals thus formed are known as hybrid orbitals.
 - Hybrid orbitals are quite useful in explaining atomic bonding properties and molecular geometry
 - Number of hybrid orbitals = number of pure orbitals
 - Hybridization happens only during the bond formation and not in an isolated gaseous atom.
 - Hybrid orbital generally form either sigma bond or contain a l.p. of electrons, but do not form pi bond



• **Types of hybridization:**

1) **sp hybridization:** mixing of one s and one p-orbital to form two new equivalent orbitals called sp hybridized orbitals.

- Each sp hybridized orbital has an equal amount of s and p character – 50% s and 50% p character.
- Shape: **Linear** (180 °)
- Eg. **BeF₂**

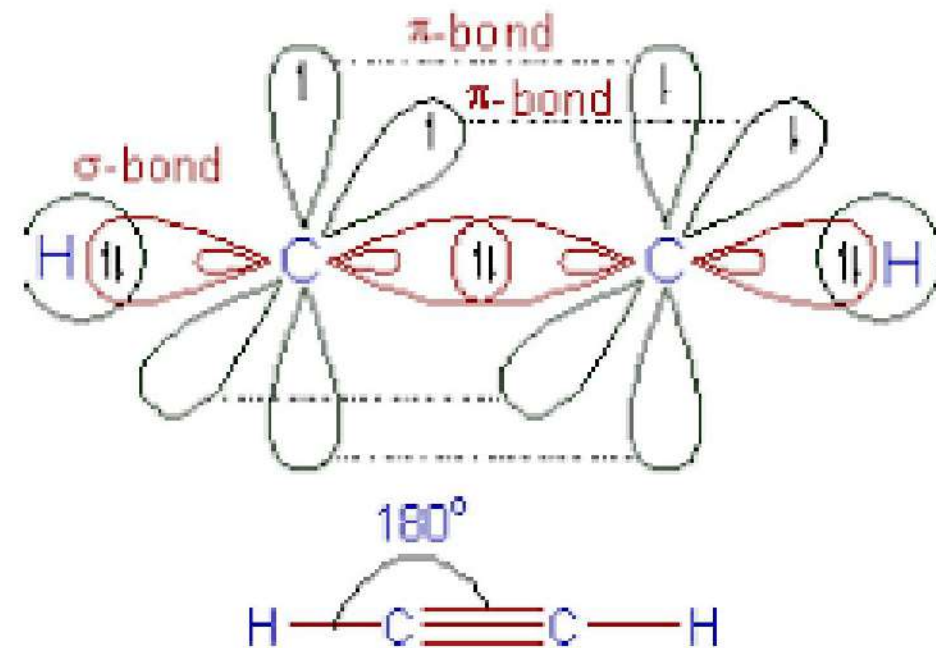
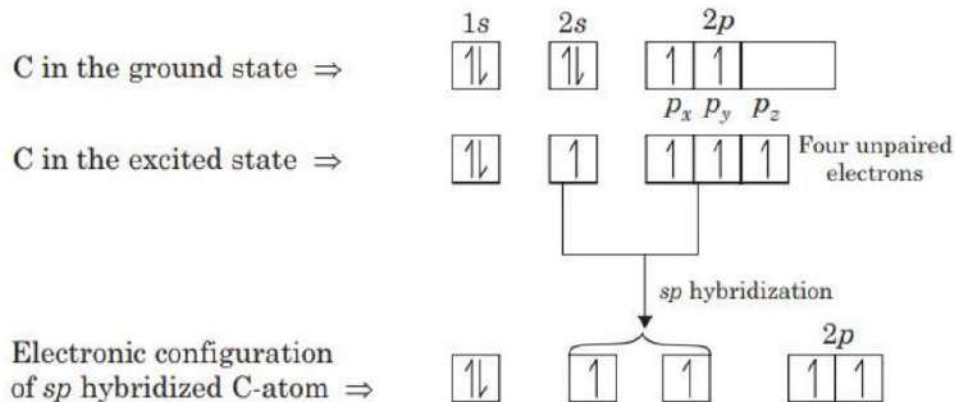


The two sp hybridized orbitals are oriented at 180 ° and the shape is linear



1) sp hybridization: Eg. Ethyne

Electronic configuration of:

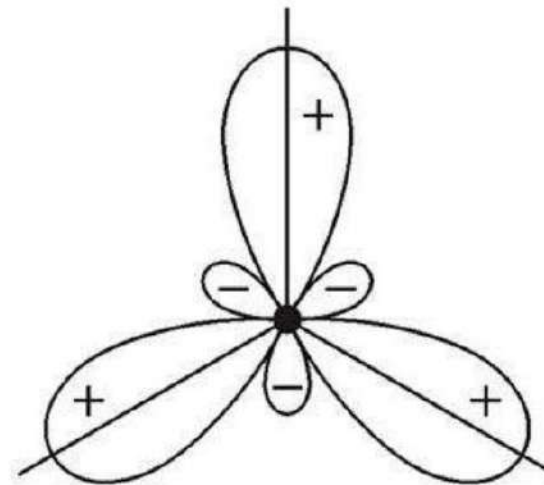
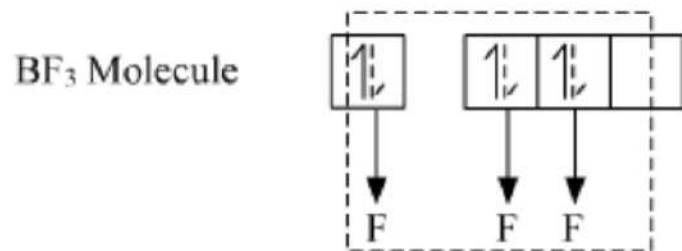
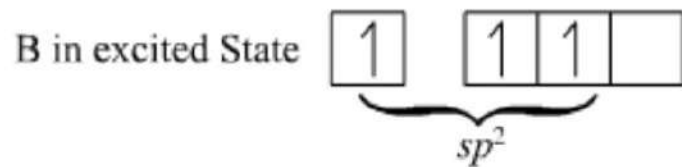
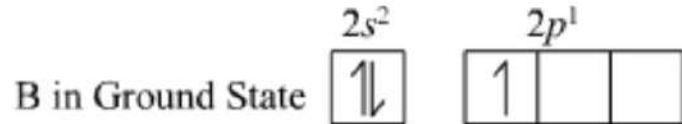


Linear structure of acetylene molecule

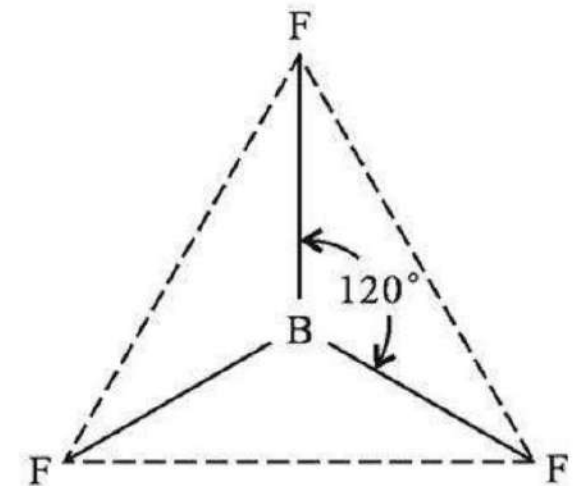


2) **sp² hybridization**: mixing of one s and two p-orbitals to form three new equivalent orbitals called sp² hybridized orbitals.

- Each sp² hybridized orbital has 33.3% s and 66.6% p character.
- Shape: **Trigonal planar** (120 °)
- Eg. **BF₃**



Three sp² hybrid orbitals

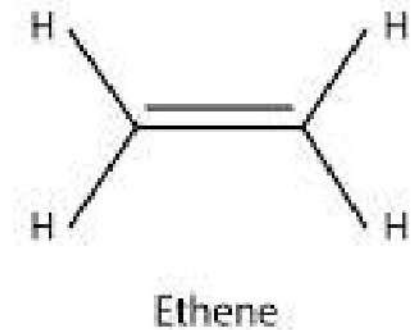
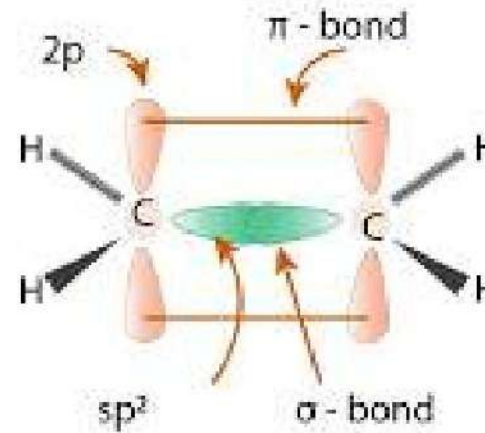
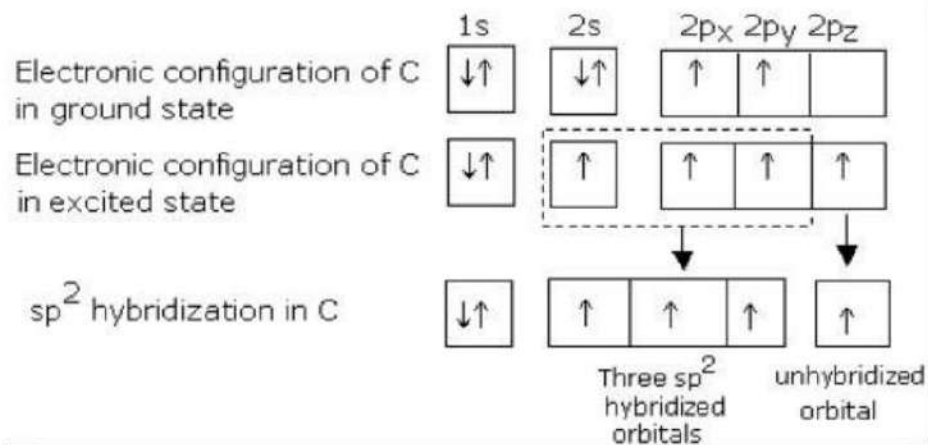


Trigonal planar

The three sp² hybridized orbitals are oriented at 120 ° and the shape is trigonal planar



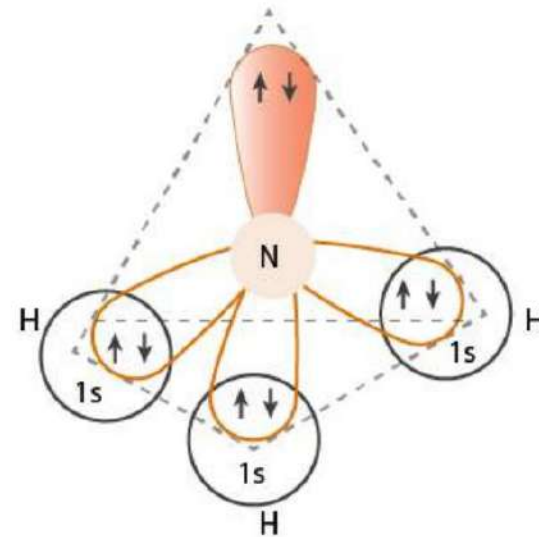
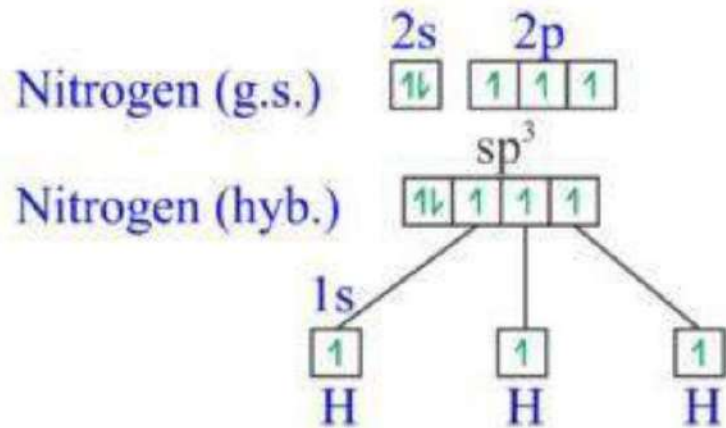
2) sp^2 hybridization: Eg. Ethene



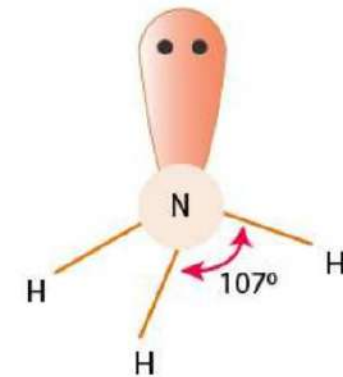


3) sp^3 hybridization: Eg. NH_3 (electronic config of N: $1s^2 2s^2 2p^3$)

- Three half-filled sp^3 orbitals of nitrogen form bonds to hydrogen's three atoms. However, the fourth sp^3 orbital that is present is a nonbonding pair of hybridized orbital and is normally used for holding the lone pair.



Orbital overlap in NH_3



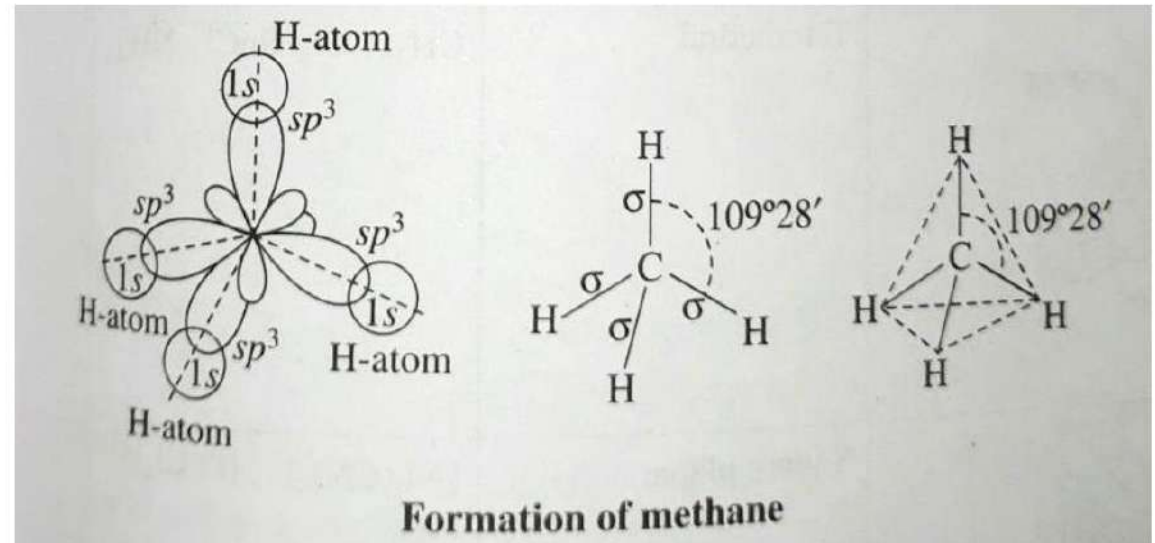
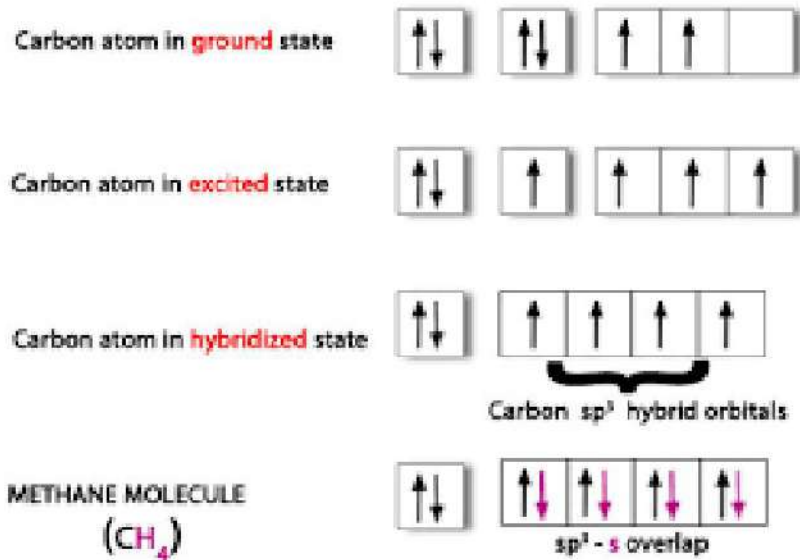
Pyramidal shape

The four sp^3 hybridized orbitals are oriented at $107^\circ 28'$ and the shape is pyramidal



3) **sp³ hybridization**: mixing of one s and three p-orbitals to form four new equivalent orbitals called sp³ hybridized orbitals.

- Each sp³ hybridized orbital has 25% s and 75% p character.
- Shape: **Tetrahedral** (109 ° 28')
- Eg. CH₄

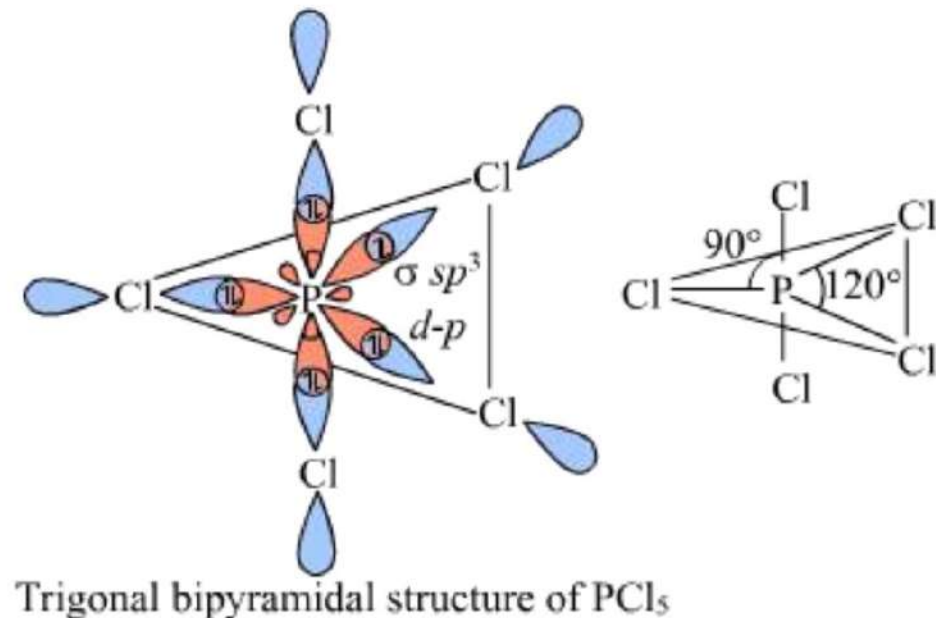
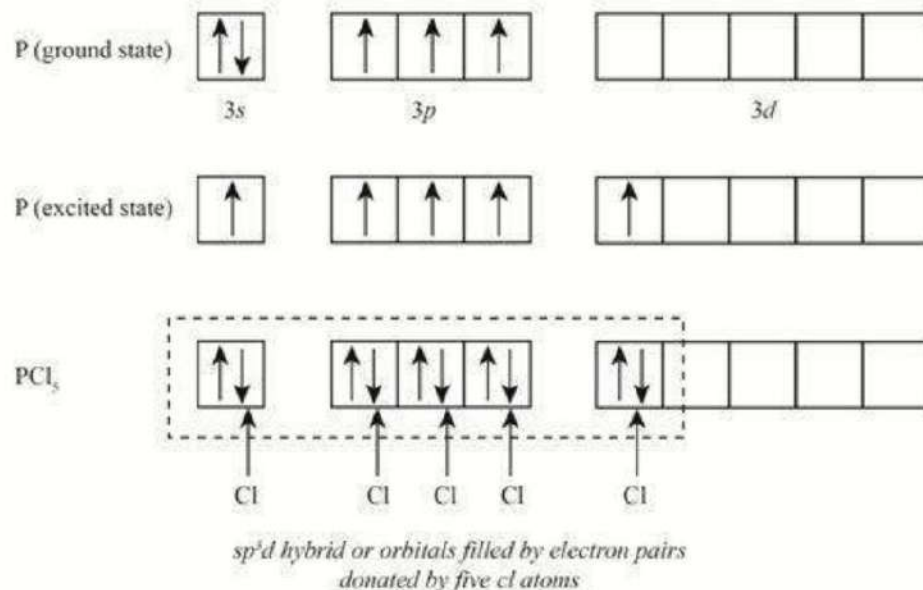


The four sp³ hybridized orbitals are oriented at 109 ° 28' and the shape is tetrahedral



4) **sp^3d hybridization:** mixing of 1s orbital, 3p orbitals and 1d orbital to form 5 sp^3d hybridized orbitals of equal energy

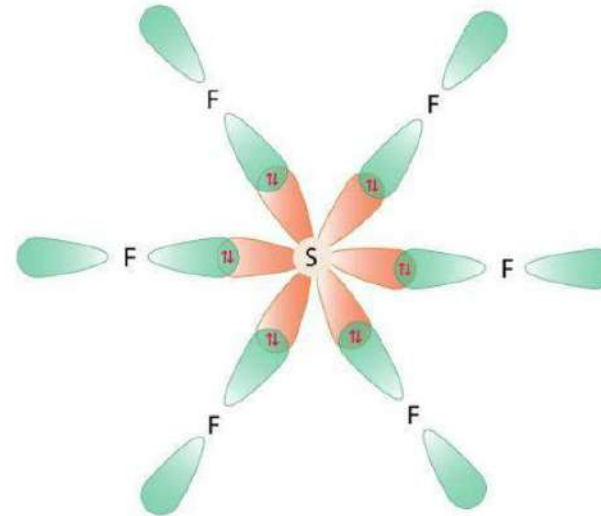
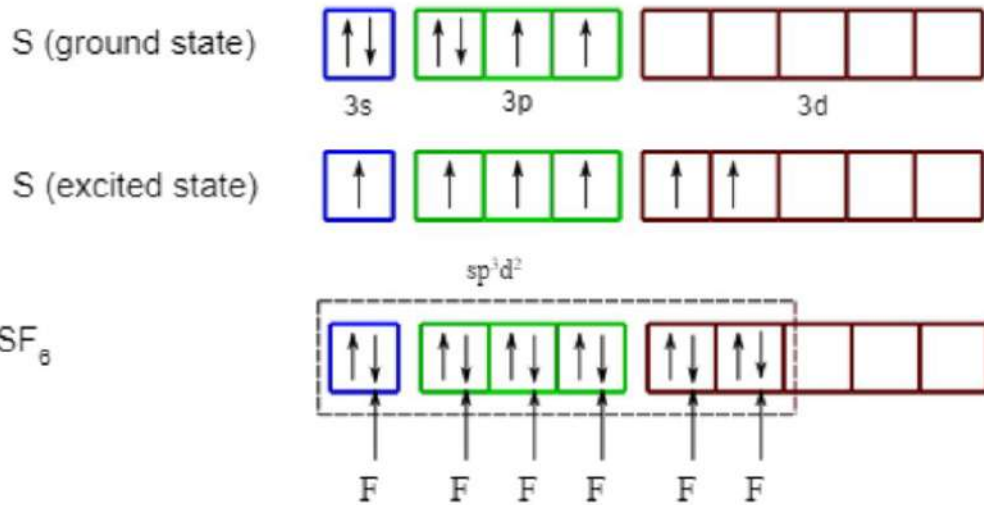
- Shape: **Trigonal bipyramidal**
- Three hybrid orbitals lie in the horizontal plane inclined at an angle of 120° to each other known as the equatorial orbitals.
- The remaining two orbitals lie in the vertical plane at 90 degrees plane of the equatorial orbitals known as axial orbitals.
- Eg. **PCl_5**



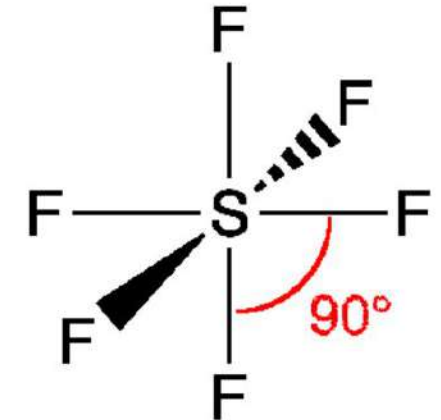


4) sp^3d^2 hybridization: has 1s, 3p and 2d orbitals, that undergo intermixing to form 6 identical sp^3d^2 hybrid orbitals.

- Shape: **Octahedral**
- Six hybrid orbitals are inclined at an angle of 90 degrees to one another.
- Eg. SF_6



Octahedral structure of sulphur hexafluoride



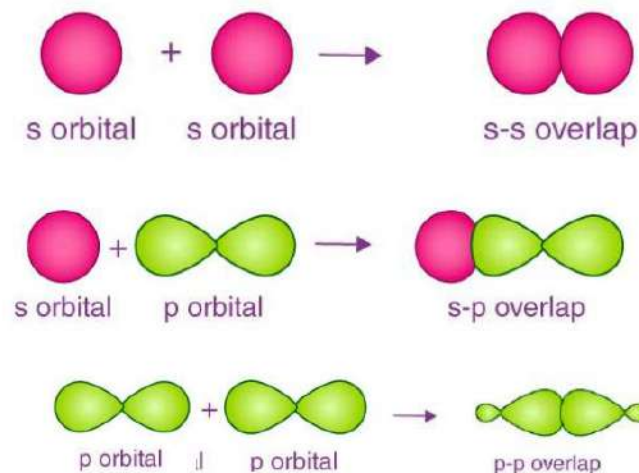
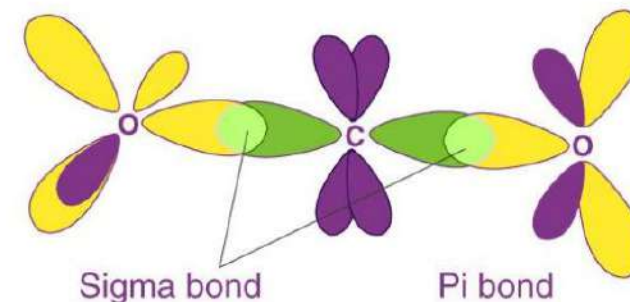


- **Sigma and Pi bonds:** Sigma and pi bonds are types of covalent bonds that differ in the overlapping of atomic orbitals. Covalent bonds are formed by the overlapping of atomic orbitals. **Sigma bonds are a result of the head-to-head overlapping of atomic orbitals whereas pi bonds are formed by the lateral overlap of two atomic orbitals.**

- **The Sigma (σ) Bond**

This type of covalent bond is formed by head-on positive (same phase) overlap of atomic orbitals along the internuclear axis. Sigma bonds are the strongest covalent bonds, owing to the direct overlapping of the participating orbitals. The electrons participating in a σ bond are commonly referred to as σ electrons. It can be formed by:

- a) s-s overlap: An s orbital must be half-filled before it overlaps with another.
- b) s-p overlap: one half filled s orbital overlaps with one half-filled p orbital along the internuclear axis, forming a covalent bond. This type of overlapping can be observed in ammonia. An NH₃ molecule features 3 sigma bonds, formed by the overlap of the 2p_x, 2p_y, and 2p_z orbitals belonging to the nitrogen atom and the 1s orbitals of the three hydrogen atoms.
- c) p-p overlap: one half-filled p orbital from each participating atom undergoes head-on overlapping along the internuclear axis.

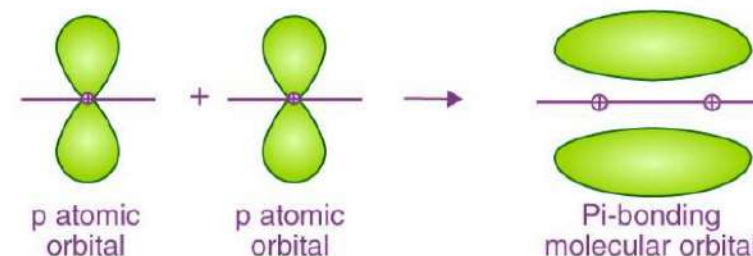




• The Pi (π) Bond

Pi bonds are formed by the sidewise positive (same phase) overlap of atomic orbitals along a direction perpendicular to the internuclear axis. During the formation of π bonds, the axes of the atomic orbitals are parallel to each other whereas the overlapping is perpendicular to the internuclear axis.

Pi Bonds are generally weaker than sigma bonds, owing to the significantly lower degree of overlapping. Generally, double bonds consist of one sigma and one pi bond, whereas a typical triple bond is made up of two π bonds and one σ bond. It is important to note that a combination of sigma and pi bonds is always stronger than a single sigma bond.



Sigma Bond	Pi Bond
The overlapping orbitals can be pure or hybrid	The overlapping orbitals must be unhybridized
These bonds are strong and have high bond 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 shape of molecules



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- **Molecular Orbital Theory:** Given by F. Hund and R. S. Mulliken to describe the structure and properties of different molecules. Each atom tends to combine together and form molecular orbitals. As a result of such arrangement, the valence electrons are considered to be associated with different nuclei in the molecule.
- Uses linear combination of atomic orbitals (LCAO) to form molecular orbitals concept.
- Salient features:
 - The atomic orbitals overlap to form new orbitals called **molecular orbitals**. When two atomic orbitals overlap they lose their identity and form new orbitals called molecular orbitals.
 - The electrons in the molecules are filled in the new energy states called the Molecular orbitals similar to the electrons in an atom being filled in an energy state called atomic orbitals. (Aufbau, Hund's and Pauli Exclusion)
 - There exist different types of molecular orbitals viz; bonding molecular orbitals, anti-bonding molecular orbitals, and non-bonding molecular orbitals. Of these, anti-bonding molecular orbitals will always have higher energy than the parent orbitals whereas bonding molecular orbitals will always have lower energy than the parent orbitals.
 - The probability of finding the electronic distribution in a molecule around its group of nuclei is given by the molecular orbital.
 - The two combining atomic orbitals should possess energies of comparable value and similar orientation. For example, 1s can combine with 1s and not with 2s.
 - The number of molecular orbitals formed is equal to the number of atomic orbitals combining.
 - The shape of molecular orbitals formed depends upon the shape of the combining atomic orbitals.



- **Linear Combination of Atomic Orbitals:** An atomic orbital is an electron wave; the waves of the two atomic orbitals may be in phase or out of phase. Suppose Ψ_A and Ψ_B represent the amplitude (or wavefunction) of the electron wave of the atomic orbitals of the two atoms A and B. Then wavefunction for the molecular orbital Ψ_{AB} obtained by linear combination of Ψ_A and Ψ_B is given as:

$\Psi_{AB} = c_1 \Psi_A + c_2 \Psi_B$ where, c_1 and c_2 are constants chosen to give a minimum energy for Ψ_{AB}
so, probability of finding an electron in a given volume space is Ψ^2

Therefore,

$$\Psi_{AB}^2 = (c_1 \Psi_A + c_2 \Psi_B)^2$$

$$\Psi_{AB}^2 = \underbrace{(c_1^2 \Psi_A^2)}_A + 2 \underbrace{c_1 c_2 \Psi_A \Psi_B}_{\text{Overlap integral}} + \underbrace{c_2^2 \Psi_B^2}_B$$

Prob of finding an
electron on atom A

Overlap integral

Prob of finding an
electron on atom B

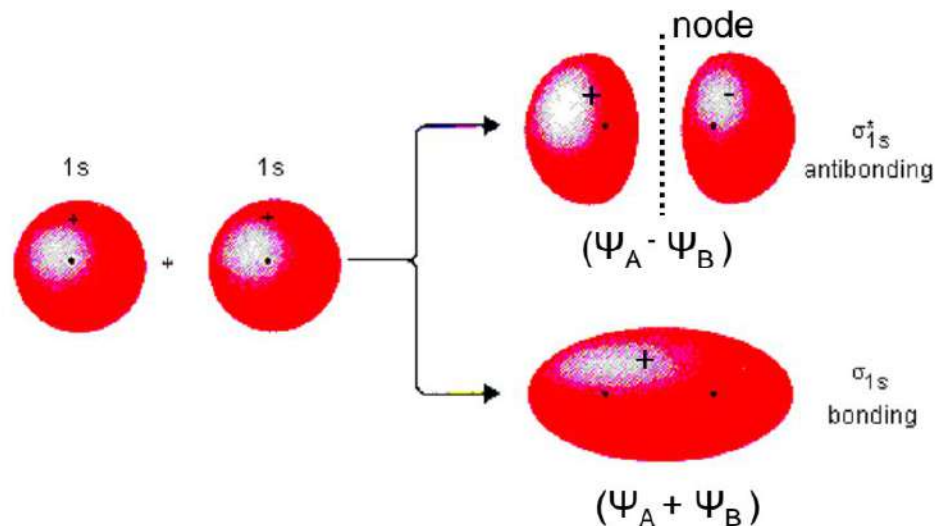
- Overlap integral represents the main difference between the electron clouds in individual atoms and in the molecule. Larger this term, stronger is the bond
- **Conditions for LCAO:**
 1. The atomic orbitals combining to form molecular orbitals should have comparable energy.
 2. The combining atoms should have the same symmetry around the molecular axis for proper combination, otherwise, the electron density will be sparse. For e.g. all the sub-orbitals of 2p have the same energy but still, 2pz orbital of an atom can only combine with a 2pz orbital of another atom but cannot combine with 2px and 2py orbital as they have a different axis of symmetry.
 3. The two atomic orbitals will combine to form molecular orbital if the overlap is proper. Greater the extent of overlap of orbitals, greater will be the nuclear density between the nuclei of the two atoms.



- **Combination of s-s orbitals:** Consider the H_2 molecule, for example. One of the molecular orbitals in this molecule is constructed by adding the mathematical wave functions for the two 1s atomic orbitals that come together to form this molecule (waves are in same phase). Another orbital is formed by subtracting one of these functions from the other (waves are out of phase). The two combinations can be written as:

$$\Psi_{AB} = N(\Psi_A + \Psi_B) \text{ where, } N \text{ is the normalizing constant}$$

and , $\Psi_{AB} = N(\Psi_A - \Psi_B)$



- Two lobes of opposite sign cancelling and therefore, zero electron density between the nuclei
- Anti-bonding molecular orbital
- Higher in energy than the original atomic orbitals

- Increased electron density between the nuclei
- Bonding molecular orbital
- Lower in energy than the original atomic orbitals

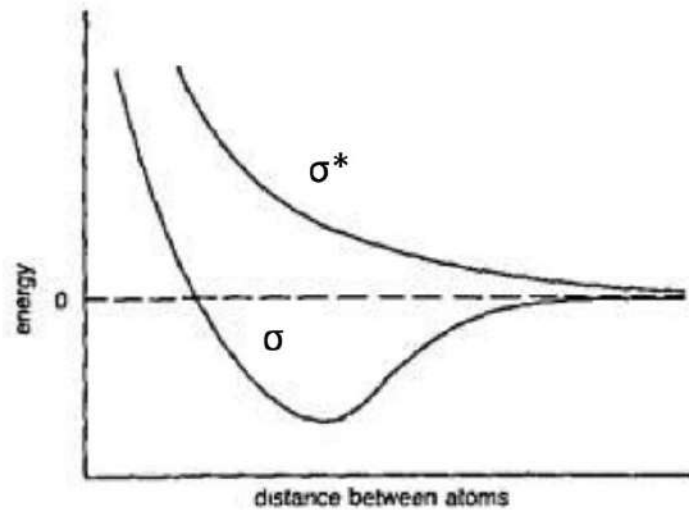


Figure 4 15 Energy of $\psi_{(g)}$ and $\psi_{(u)}$ molecular orbitals

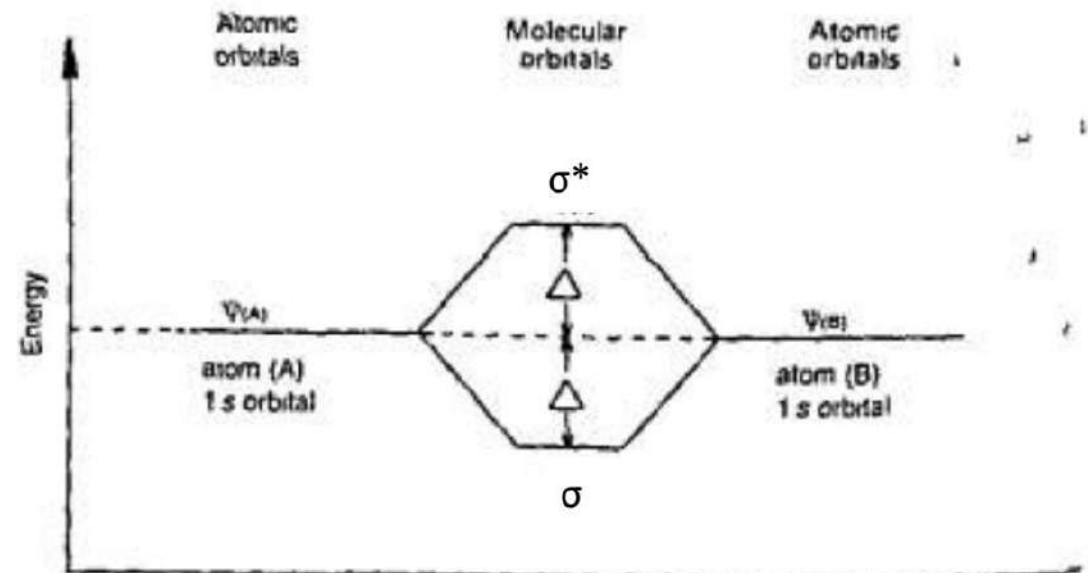


Figure 4 16 Energy levels of $s-s$ atomic and molecular orbitals

Δ = stabilization energy



- **Combination of s-p orbitals:** An s orbital may combine with a p orbital if the lobes of the p orbital are pointing along the axis joining the nuclei.

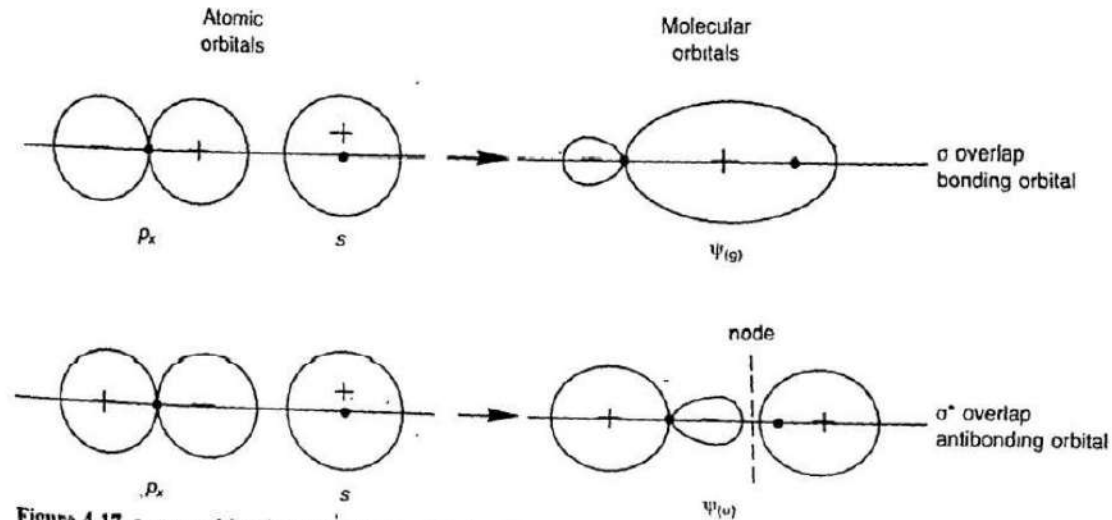
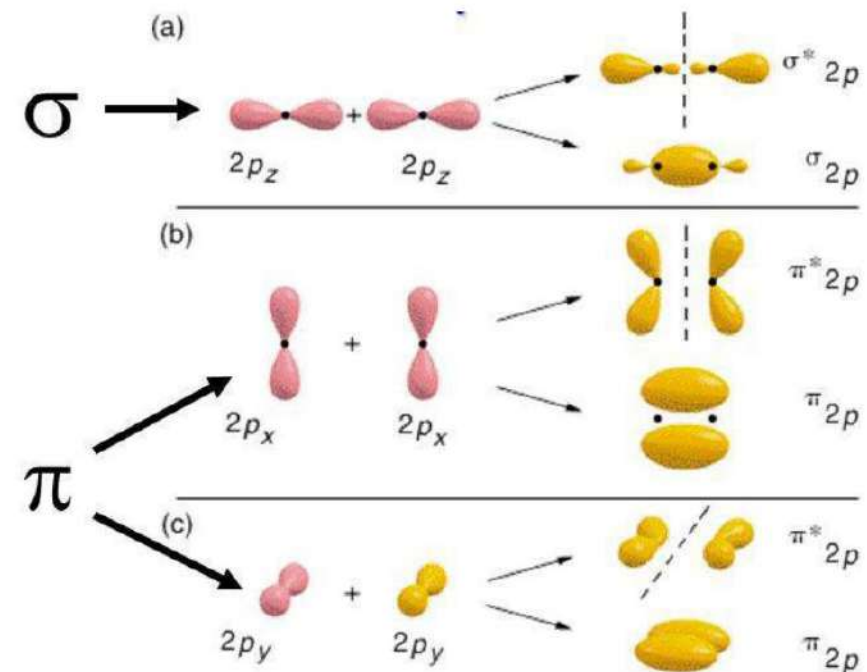


Figure 4.17 s - p combination of atomic orbitals.



- **Combination of p-p orbitals:**

- a) overlap of two p orbitals along the internuclear axis results in the generation of σ_{2p} bonding and σ_{2p}^* antibonding orbitals.
- b) Overlap of two p orbitals with lobes perpendicular to the internuclear axis results in the formation of π_{2p} bonding and π_{2p}^* antibonding orbitals.



- 1) 1 sigma bond through overlap of orbitals along the internuclear axis.
- 2) 2 pi bonds through overlap of orbitals above and below (or to the sides) of the internuclear axis.



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Molecular Orbital Theory	
Bonding Molecular Orbitals	Anti-Bonding Molecular Orbitals
Molecular orbitals formed by the additive effect of the atomic orbitals is called bonding molecular orbitals	Molecular orbitals formed by the subtractive effect of atomic orbitals is called anti-bonding molecular orbitals
Probability of finding the electrons is more in the case of bonding molecular orbitals	Probability of finding electrons is less in antibonding molecular orbitals. There is also a node between the anti-bonding molecular orbital between two nuclei where the electron density is zero.
The electron density, in the bonding molecular orbital in the internuclear region, is high. As a result, the nuclei are shielded from each other and hence the repulsion is very less.	The electron density in the antibonding molecular orbital in the internuclear region is very low and so the nuclei are directly exposed to each other. Therefore the nuclei are less shielded from each other.
The bonding molecular orbitals are represented by σ , π , δ .	The corresponding anti-bonding molecular orbitals are represented by σ^* , π^* , δ^* .



- **Order of energy of molecular orbitals:**

- The increasing order of energies of various molecular orbitals in simple homonuclear diatomic molecules is given below:



where, $\pi 2p_x$ and $\pi 2p_y$; and $\pi^* 2p_x$ and $\pi^* 2p_y$ are of same energy and are therefore, degenerate

- For molecules like Li, Be, B, C and N, the order of energy changes as:



Reason: This phenomenon is explained by **s-p mixing**. All the elements in the second period before oxygen have the small difference in energy between 2s and 2p_z orbitals, and they also have same symmetry. This results in s-p mixing (combination), which lowers the energy of the $\sigma(2s)$ and $\sigma^*(2s)$ and increases the energy of the $\sigma(2p_z)$ and $\sigma^*(2p_z)$ molecular orbitals. By moving towards right in a period, the s orbital gets more stabilized than the p orbital and the difference in their energies increases, making the s-p mixing for oxygen and higher atoms much smaller.



- **Bond Order:**

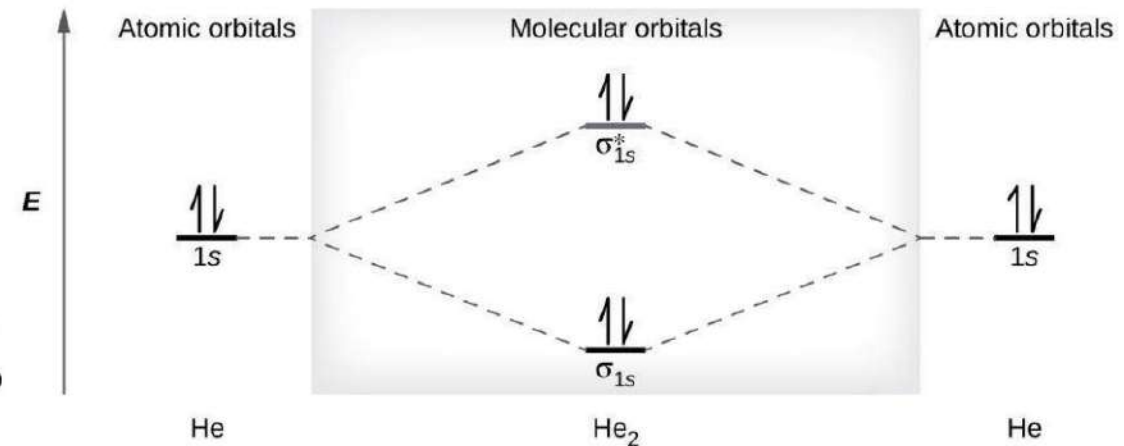
- Bond order is the number of chemical bonds between a pair of atoms.
- Bond order is an index of bond strength.
- Bond order is defined as half the difference between the number of bonding and antibonding electrons.
- **Bond Order = $\frac{1}{2} [N_b - N_a]$** where,
Nb is that the number of bonding electrons
Na is that the number of antibonding electrons
- Stable bonds have a positive bond order.
- If BO is 1, 2 or 3, it implies the presence of single, double or triple bond, respectively
- If BO is zero, it implies that there is no bond between two atoms i.e. molecule does not exist

- **Why He₂ does not exist?**

E.C. of He: $(\sigma 1s)^2$

$$\text{BO: } \frac{1}{2} [2-2] = 0$$

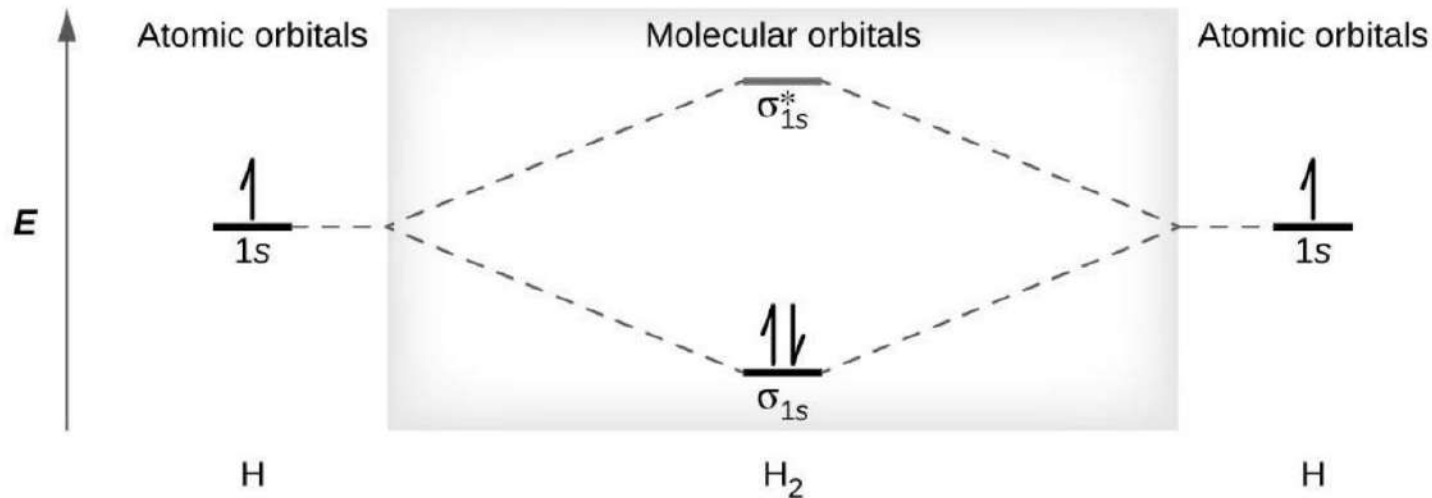
Two helium atoms do not combine to form a dihelium molecule, He₂, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. The net energy change would be zero, so there is no driving force for helium atoms to form the diatomic molecule.





- **Molecular orbital diagram for simple homonuclear diatomic molecules:**

1. **Hydrogen molecule (H_2):** When the atomic orbitals of the two H-atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital. A dihydrogen molecule, H_2 , readily forms, because the energy of a H_2 molecule is lower than that of two H atoms. The σ_{1s} orbital that contains both electrons is lower in energy than either of the two 1s atomic orbitals. A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ_{1s} bonding orbital; the electron configuration is $(\sigma_{1s})^2$.



A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$BO \text{ in } H_2 = (2-0)/2 = 1$$

Because the bond order for the H-H bond is equal to 1, the bond is a single bond.

Diamagnetic molecule (no unpaired electrons)



2. Nitrogen molecule (N₂):

7 electrons in N atom: $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x^2, \pi 2p_y^2)(\sigma 2p_z)^2$

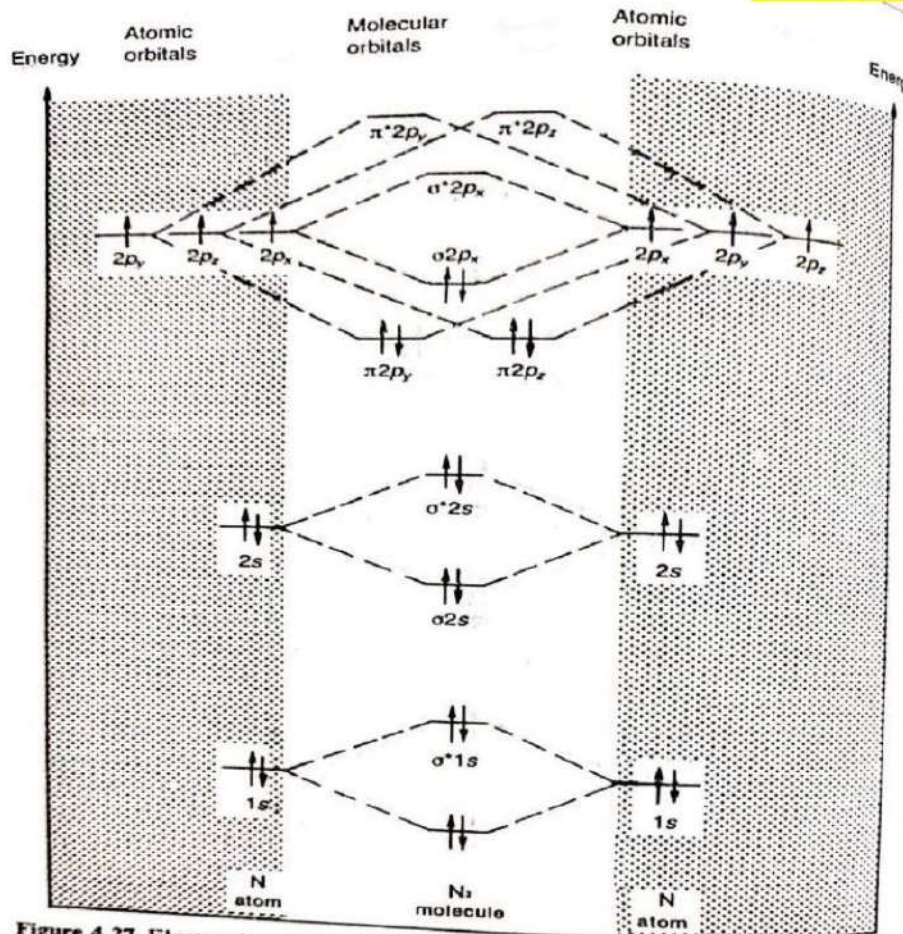


Figure 4.27 Electronic configuration, atomic and molecular orbitals for nitrogen.

$$\text{BO in N}_2 = (10 - 4) / 2 = 3$$

- ⇒ Triple bond between two N atoms
- ⇒ Diamagnetic molecule



3. Oxygen molecule (O₂): 8 electrons in O atom: $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x^2, \pi 2p_y^2)(\pi^* 2p_x^1, \pi^* 2p_y^1)$

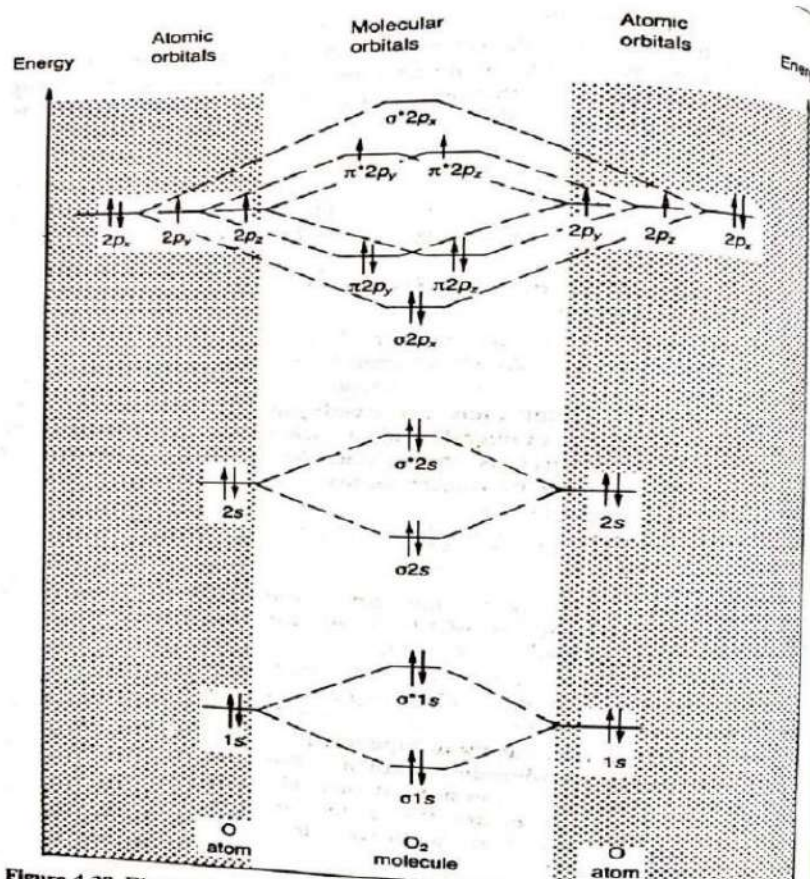


Figure 4.28 Electronic configuration, atomic and molecular orbitals for oxygen molecule.

$$BO \text{ in } O_2 = (10 - 6) / 2 = 2$$

- ⇒ Double bond between two O atoms
- ⇒ Paramagnetic molecule



4.

Fluorine molecule (F_2):

9 electrons in F atom: $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x^2, \pi 2p_y^2)(\pi^* 2p_x^2, \pi^* 2p_y^2)$

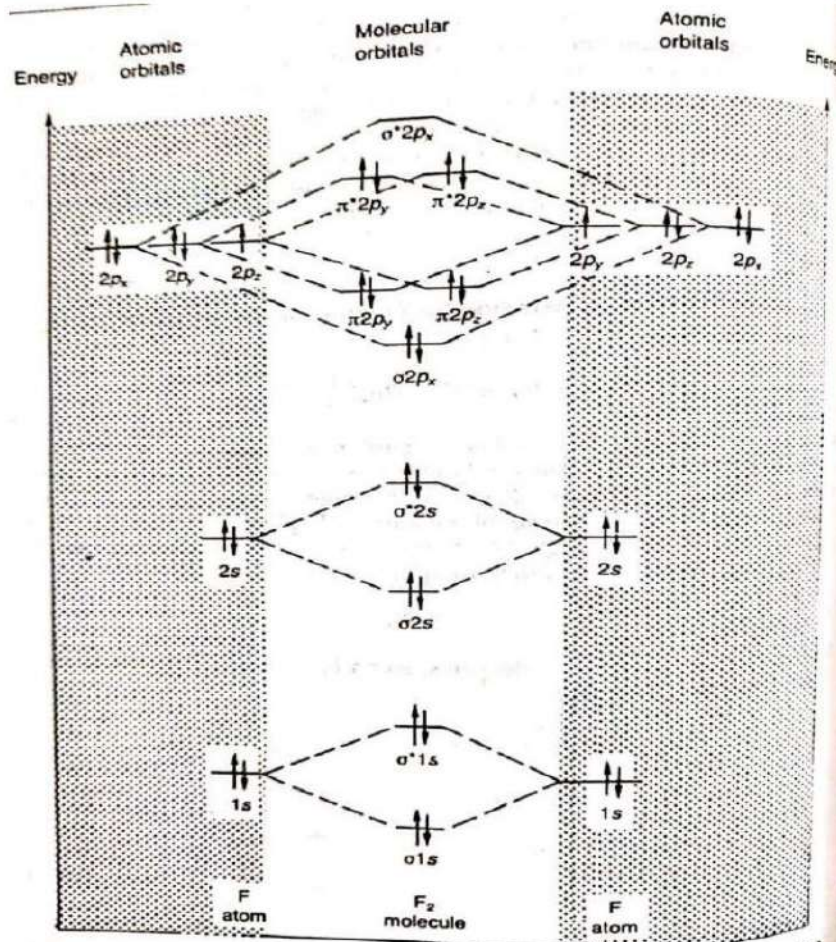


Figure 4.29 Electronic configuration, atomic and molecular orbitals for fluorine

$$BO \text{ in } F_2 = (10 - 8) / 2 = 1$$

- ⇒ Single bond between two F atoms
- ⇒ Diamagnetic molecule



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Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements		
Molecule	Electron Configuration	Bond Order
Li ₂	(σ2s) ²	1
Be ₂ (unstable)	(σ2s) ² (σ*2s) ²	0
B ₂	(σ2s) ² (σ*2s) ² (π2px,π2py) ²	1
C ₂	(σ2s) ² (σ*2s) ² (π2px,π2py) ⁴	2
N ₂	(σ2s) ² (σ*2s) ² (π2px,π2py) ⁴ (σ2pz) ²	3
O ₂	(σ2s) ² (σ*2s) ² (σ2pz) ² (π2px,π2py) ⁴ (π*2px,π*2py) ²	2
F ₂	(σ2s) ² (σ*2s) ² (σ2pz) ² (π2px,π2py) ⁴ (π*2px,π*2py) ⁴	1
Ne ₂ (unstable)	(σ2s) ² (σ*2s) ² (σ2pz) ² (π2px,π2py) ⁴ (π*2px,π*2py) ⁴ (σ*2pz) ²	0



Molecular Structure

Valence Shell Electron Pair Repulsion Theory

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
	Linear					
	Trigonal Planar					
	Tetrahedral					
	Trigonal Bipyramidal					
	Octahedral					

Hybridization

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 Bipyramidal	120, 90	sp ³ d
AX ₆	Octahedral	90	sp ³ d ²
AX ₂ N	Bent	120	sp ²
AX ₂ N ₂	Bent	109.5	sp ³
AX ₃ N	Trigonal Pyramidal	109.5	sp ³

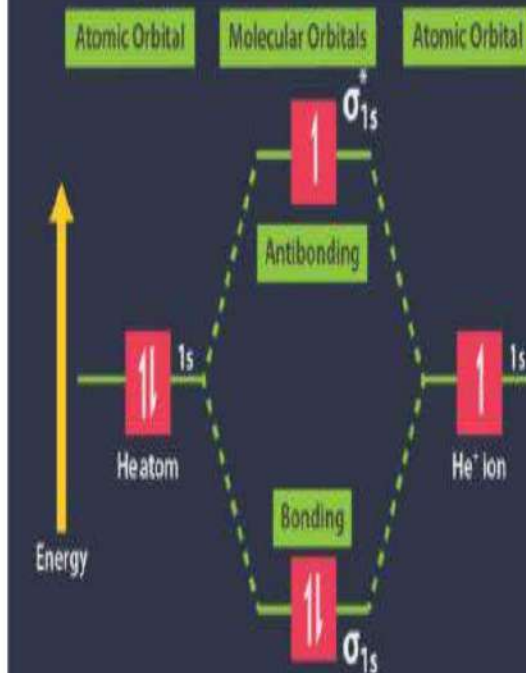
$$\text{Hybridization} = \frac{1}{2} [V + M - C + A]$$

V = Valence electrons
 M = Monovalent atoms
 C or A = Number of Cations or Anions

Example, NH₄⁺
 Hybridization = $\frac{1}{2} [5 + 4 - 1]$

- H=2 → sp
- H=3 → sp²
- H=4 → sp³
- H=5 → sp³d
- H=6 → sp³d²

Molecular Orbital Theory



VSEPR	Valence Bond Theory
VSEPR theory is the theory that predicts the geometry of a molecule	Valence bond theory is a theory that explains the chemical bonding in a covalent bond
Based on the repulsions between lone electron pairs and bond electron pairs	Based on the overlapping of orbitals in order to form a chemical bond
Does not give details about orbitals present in atoms of a molecule	Give details about orbitals present in atoms of a molecule
Indicates the geometry of molecules	Does not indicate the geometry of molecules
Does not indicate the types of bonds present between atoms	Indicate the types of bonds present between atoms



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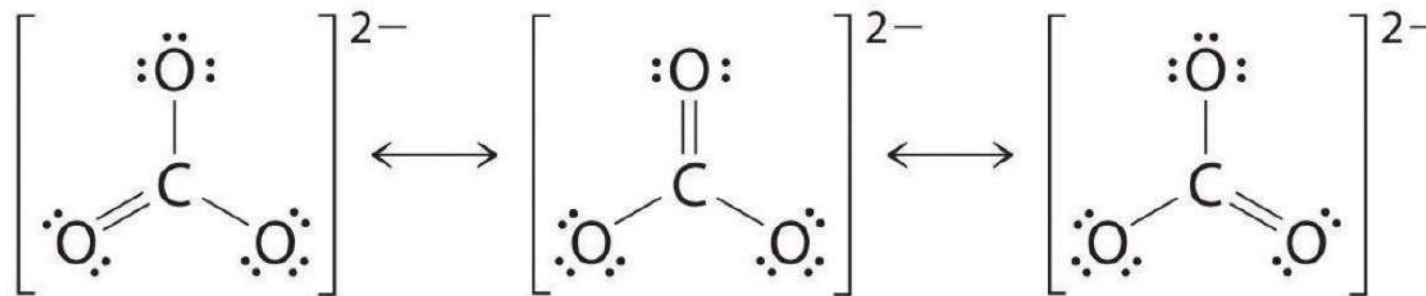
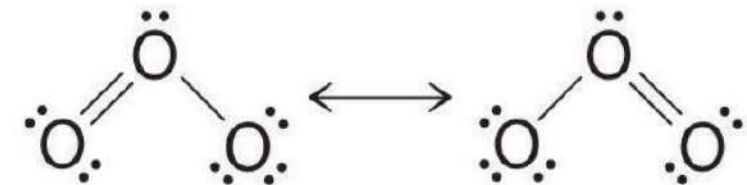
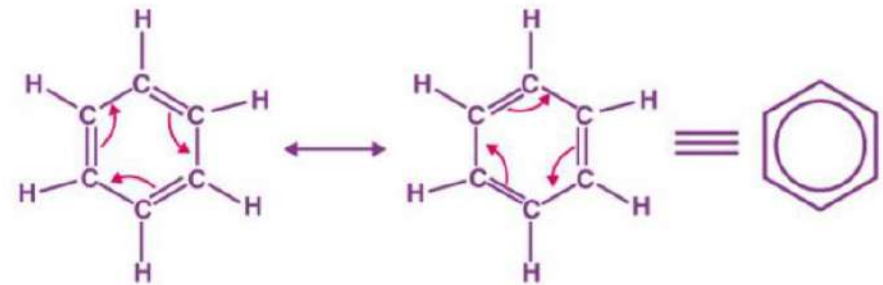


- **Resonance:** Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula.
- In many cases, a single Lewis structure fails to explain the bonding in a molecule/polyatomic ion due to the presence of partial charges and fractional bonds in it. In such cases, resonance structures are used to describe chemical bonding.
- It describes the bonding in particular molecules or ions by merging many contributory structures or forms, jointly called canonical structures or resonance structures within the theory of valence bonding into a hybrid resonance (or hybrid structure).
- Resonance structures are sets of Lewis structures that describe the delocalization of electrons in a polyatomic ion or a molecule.
- The combination of possible resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule.
- In general, molecules with multiple resonance structures will be more stable than one with fewer and some resonance structures contribute more to the stability of the molecule than others.



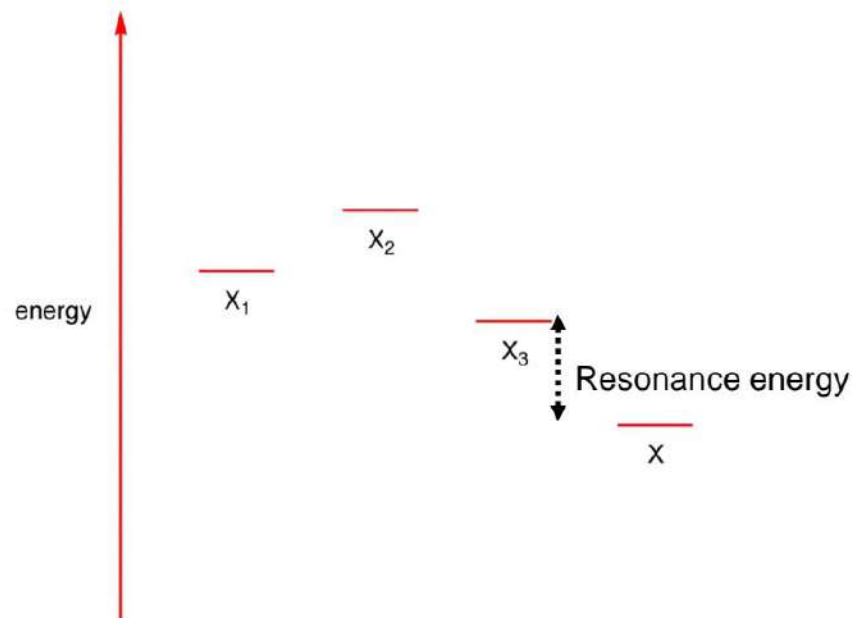
• **Examples:**

1. **Benzene:** The benzene molecule is stabilized by resonance, the pi electrons are delocalized around the ring structure. This delocalization causes each carbon-carbon bond to have a bond order of 1.5, implying that they are stronger than regular C-C sigma bonds.
2. **Ozone (O₃):** Both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O₂ (120.7 pm).
3. **Carbonate ion (CO₃)²⁻:** All C–O bond lengths are identical and shorter than C=O but greater than C–O

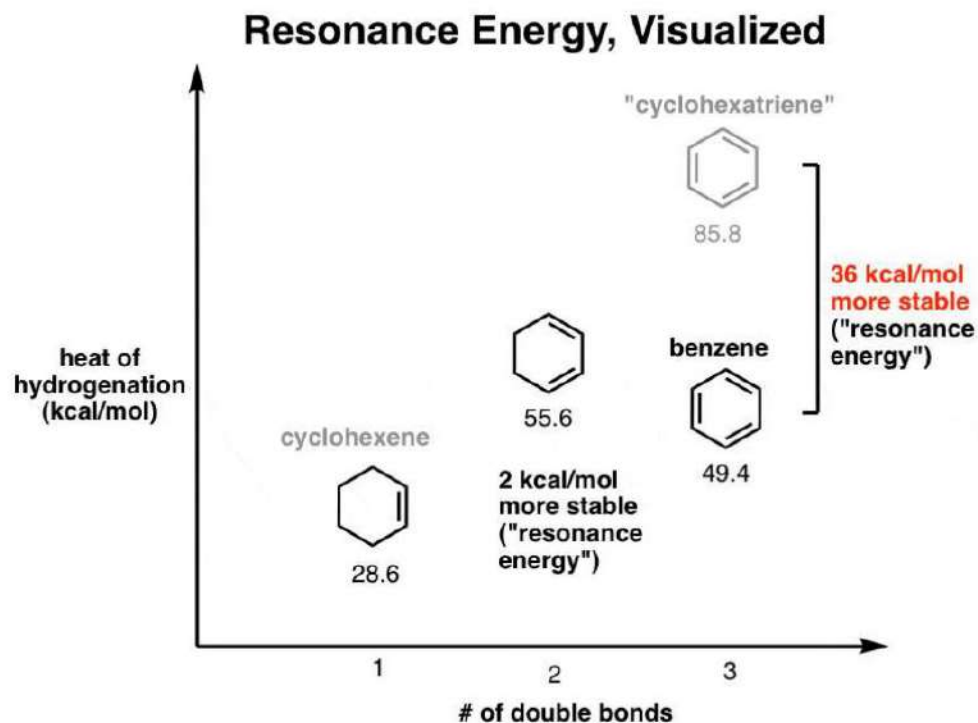




- Resonance energy:** The difference in energy between the actual molecule and the canonical form of the lowest energy is called the Resonance Energy. The resonance energy of a molecule is expressed in kcal/mole or kJ/mole.



Resonance-stabilized molecule X (hybrid) has three resonance forms (X_1 , X_2 , and X_3)



Resonance energy in benzene molecule as measured by heat of hydrogenation



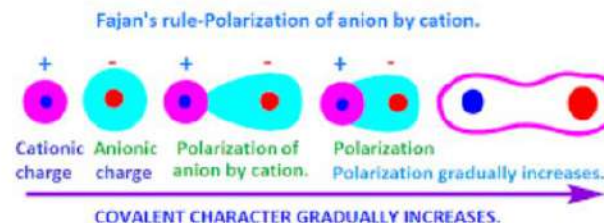
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- **Fajans' Rules:** by Kazimierz Fajans in 1923. These rules predict whether a chemical bond will be covalent or ionic.
- **Polarizing power:** It is the extent to which a cation can polarize an anion. It is proportional to charge density. Charge density is the ratio of charge to volume. Polarizing power \propto Charge density. More the charge density, greater is the polarizing power for that cation.
- **Polarizability:** It is the extent to which an ion can be polarized. Polarization is the distortion of a spherically symmetric electron cloud to an unsymmetric cloud.
- Rules summarizing the factors favoring polarization and hence covalency:
 1. *A small positive ion favors covalency.* In small ions the positive charge is concentrated over a smaller area. This makes the ion highly polarizing, and very good at distorting the negative ions.
 2. *Large negative ions favor covalency.* Large ions are highly polarizable, that is easily distorted by the positive ion, because the outermost electrons are shielded from the charge on the nucleus.
 3. *The charge of Cation:* Greater the charge of cation, greater is the covalent character of the ionic bond.
 4. Polarization and hence covalency is favored if the positive ion does not have a noble gas configuration. e.g. many transition metals
- Amongst the alkali chlorides, which one is the most covalent? Since the anion is the same, we have to compare the cations. According to Fajans' rules, smaller the cation, more is the covalency. Therefore, LiCl is the most covalent.



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- Amongst the anions, larger the size more would be the covalency. Therefore the order is: **NaF < NaCl < NaBr < NaI**
- Smaller the cation more is the covalency. Therefore, the order is: **CsF < RbF < KF < NaF < LiF**





Pauling's method for calculation of ionic radii:

- Pauling has calculated the radii of the ions on the basis of the observed internuclear distances in four crystals namely NaF, KCl, RbBr and CsI. In each ionic crystal the cations and anions are isoelectronic with inert gas configuration.
- Assumptions:
 - The cations and anions of an ionic crystal are assumed to be in contact with each other and hence the sum of their radii will be equal to the inter nuclear distance between them.

$$r(\text{C}^+) + r(\text{A}^-) = d(\text{C}^+\text{-A}^-)$$

where, $r(\text{C}^+)$ = radius of cation, C^+ ; $r(\text{A}^-)$ = radius of anion, A^- ; and $d(\text{C}^+\text{-A}^-)$ = internuclear distance between C^+ and A^- ions in C^+A^- ionic crystal

- For a given noble gas configuration, the radius of an ion is inversely proportional to its effective nuclear charge. i.e. $r(\text{C}^+) = 1/Z_{\text{eff}}(\text{C}^+)$ and $r(\text{A}^-) = 1/Z_{\text{eff}}(\text{A}^-)$
where, $Z_{\text{eff}}(\text{C}^+)$ & $Z_{\text{eff}}(\text{A}^-)$ are the effective nuclear charges of cation (C^+) and anion (A^-) respectively.

On combining,

$$r(\text{C}^+) / r(\text{A}^-) = Z_{\text{eff}}(\text{A}^-) / Z_{\text{eff}}(\text{C}^+)$$

we know $Z_{\text{eff}} = Z - \sigma$, where, Z = atomic number and σ = screening constant

$$r(\text{C}^+) / r(\text{A}^-) = Z(\text{A}^-) - \sigma(\text{A}^-) / Z(\text{C}^+) - \sigma(\text{C}^+)$$

- Find the radii of Na^+ and F^- in NaF crystal. Given: $d(\text{Na-F})$: 2.31 Å and σ for ions with $ns^2 np^6$: 4.5

Ans: $Z_{\text{Na}} = 11$ and $Z_{\text{F}} = 9$,

$$r(\text{Na}^+) / r(\text{F}^-) = 9 - 4.5 / 11 - 4.5 = 4.5 / 6.5$$

$$\Rightarrow 6.5 r(\text{Na}^+) - 4.5 r(\text{F}^-) = 0$$

$$\text{and, } r(\text{Na}^+) + r(\text{F}^-) = 2.31$$

solving the above two equations,

$$r(\text{Na}^+) = 0.945 \text{ \AA} \text{ and } r(\text{F}^-) = 1.365 \text{ \AA}$$



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Engineering Chemistry-I (BS-109)

Thermochemistry

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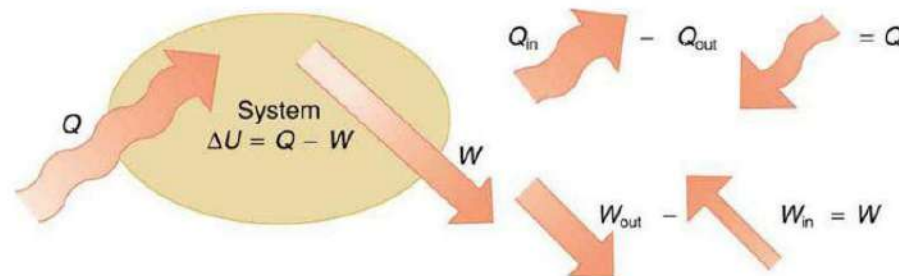


- **What is the difference between Thermodynamics and Thermochemistry?**

Thermodynamics is the branch of physical science that deals with the relations between heat and other forms of energy such as mechanical, electrical, or chemical energy.

Thermochemistry is the quantitative study of the relation between heat and chemical reactions. It primarily deals with the transfer of heat between a chemical system and its surroundings when a change of phase or a chemical reaction takes place within the system.

- Thermochemistry, in fact, implies the first law of thermodynamics to a chemical reaction. According to this law, “Energy can neither be created nor can be destroyed, but can be converted from one state to the other” (Conservation of Energy)
- In other words, change in internal energy of a system equals the net heat transfer into the system minus the net work done by the system.
- In equation form, the first law of thermodynamics is $\Delta U = Q - W$, where ΔU is the change in internal energy, U of the system. Q is the net heat transferred into the system—that is, Q is the sum of all heat transfer into and out of the system. W is the net work done by the system—that is, W is the sum of all work done on or by the system.





- **Change of internal energy in a chemical reaction:**

In chemical systems, the most common type of work is pressure-volume (PV) work, in which the volume of a gas changes. Substituting this in for work in the above equation, we can define the change in internal energy for a chemical system:

$$\Delta U = Q - P\Delta V$$

Let's examine the internal energy change, ΔU , at constant volume. At constant volume, $\Delta V = 0$, the equation for the change in internal energy reduces to the following:

$$\Delta U = Q_V \dots \dots \dots \text{Heat exchanged at constant } V$$

So, let U_R be the internal energy of reactants and U_P be that of products,

$$\Delta U = U_P - U_R = Q_V \dots \dots \dots \text{Heat of reaction at constant } V$$

- This internal energy is often very difficult to calculate in real life settings, though, because chemists tend to run their reactions in open flasks and beakers that allow gases to escape to the atmosphere. Therefore, volume is not held constant, and calculating ΔU becomes problematic. To correct this, the concept of *enthalpy* is considered, which is much more commonly used by chemists.



- **Change of enthalpy in a chemical reaction:**

Change in enthalpy of a given reaction can be expressed as follows:

$$\Delta H = \Delta U + P\Delta V$$

When you run a chemical reaction in a laboratory, the reaction occurs at constant pressure, because the atmospheric pressure around us is relatively constant.

$$\Delta U = Q - W = Q - P\Delta V$$

Substituting to combine these two equations, we have:

$$\Delta H = Q - P\Delta V + P\Delta V = Q_p$$

Thus, at constant pressure, the change in enthalpy is simply equal to the heat released/absorbed by the reaction.

- In general, if H_R is the enthalpy of reactants and H_P is the enthalpy of products, then

$$\Delta H = H_P - H_R = Q_p \dots \dots \text{Enthalpy of reaction}$$

- $\Delta H = \sum a_i H_P - \sum b_i H_R$, where a_i and b_i are stoichiometric coefficients of products and reactants, respectively

e.g. for a reaction, $\text{Fe}_2\text{O}_3 (\text{s}) + 3\text{H}_2 (\text{g}) \rightarrow 2\text{Fe} (\text{s}) + 3\text{H}_2\text{O} (\text{l})$

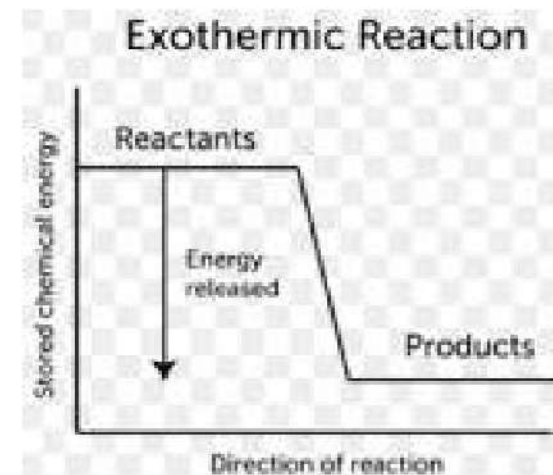
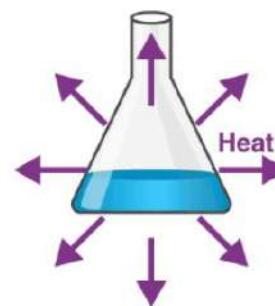
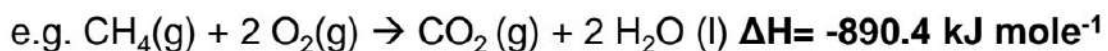
$$\Delta H = [2H_{(\text{Fe}, \text{s})} + 3H_{(\text{H}_2\text{O}, \text{l})}] - [H_{(\text{Fe}_2\text{O}_3, \text{s})} + 3H_{(\text{H}_2, \text{g})}]$$

- **Enthalpy of a reaction:** The amount of heat evolved or absorbed in a chemical reaction, when number of moles of the reactants by the chemical reaction have completely reacted

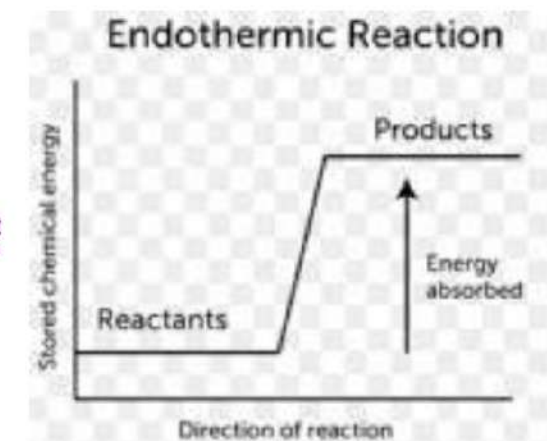
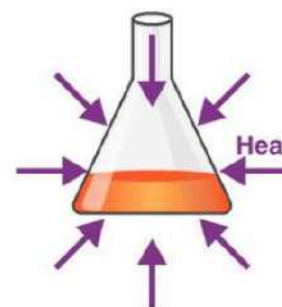
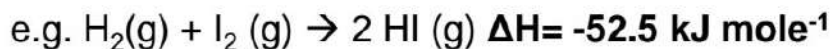


- Exothermic and Endothermic reactions:

Exothermic reactions: A reaction that releases energy in the form of heat. Here, $\Sigma H_P < \Sigma H_R \Rightarrow \Delta H = \text{negative}$



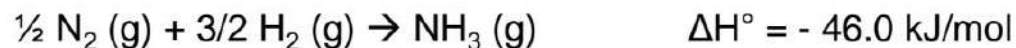
Endothermic reactions: A reaction wherein heat is absorbed by the system from the surroundings. Here, $\Sigma H_P > \Sigma H_R \Rightarrow \Delta H = \text{positive}$





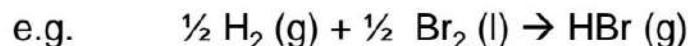
- **Standard enthalpy of reaction:**

When all the chemical species in a chemical equation are present in the respective standard states, the enthalpy of reaction determined at 25 °C and 1 atm pressure, then it is known as standard enthalpy of reaction (ΔH°).



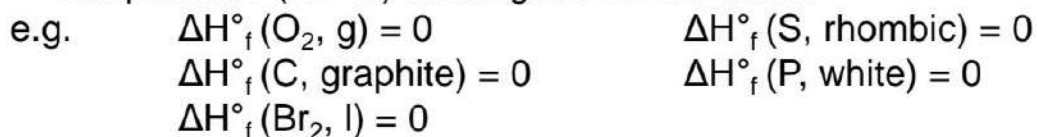
- **Standard enthalpy of formation (ΔH°_f):** The standard enthalpy of formation of a compound is the change in the standard enthalpy when one mole of the compound is formed starting from the requisite amounts of elements in their stable states of aggregation.

$$\Delta H^\circ_f = \sum H^\circ_f \text{ Products} - \sum H^\circ_f \text{ Reactants}$$



$$\Delta H^\circ_f = [H^\circ_{(\text{HBr}, \text{g})}] - [\frac{1}{2} H^\circ_{(\text{H}_2, \text{g})} + \frac{1}{2} H^\circ_{(\text{Br}_2, \text{l})}]$$

- The standard enthalpy of formation of every element in its stable state of aggregation at 1 bar pressure and at specified temperature (25 °C) is assigned a zero value.

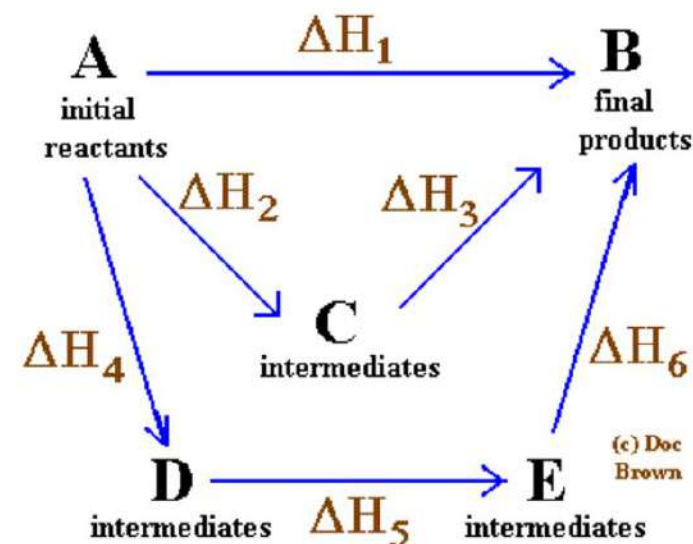




- **Hess's Law of constant heat summation:** Named after Russian Chemist and Doctor Germain Hess. According to this law, "The heat absorbed or evolved in a given chemical equation is the same whether the process occurs in one step or several steps"
- All steps have to proceed at the same temperature and the equations for the individual steps must balance out.
- It is a consequence of the first law of thermodynamics and need not be considered a separate thermodynamic law; in thermochemistry, however, it retains its identity because of its importance as the basis for calculating heats of reactions.
- Hess's law can be written as $\Delta H^\circ = \Sigma \Delta H_n$, where ΔH° is the heat absorbed or evolved and $\Sigma \Delta H_n$ is the sum of the heat absorbed or evolved in the individual n steps of the reaction.
- The chemical equation can be treated as ordinary algebraic expressions and can be added or subtracted to yield the required equation.

Reactant A can form product B by following three different steps. C, D and E are intermediates in the other stepwise reactions. Hess' law states that the enthalpy of the reaction (ΔH_1) is the same irrespective of the path.

So, the enthalpy of direct single-step reaction and other paths giving intermediates C, D and E should be the same. $\Delta H_1 = \Delta H_2 + \Delta H_3 = \Delta H_4 + \Delta H_5 + \Delta H_6$.





- **Applications of Hess's Law:**

1. **Determination of enthalpy of a reaction.** Sometimes, it is difficult to determine the enthalpy of a reaction experimentally, e.g. enthalpy change in the following reaction



can be estimated from the following two reactions:



on adding eqns 2 and 3, we get eq 1:

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2$$

$$\Delta_r H = -26.417 + (-67.637) = -94.054 \text{ kcal}$$

2. **Determination of lattice energy of a crystal (Born-Haber cycle).** Lattice energy is defined as the energy released when number of positive and negative ions combine to form one mole of the ionic compound.

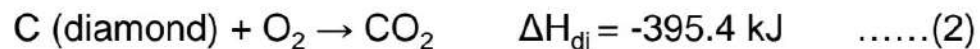
- Larger the lattice energy, more stable is the ionic compound and more tightly the ions are held.



3. Enthalpy change in a physical change

Carbon and diamond are allotropes of carbon. But measuring the energy change in the conversion of graphite to diamond cannot be determined, as the process cannot be carried out. Still, the heat changes for this hypothetical physical change can be calculated using Hess law.

Graphite and diamond combine with oxygen with the heat of reaction as -393.4 kJ and – 395.4 kJ respectively.



Subtracting (2) from (1)



Enthalpy change in the allotrope transition of graphite to diamond is endothermic of 2 kJ.



- **Variation of enthalpy of a reaction with temperature (Kirchhoff's Relation):** is equality expressing the temperature dependence of the thermal quantities linked with a chemical reaction through the difference in heat capacities between the products and reactants.
- The heat change accompanying chemical or physical processes generally depends on the temperature at which the process takes place.
- Kirchhoff equation relates the heat of reaction with the definite heats of a structure before and after the reaction.
- Consider a reaction, $aA + bB \rightarrow cC + dD$, the enthalpy change for the above reaction will be:

$$\Delta H = \sum a_i H_p - \sum b_i H_R$$
$$\Delta H = [cH_C + dH_D] - [aH_A + bH_B] \text{ -----(1)}$$

On differentiating the above equation w.r.t. temperature at constant pressure, we get

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_P = c \left(\frac{\partial H_C}{\partial T} \right)_P + d \left(\frac{\partial H_D}{\partial T} \right)_P - a \left(\frac{\partial H_A}{\partial T} \right)_P - b \left(\frac{\partial H_B}{\partial T} \right)_P$$

The variation of enthalpy of a substance with temperature at a given pressure is given by:

$$\left(\frac{dH}{dT} \right)_P = C_p \quad \text{where } C_p \text{ is the heat capacity}$$

On substituting it in above eq:

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_P = c C_{p,C} + d C_{p,D} - a C_{p,A} - b C_{p,B} = \Delta C_p \text{ ---(2)}$$



where, $\Delta C_p = \left(\text{Sum of heat capacities of products} \right) - \left(\text{Sum of heat capacities of reactants} \right)$

So, Eq (2) is called KIRCHHOFF'S Equation. It states that variation of ΔH of a reaction with temperature at constant pressure is equal to ΔC_p of system. We can write it as.

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_p = \Delta C_p \quad \text{or} \quad d(\Delta H) = \Delta C_p dT \quad \dots (3)$$

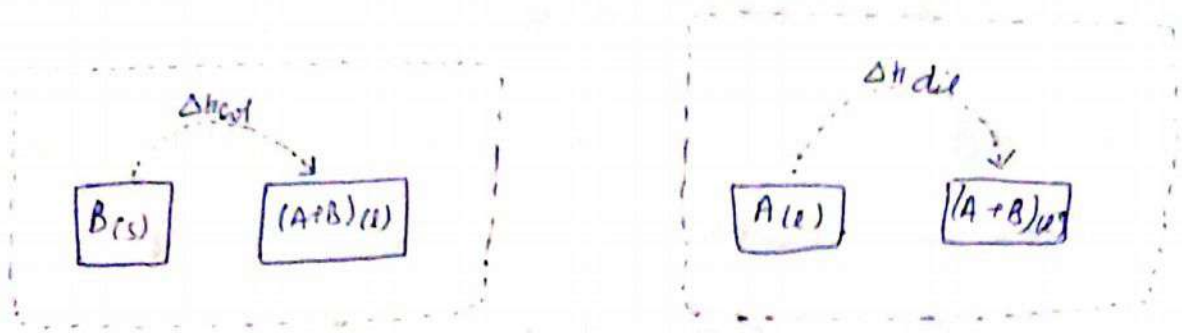
If taking temperature range from T_1 to T_2 , Eq (3) can be easily integrated, we get:

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p dT = \Delta C_p \int_{T_1}^{T_2} dT$$

or

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

• Heat of solution and heat of dilution:

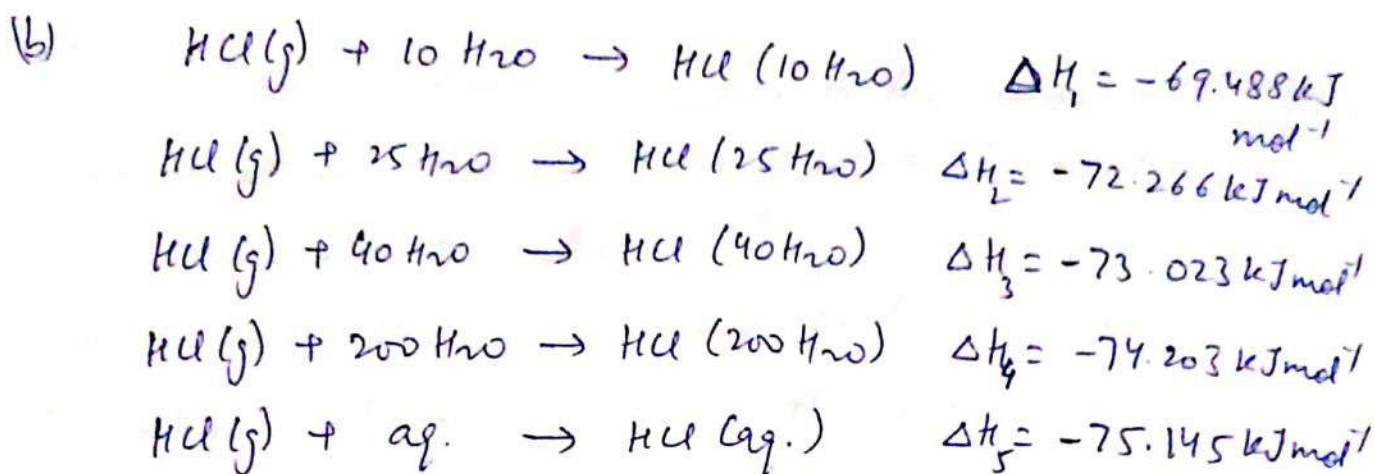
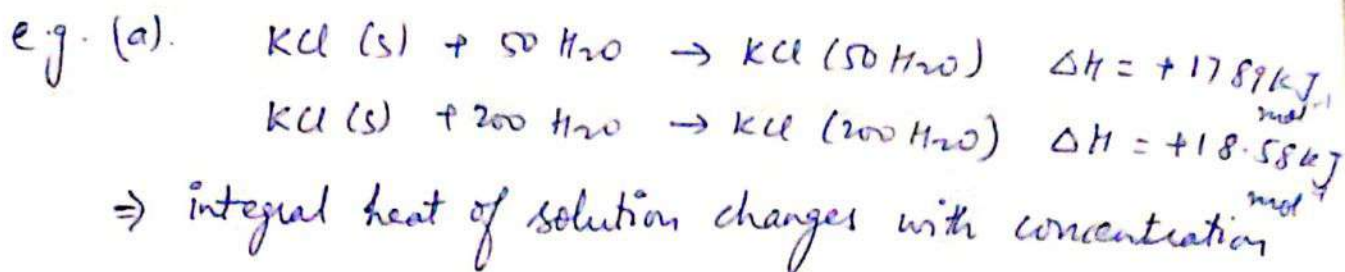


Solution process

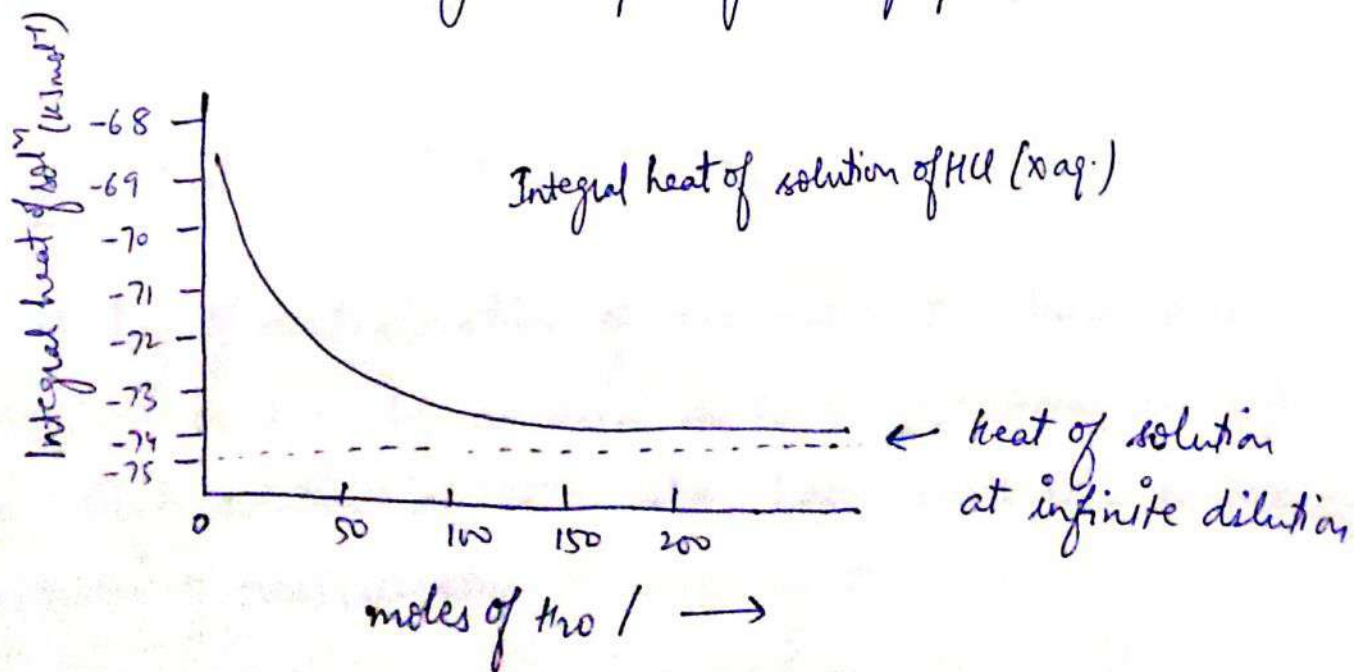
Dilution process

A: solvent
B: solute

- The processes of solution (dissolution) and dilution are related.
- During a solution process, a solute is transferred from a pure solute phase (solid, liquid, or gas) to a solvent or solution phase.
- During a dilution process, solvent is transferred from a pure solvent phase to a solution phase.
- The dissolution of solute in a solvent is often accompanied by either evolution or absorption of heat. The amount of heat evolved or absorbed depends on the nature of solute and the solvent and also on the composition of the solution.
- "The enthalpy change when one mole of the solute is dissolved in a definite amount of solvent to produce a solution of desired concentration is known as integral enthalpy of solution at the given concentration."



where, ΔH_5 represents the limit of enthalpy change when 1 mol of HCl (g) is dissolved in a very large quantity of water. The resultant solution is known as an infinite diluted solution. The value of ΔH at infinite dilution can be obtained by extrapolating the graph.

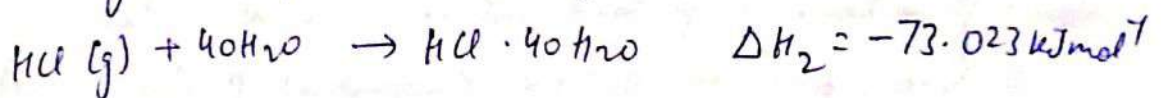
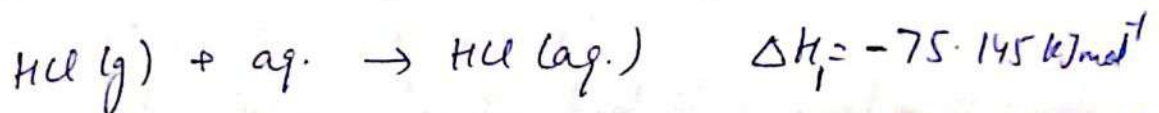
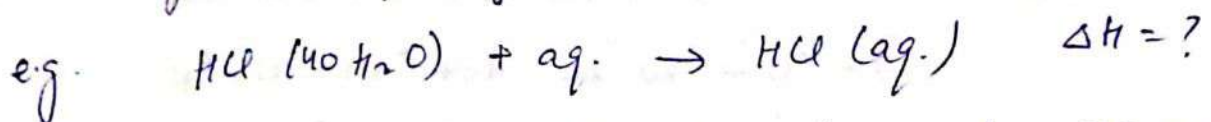


At infinite dilution, the heat change becomes constant

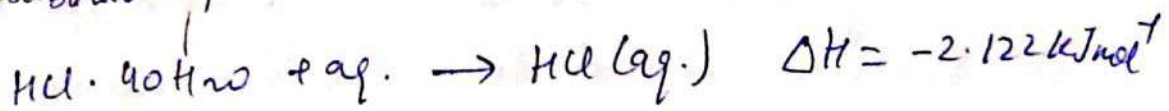
→ Now that, the enthalpy of solution of a solute varies with its concentration implies that there must be a change of enthalpy when a solution is diluted by adding more solvent.

" The integral enthalpy of dilution is the change in enthalpy when a solution containing 1 mole of solute is diluted from one concentration to another "

Acc. to Hess's law, it is equal to the difference between the integral enthalpies of solution at the two concentrations.

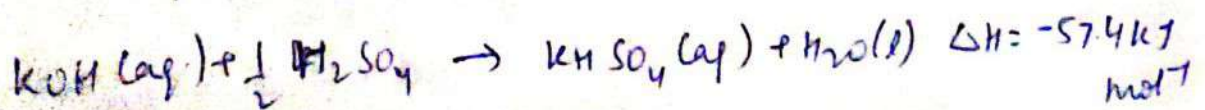
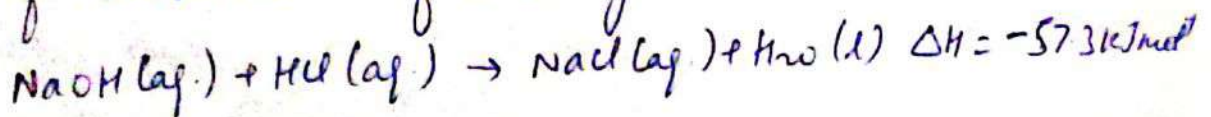


on subtraction,

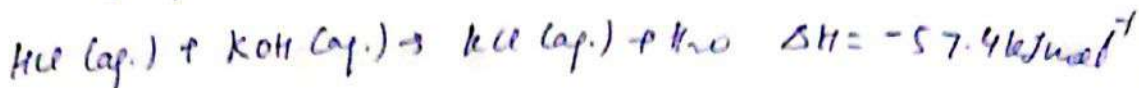
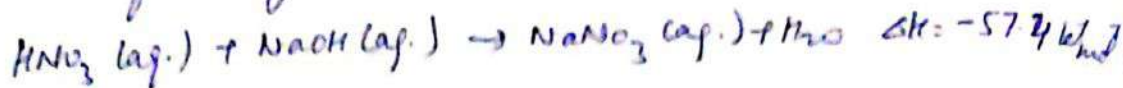


• Heat of neutralization ($\Delta H_{\text{neut.}}$):

→ Enthalpy of neutralization of one mole of a base such as NaOH or KOH by an acid such as HCl, HNO₃ and H₂SO₄ in dilute solution at 25°C and 1 atm pressure is called enthalpy of neutralization of base by the acid.

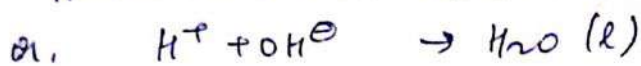
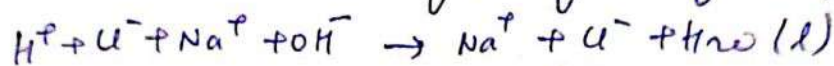


Similarly, the enthalpy change accompanying the neutralization of 1 mole of an acid by a base in dilute solutions at 25°C and 1 atm pressure is known as standard enthalpy of neutralization of acid by the base.



⇒ Amount of heat evolved (exothermic) when 1 mole of an acid is neutralized by 1 mole of base in large excess of water.

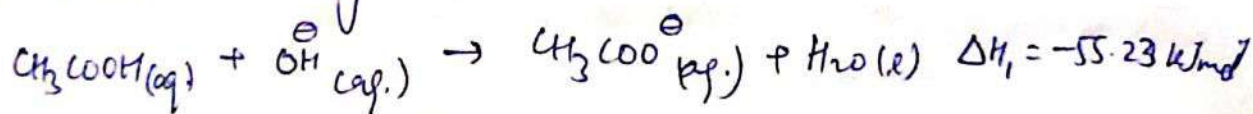
→ When acid and base are both strong, they undergo complete dissociation,



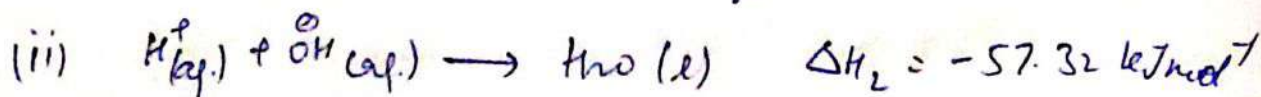
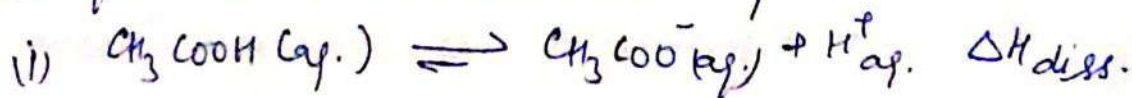
∴ heat of neutralization is actually the heat of formation of 1 mole of water from 1 mole of hydrogen & hydroxide ions, and this is always equivalent to 13.7 kcal or 57.32 kJ of heat.

→ However, when a weak acid or a weak base is neutralized, the ΔH_{neu} changes as there is no complete dissociation of ions.

eg. weak acid and strong base:



this equation can be considered in 2 steps:



Acc to Hess's law,

$$\Delta H_1 = \Delta H_{\text{diss}} + \Delta H_2$$

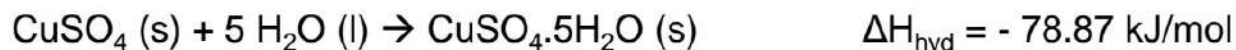
$$\begin{aligned} \Delta H_{\text{diss}} &= \Delta H_1 - \Delta H_2 \\ &= -55.23 - (-57.32) \\ &= 2.09 \text{ kJ mol}^{-1} \end{aligned}$$



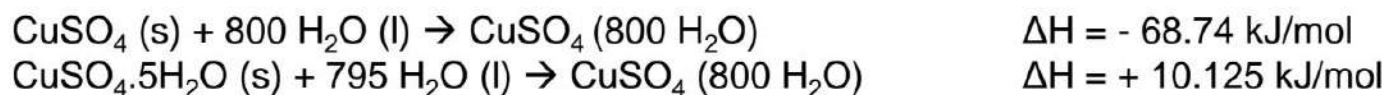
- **Heat of hydration:**

The enthalpy change when a given anhydrous or partially hydrated salt combines with the requisite amount of water to form a new hydrated stable salt.

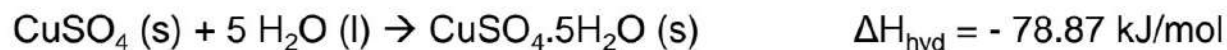
e.g. hydration of anhydrous cupric sulphate :



- In order to dissolve an ionic solid, water molecules must break up the interactions between all of the ions in the solid. To do this, they orient themselves such that they effectively reduce the localized charge on the ions. This is called hydration.
- Hydration of ions is a thermodynamically favorable process, and as such can **release heat i.e. $\Delta H = \text{negative}$**
- Enthalpy of hydration can be readily calculated from the integral enthalpies of solution of the hydrated and anhydrous salts.

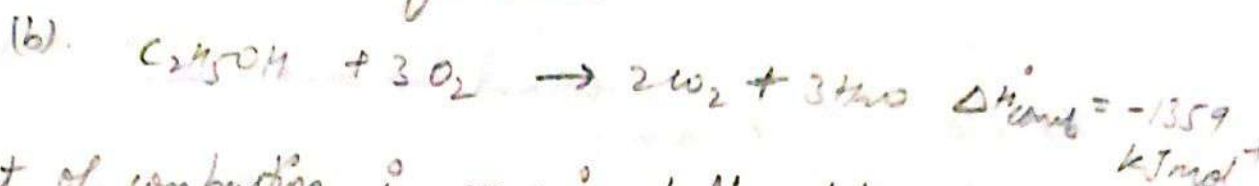
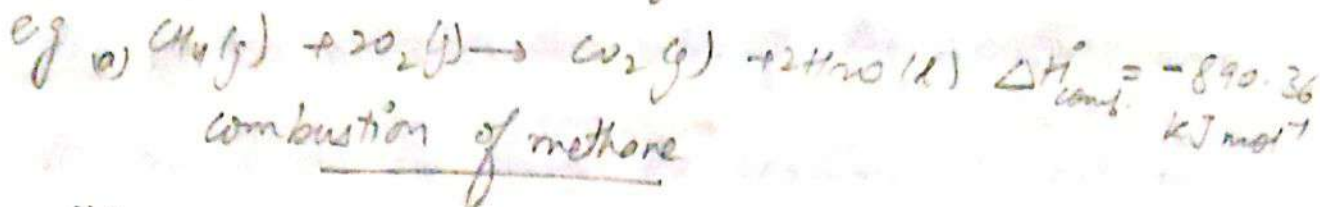


subtracting the two, we get



• Heat of Combustion (ΔH_{comb}):

It is the enthalpy change when 1 mole of a compound combines with the requisite amount of oxygen to give products in their stable forms.



Heat of combustion is experimentally determined in a "bomb calorimeter", which is a pressure vessel internally enamelled with platinum.

• Flame temperature:

→ Adiabatic flame temperature is a temperature which the system attains if the changes in the system are carried out under adiabatic conditions. It is the maximum temperature of the combustion gas that can be reached during combustion.

→ For an isobaric (const pressure) adiabatic process, the flame temperature can be calculated using the Kirchhoff's eq

$$\frac{d(\Delta H)}{dT} = \Delta C_p \quad \text{or} \quad d(\Delta H) = \Delta C_p dT$$

on integration,

$$\int d(\Delta H) = \Delta C_p \int_{T_i}^{T_f} dT$$

T_i : initial temp^r

T_f : final temp^r

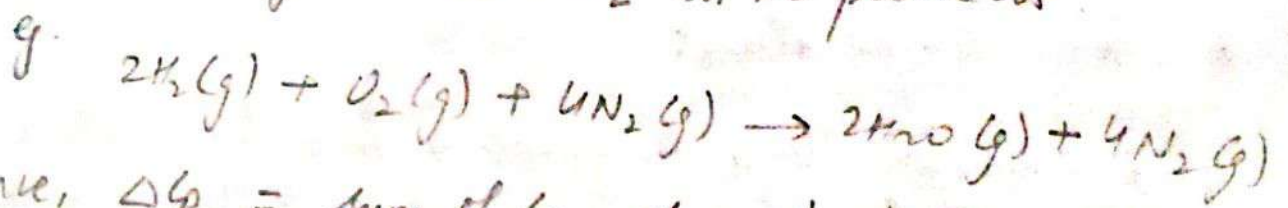
(flame temp^r)

Assumption:
over great temp^r
range, $\Delta C_p = \text{const}$ ⇒

$$\Delta H = \Delta C_p (T_f - T_i)$$

→ Comment on ΔC_p : The flame temp^r would obviously depend on the composition and heat capacities of the resultant gases. In the flames produced by combustion of fuels in air, unreacted nitrogen, present in the atmosphere, is also heated up along with the gaseous products to the flame temperature.

→ Since air contains about 20% O_2 and 80% N_2 by volume, the combustion involving 1 mole of O_2 is associated with 4 moles of unreacted N_2 in the products.



Hence, $\Delta C_p =$ sum of C_p s of products + C_p of 4 moles of unreacted N_2 per mole of O_2

$$\Rightarrow \Delta C_p = \sum C_{p, \text{products}} + 4C_{p, N_2}$$

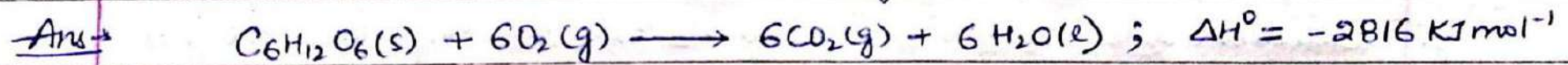


1. Comment by a student, "In an endothermic reaction, if heat is taken in during the reaction, the temperature should go up, not down." Clear the doubt.

Ans → If reaction being endothermic, the energy taken in is being consumed to break the bonds in reactants so that it does not have chance to appear as heat and raise the temperature.



2. Enthalpy of combustion of glucose $C_6H_{12}O_6(s)$ is $-2816 \text{ kJ mol}^{-1}$ at 25°C . Calculate ΔH_f° ($C_6H_{12}O_6$). The ΔH_f° value for $CO_2(g)$ and $H_2O(l)$ are -393.5 and $-285.9 \text{ kJ mol}^{-1}$, respectively.



Since, $\Delta H = \sum \Delta H_f^\circ$ (products) - $\sum \Delta H_f^\circ$ (reactants), we find that

$$-2816 \text{ kJ mol}^{-1} = [6(-393.5) + 6(-285.9)] - [\Delta H_f^\circ(C_6H_{12}O_6) + \Delta H_f^\circ(O_2) \times 6]$$

$$-2816 \text{ kJ mol}^{-1} = [(-2361) + (-1715.4)] - [\Delta H_f^\circ(C_6H_{12}O_6)] \quad \text{as, } \Delta H_f^\circ(O_2) = 0$$

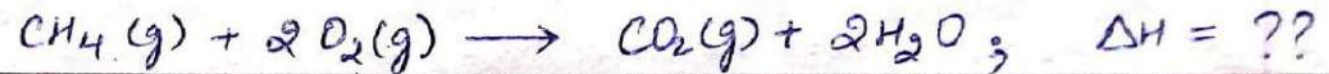
$$\Delta H_f^\circ(C_6H_{12}O_6) = -1260.4 \text{ kJ mol}^{-1}$$



3. Calculate enthalpy of combustion of methane at 25°C and 1 atm pressure.

Where $\Delta H_f^\circ(\text{CH}_4(\text{g})) = -74.8 \text{ kJ mol}^{-1}$, $\Delta H_f^\circ(\text{CO}_2(\text{g})) = -393.5 \text{ kJ mol}^{-1}$ and
 $\Delta H_f^\circ(\text{O}_2(\text{g})) = 0 \text{ kJ mol}^{-1}$, $\Delta H_f^\circ(\text{H}_2\text{O}(\text{l})) = -285.9 \text{ kJ mol}^{-1}$

Ans → The combustion of methane is represented as:

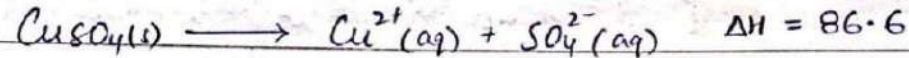


$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{CO}_2) + 2\Delta H_f^\circ(\text{H}_2\text{O}) - \Delta H_f^\circ(\text{CH}_4) - 2\Delta H_f^\circ(\text{O}_2) \\ &= (-393.5) + 2(-285.9) - (-74.8) - 2(0) \\ &= -890.5 \text{ kJ mol}^{-1}\end{aligned}$$



4. The Heat evolved on dissolving $\text{CuSO}_4(\text{s})$ in water is 86.6 kJ mol^{-1} .
If $\Delta H_f^\circ(\text{Cu}^{2+})$ is 64.4 kJ mol^{-1} , what is $\Delta H_f^\circ(\text{SO}_4^{2-})$?
 $\Delta H_f^\circ(\text{CuSO}_4(\text{s})) = -770.0 \text{ kJ mol}^{-1}$.

Ans Reaction can be written as.



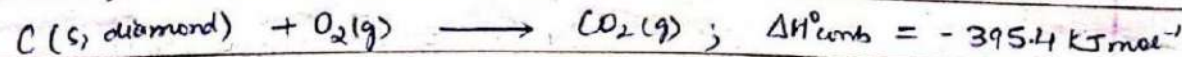
so,

$$\Delta H = \Delta H_f^\circ(\text{Cu}^{2+}) + \Delta H_f^\circ(\text{SO}_4^{2-}) - \Delta H_f^\circ(\text{CuSO}_4(\text{s}))$$

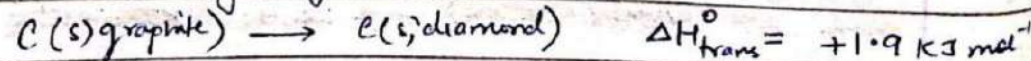
$$86.6 = 64.4 + \Delta H_f^\circ(\text{SO}_4^{2-}) - (-770.0)$$

$$\Delta H_f^\circ(\text{SO}_4^{2-}) = -747.8 \text{ kJ mol}^{-1}$$

5. Calculate the enthalpy change for the transition graphite \rightleftharpoons diamond from the $\Delta H_{\text{comb}}^\circ$ values of $-393.5 \text{ kJ mol}^{-1}$ and $-395.4 \text{ kJ mol}^{-1}$ for graphite and diamond, respectively.

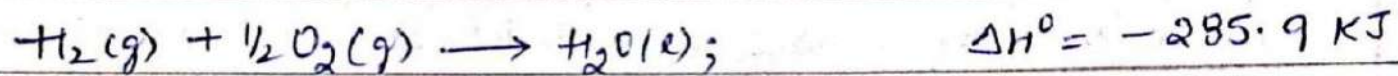
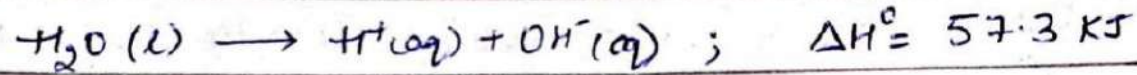


Subtraction of second reaction from first,

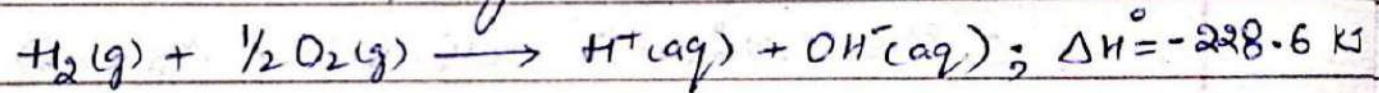




6. Calculate the enthalpy of formation of OH^- ions at 25°C from following thermo-chemical data:



Ans → Adding above two reactions, we get -



$$\therefore \Delta H^\circ = \Delta H_f^\circ(\text{H}^+) + \Delta H_f^\circ(\text{OH}^-) - \Delta H_f^\circ(\text{H}_2(\text{g})) - \frac{\Delta H_f^\circ(\text{O}_2(\text{g}))}{2}$$

$$-228.6 = 0 + \Delta H_f^\circ(\text{OH}^-) - (0) - (0/2)$$

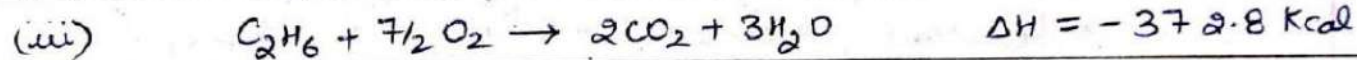
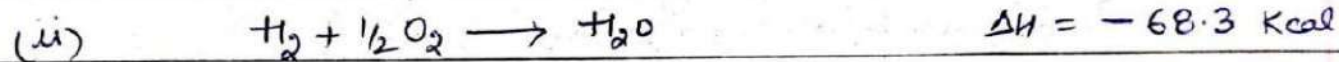
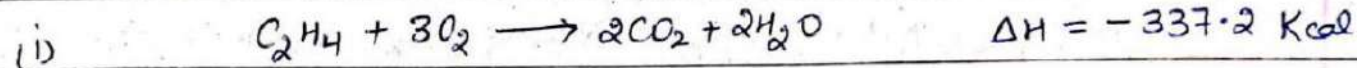
by convention $\Delta H_f^\circ(\text{H}^+) = 0$.

$$\therefore \Delta H_f^\circ(\text{OH}^-_{\text{aq}}) = -228.6 \text{ KJ}$$

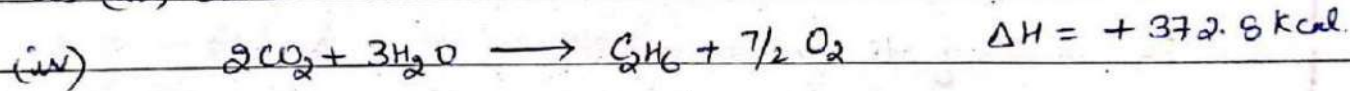


7 Heat of combustion of ethylene, hydrogen, and ethane are 337.2, 68.3, 372.8 Kcal mol⁻¹ at a definite temperature. Calculate heat of reaction of
$$\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$$

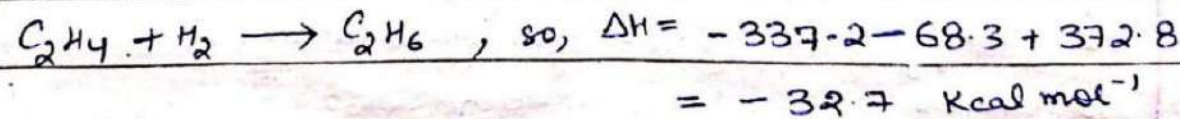
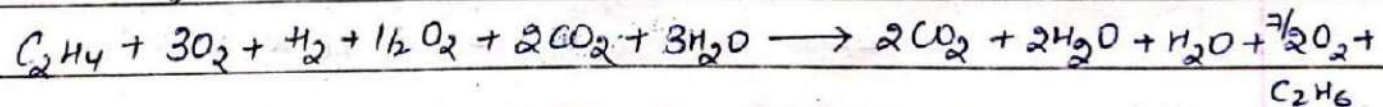
Ans Given



as (iii) can be written as

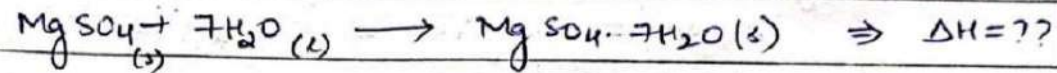


on adding (i), (ii) and (iv) we have,

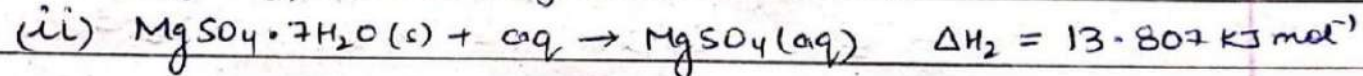
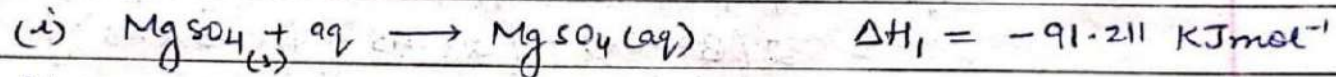




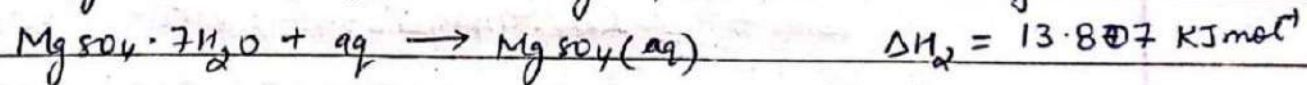
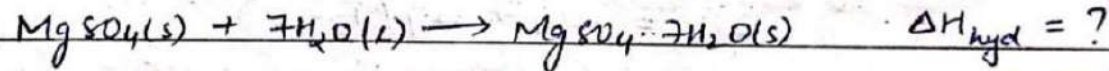
8. At 25°C , 1 mole of MgSO_4 was dissolved in water. The heat evolved was found to be 91.211 kJ . 1 mole of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ on dissolution gives a solution of the same composition accompanied by an absorption of 13.807 kJ . Find enthalpy of hydration.



Ans Given that:



So, eq (i) can be considered in two steps.



as per Hess law \rightarrow

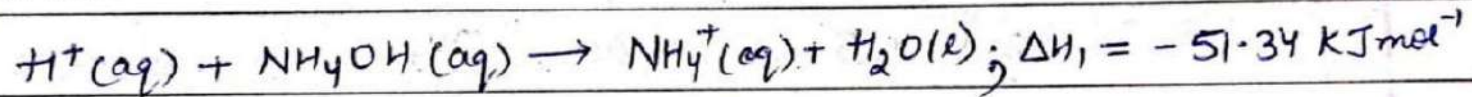
$$\Delta H_1 = \Delta H_{\text{hydr}} + \Delta H_2$$

$$\text{So, } \Delta H_{\text{hyd}} = \Delta H_1 - \Delta H_2 = -91.211 - 13.807 = -105.018 \text{ kJ mol}^{-1}$$

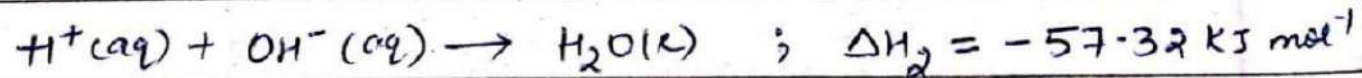
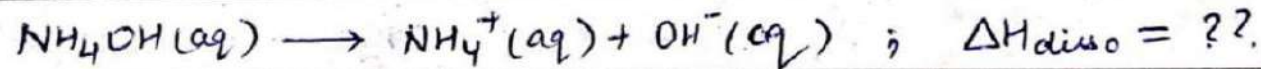


9. Enthalpy of neutralization of HCl by NaOH is $-57.32 \text{ kJ mol}^{-1}$ and by NH_4OH is $-51.34 \text{ kJ mol}^{-1}$. Calculate enthalpy of dissociation of NH_4OH .

Ans → Given that:



This reaction can be considered in two steps:



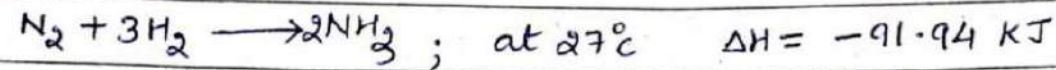
So, according to Hess law,

$$\Delta H_1 = \Delta H_{\text{diss}} + \Delta H_2$$

$$\begin{aligned} \Delta H_{\text{diss}} &= \Delta H_1 - \Delta H_2 = (-51.34 + 57.32) \text{ kJ mol}^{-1} \\ &= 5.98 \text{ kJ mol}^{-1} \end{aligned}$$



10. The enthalpy of reaction (ΔH) for the formation of ammonia according to the reaction



What will be the enthalpy of reaction (ΔH) at 50°C ? The molar heat capacity at constant pressure at 27°C for N_2 , H_2 & NH_3 are 28.45, 28.32 & 37.07 joules, respectively.

Ans → According to Kirchoff equation,

$$d(\Delta H) = \Delta C_p dT \quad \text{or} \quad \Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

$$\Delta H_1 = -91.94 \text{ KJ} ; T_1 = 300\text{K} ; T_2 = 323\text{K} ;$$

$$\text{So, } \Delta C_p = C_{p, \text{ products}} - C_{p, \text{ reactants}}$$

$$= 2(37.07) - [28.45 + (28.32 \times 3)]$$

$$= -39.28 \text{ JK}^{-1} = -39.28 \times 10^{-3} \text{ KJ K}^{-1}$$

assuming C_p do not change with temperature, ΔH_2 at 50°C , will be

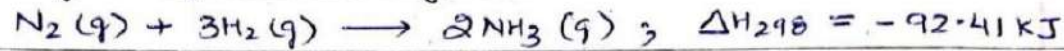
$$\Delta H_2 = \Delta H_1 + \Delta C_p (T_2 - T_1)$$

$$= (-91.94) + (-39.28 \times 10^{-3})(323 - 300)$$

$$= -92.85 \text{ KJ}$$



11. Calculate the enthalpy change at 125°C for the reaction



Molar heat capacities (in $\text{JK}^{-1}\text{mol}^{-1}$) for various gases involved in the reaction vary with temperature as follows:

$$C_p(\text{N}_2) = 27.26 + 5.23 \times 10^{-3}T - 4.18 \times 10^{-9}T^2$$

$$C_p(\text{H}_2) = 29.02 + 8.35 \times 10^{-4}T + 20.80 \times 10^{-7}T^2$$

$$C_p(\text{NH}_3) = 25.86 + 32.94 \times 10^{-2}T - 30.42 \times 10^{-7}T^2$$

Ans $\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT$

$$\Delta C_p = 2C_p(\text{NH}_3) - C_p(\text{N}_2) - 3C_p(\text{H}_2)$$

$$\Delta C_p = -62.60 + 63.14 \times 10^{-3}T - 123.20 \times 10^{-7}T^2$$

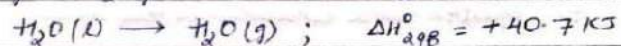
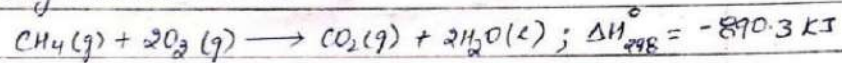
Hence, $\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} [-62.60 + 63.14 \times 10^{-3}T - 123.20 \times 10^{-7}T^2] dT$

$$\Delta H_{398} - \Delta H_{298} = \left[-62.60 + \frac{63.14 \times 10^{-3}}{2}T^2 - \frac{123.20 \times 10^{-7}}{3}T^3 \right]_{298}^{398}$$

$$\Delta H_{398} = -96.50 \text{ kJ}$$

12. In a Bunsen burner, CH_4 gas is premixed with sufficient air to allow complete combustion and at flame temperature water is converted to steam.

Using the following thermochemical data:

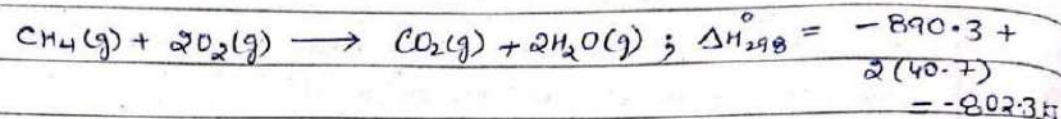


Calculate flame temperature. Assume gaseous product behave ideally.

$$\Sigma C_p = 41.8 \text{ J K}^{-1} \text{ mol}^{-1} \text{ \& initial } T = 25^\circ\text{C}$$



Ans. From given equation, we have, at flame temperature (when water is in gaseous state)



$$\Delta C_p \text{ of gaseous products } (\text{CO}_2, \text{H}_2\text{O} \& \text{N}_2) = 41.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

When,

1 O_2 reacted, 4 N_2 remain unreacted, hence total moles of gaseous products

$$\text{will be} = 1 + 2 + (4 \times 2) = 11$$

So, now, flame temperature (T_f) is attained when 802.3 kJ of heat is liberated above is used to heat 11 moles of gases.

By Kirchoff equation,

$$\Delta H = \Delta C_p (T_f - T_i)$$

$$\Delta H_{\text{heating}} \rightarrow 802.3 \times 10^3 \text{ J} = (11 \times 41.8) \text{ J K}^{-1} \times (T_f - T_i)$$

$$\text{adiabatic, } \Delta H = 0 \quad T_f - T_i = \frac{802.3 \times 10^3 \text{ J}}{459.6 \text{ J K}^{-1}} = 1746 \text{ K}$$

$$\text{So, } T_f = 1746 + T_i = 1746 + 298 = \boxed{2043 \text{ K}}$$