

CHEMICAL KINETICS & REDIOACTIVITY

RATE/VELOCITY OF CHEMICAL REACTION :

$$\text{Rate} = \frac{\Delta c}{\Delta t} = \frac{\text{mol/lit.}}{\text{sec}} = \text{mol lit}^{-1} \text{ time}^{-1} = \text{mol dm}^{-3} \text{ time}^{-1}$$

Types of Rates of chemical reaction :

For a reaction $R \longrightarrow P$

$$\text{Average rate} = \frac{\text{Total change in concentration}}{\text{Total time taken}}$$

$$R_{\text{instantaneous}} = \lim_{t \rightarrow 0} \left[\frac{\Delta c}{\Delta t} \right] = \frac{dc}{dt} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Relation between reaction rates of different species involved in a reaction :

For the reaction : $N_2 + 3H_2 \longrightarrow 2NH_3$

$$\text{Rate of disappearance of } N_2 = -\frac{d[N_2]}{dt};$$

$$\text{Rate of disappearance of } H_2 = -\frac{d[H_2]}{dt}; \text{ Rate of appearance of } NH_3 = \frac{d[NH_3]}{dt}$$

$$\text{Rate of reaction} = -\frac{d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

RATE LAW (DEPENDENCE OF RATE ON CONCENTRATION OF REACTANTS) :

$$\text{Rate} = K (\text{conc.})^{\text{order}} \quad - \text{differential rate equation or rate expression}$$

Where K = Rate constant = specific reaction rate = rate of reaction when concentration is unity
unit of K = $(\text{conc.})^{1-\text{order}} \text{ time}^{-1}$

Order of reaction :

$m_1 A + m_2 B \longrightarrow \text{products.}$

$R \propto [A]^p [B]^q$ Where p may or may not be equal to m_1 & similarly q may or may not be equal to m_2 .
 p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and $(p + q)$ is overall order of the reaction.

Note : Order of a reaction can be 'zero' or any whole number, can be a fractional number and it can even be negative with respect to a particular reactant. But overall order is not found to be negative for any reaction till observed.

INTEGRATED RATE LAWS :

C_0 or 'a' is initial concentration and C_t or $a - x$ is concentration at time 't'

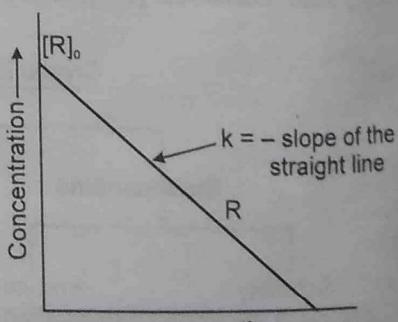
(a) zero order reactions :

$$\text{Rate} = k [\text{conc.}]^0 = \text{constant}$$

$$\text{Rate} = k = \frac{C_0 - C_t}{t} \quad \text{or} \quad C_t = C_0 - kt$$

$$\text{Unit of } K = \text{mol lit}^{-1} \text{ sec}^{-1}, \text{ Time for completion} = \frac{C_0}{k}$$

$$\text{at } t_{1/2}, C_t = \frac{C_0}{2}, \text{ so } kt_{1/2} = \frac{C_0}{2} \Rightarrow t_{1/2} = \frac{C_0}{2k} \quad \therefore t_{1/2} \propto C_0$$



(b) First Order Reactions :

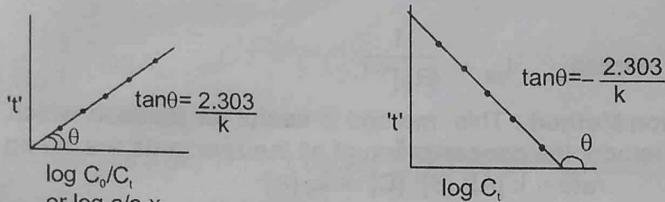
(i) Let a 1st order reaction is, A → Products

$$t = \frac{2.303}{k} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

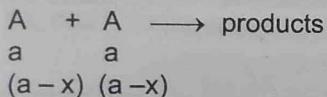
$$\Rightarrow t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} = (\text{Independent of initial concentration}) ; \quad t_{\text{Avg.}} = \frac{1}{k} = 1.44 t_{1/2} \checkmark$$

Graphical Representation :

$$t = -\frac{2.303}{k} \log C_t + \frac{2.303}{R} \log C_0$$

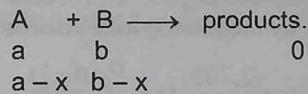


(c) Second order reaction :

2nd order Reactions
Two types

$$\therefore \frac{dx}{dt} = k (a-x)^2$$

$$\Rightarrow \frac{1}{(a-x)} - \frac{1}{a} = kt$$



$$\frac{dx}{dt} = k (a-x)(b-x)$$

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

(d) Psuedo first order reaction :

A second order (or of higher order) reactions can be converted into a first order reaction if the other reactant is taken in large excess. Such first order reactions are known as psuedo first order reactions.

∴ For A + B → Products [Rate = K [A]¹ [B]¹]

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}. \quad \text{Now if 'B' is taken in large excess } b \gg a.$$

$$\Rightarrow k = \frac{2.303}{bt} \log \frac{a}{a-x} \quad \therefore \quad \text{'b' is very large can be taken as constant}$$

$$\Rightarrow kb = \frac{2.303}{t} \log \frac{a}{a-x} \quad \Rightarrow \quad k' = \frac{2.303}{t} \log \frac{a}{a-x}, k' \text{ is psuedo first order rate constant}$$

(e) nth order reaction

A → product

$$\text{Rate} = KC_A^n$$

$$t = \frac{1}{k(n-1)} \left[\frac{1}{C_{A^0}^{n-1}} - \frac{1}{C_A^{n-1}} \right] \quad n \neq 1$$

$$t_{r_2} = \frac{2^{n-1} - 1}{k(n-1) C_{A^0}^{n-1}}$$

METHODS TO DETERMINE ORDER OF A REACTION

(a) **Initial rate method** : In this method initial rate of a reaction is determined by varying the concentration of one of the reactants while others are kept constant.

$$r = k [A]^a [B]^b [C]^c \quad \text{if} \quad [B] = \text{constant}$$

$$[C] = \text{constant}$$

then for two different initial concentrations of A we have

$$r_1 = k [A_{01}]^a, \quad r_2 = k [A_{02}]^a \quad \Rightarrow \quad \frac{r_1}{r_2} = \left(\frac{[A_{01}]}{[A_{02}]} \right)^a$$

(b) **Using integrated rate law** : It is method of trial and error. We have to check that the kinetical data (experimental data) best fits into which rate law. The comparison can also be done graphically.

(c) **Method of half lives** : The half life of different order of reaction is found to depend differently on initial rate of reaction.

$$\text{for } n^{\text{th}} \text{ order reaction} \quad t_{1/2} \propto \frac{1}{[R_0]^{n-1}}$$

(d) **Ostwald Isolation Method** : This method is useful for reaction which involve a large number of reactants. In this method, the concentration of all the reactants are taken in large excess except that of one, so if $\text{rate} = k [A]^a [B]^b [C]^c = k_0 [A]^a$. Then value of 'a' can be calculated by previous methods and similarly 'b' and 'c' can also be calculated.

METHODS TO MONITOR THE PROGRESS OF THE REACTION :

(a) Progress of gaseous reaction can be monitored by measuring total pressure at a fixed volume & temperature or by measuring total volume of mixture under constant pressure and temperature.

$$\therefore k = \frac{2.303}{t} \log \frac{P_0(n-1)}{nP_0 - P_t} \quad \{ \text{Formula is not applicable when } n = 1, \text{ the value of } n \text{ can be fractional also.} \}$$

(b) **By titration method :**

$$1. \quad \therefore a \propto V_0 \quad a - x \propto V_t \quad \Rightarrow \quad k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

2. Study of acid hydrolysis of an ester.

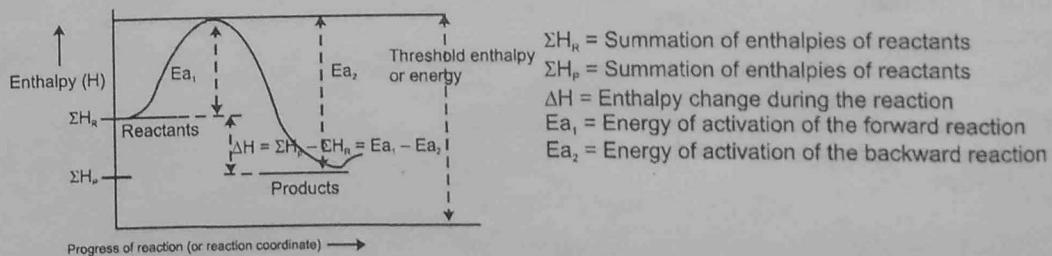
$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

(c) **By measuring optical rotation produced by the reaction mixture :**

$$k = \frac{2.303}{t} \log \left(\frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty} \right)$$

EFFECT OF TEMPERATURE ON RATE OF REACTION.

$$\text{T.C.} = \frac{K_t + 10}{K_t} \approx 2 \text{ to } 3 \quad (\text{for most of the reactions})$$

Arrhenius theory of reaction rate.

$$E_p > E_r \rightarrow \text{endothermic}$$

$$E_p < E_r \rightarrow \text{exothermic}$$

$$\Delta H = (E_p - E_r) = \text{enthalpy change}$$

$E_{\text{threshold}} = \text{min. energy of reactant molecules so they can lead to the transition or product formation.}$
 $E_a = \text{activation energy (it is excess energy of reactant molecules w.r.t. avg energy level so that these can lead into product formation).}$

$E_{\text{af}} = \text{activation energy of forward rxn.}$

$E_{\text{ab}} = \text{activation energy of backward.}$

$$\Delta H = E_{\text{af}} - E_{\text{ab}}$$

$$E_{\text{threshold}} = E_{\text{af}} + E_r = E_b + E_p$$

Arrhenius equation

$$k = A e^{-E_a/RT}$$

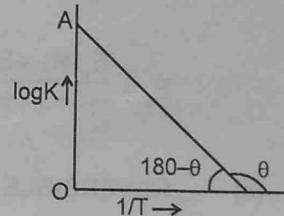
$$r = k [\text{conc.}]^{\text{order}}$$

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

$$\log k = \left(-\frac{E_a}{2.303 R} \right) \frac{1}{T} + \log A$$

So from this it is evident that a plot of $\log k$ versus $\frac{1}{T}$ will be a straight line of

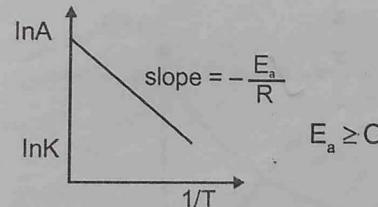
the slope equal to $-\frac{E_a}{2.303 R}$ and intercept equal to $\log A$ as shown below :



If k_1 and k_2 be the rate constant of a reaction at two different temperature T_1 and T_2 respectively, then we have

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

❖ $\ln k = \ln A - \frac{E_a}{RT}$



$T \rightarrow \infty, K \rightarrow A.$
 $K \neq A$

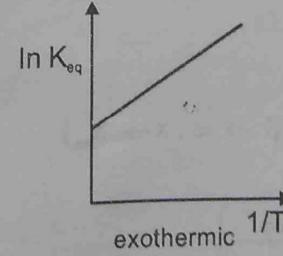
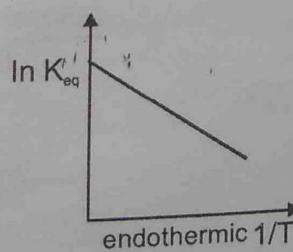
REVERSIBLE REACTIONS

$$k_f = A_f e^{-E_{\text{af}}/RT}$$

$$k_b = A_b e^{-E_{\text{ab}}/RT}$$

$$K_{\text{eq}} = \frac{K_f}{K_b} = \left(\frac{A_f}{A_b} \right) e^{-(E_{\text{af}} - E_{\text{ab}})/RT}$$

$$\ln K_{\text{eq}} = -\frac{\Delta H}{RT} + \ln \left(\frac{A_f}{A_b} \right)$$



(i) PARALLEL REACTION



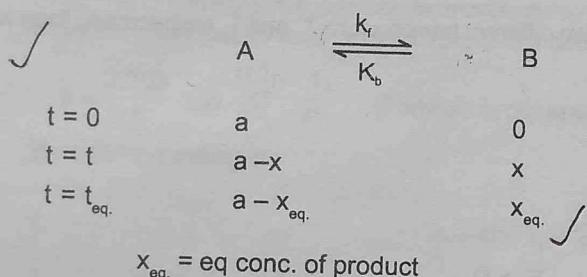
E_{A1} = activation energy for $A \rightarrow B$; E_{A2} = activation energy for $A \rightarrow C$

$$\frac{[B]_t}{[C]_t} = \frac{K_1}{K_2}$$

$$\% B = \frac{K_1}{K_1 + K_2} \times 100$$

$$\% C = \frac{K_2}{K_1 + K_2} \times 100$$

$$E_a = \frac{E_{a1} K_1 + E_{a2} K_2}{K_1 + K_2}$$

(ii) REVERSIBLE 1ST ORDER REACTION (both forward and backward)

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0 \text{ At eq. } (\because \text{At equilibrium conc. is not changed}) \checkmark$$

$$\Rightarrow \frac{1}{K_f + K_b} \ln \left(\frac{K_f a}{K_f a - (k_f + k_b)x} \right) = t$$

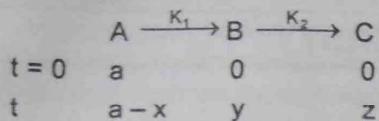
$$x = \frac{K_f a}{K_f + K_b} \left(1 - e^{-(k_f + k_b)t} \right)$$

$$K_{eq.} = \frac{K_f}{K_b} = \frac{[B]_{eq.}}{[A]_{eq.}} = \frac{x_{eq.}}{(a - x_{eq.})}$$

$$\frac{K_f + K_b}{K_f} = \frac{a}{x_{eq.}}$$

$$x = x_{eq.} \left(1 - e^{-(K_f + K_b)t} \right) (t \rightarrow \infty, x \rightarrow x_{eq.})$$

$$K_f + K_b = \frac{1}{t} \ln \left(\frac{x_{eq.}}{x_{eq.} - x} \right)$$

(iii) SEQUENTIAL 1ST ORDER REACTION

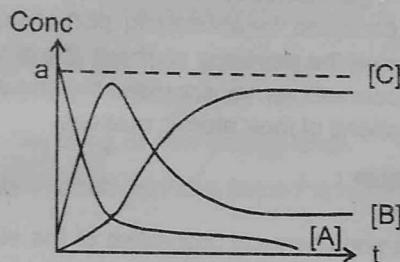
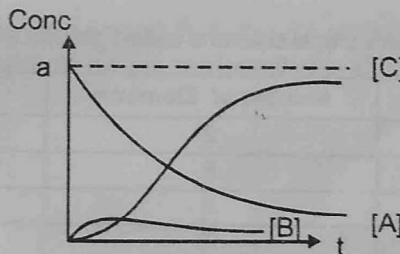
all first order equation

$$[A] = [A] e^{-k_1 t}$$

$$x = a(1 - e^{-k_1 t})$$

$$y = \frac{k_1 a}{k_2 - k_1} \{e^{-k_1 t} - e^{-k_2 t}\}$$

$$\sqrt{B_{(\max.)}} = \frac{1}{(k_1 - k_2)} \ln \frac{k_1}{k_2}$$

CASE-I $k_1 \gg k_2$ CASE II: $k_2 \gg k_1$ 

- ❖ Writing mechanism for complex reaction.
- Rate depends on slowest step.
- Write the rate law on the bases of slowest step.
- In the written rate law involves the intermediate concentration terms, then replace them by using P.S.S.A approach.

$$\frac{d[\text{intermediate}]}{dt} = 0$$

INORGANIC CHEMISTRY

PERIODIC TABLE & PERIODICITY

Development of Modern Periodic Table :

(a) Dobereiner's Triads : He arranged similar elements in the groups of three elements called as triads , in which the atomic mass of the central element was merely the arithmetic mean of atomic masses of other two elements or all the three elements possessed nearly the same atomic masses.

(b) Newland's Law of Octave : He was the first to correlate the chemical properties of the elements with their atomic masses. According to him if the elements are arranged in the order of their increasing atomic masses the eighth element starting from given one is similar in properties to the first one. This arrangement of elements is called as Newland's law of Octave.

(c) Lothen Meyer's Classification : He determined the atomic volumes by dividing atomic masses with their densities in solid states.

He plotted a graph between atomic masses against their respective atomic volumes for a number of elements. He found the observations ; (i) elements with similar properties occupied similar positions on the curve, (ii) alkali metals having larger atomic volumes occupied the crests, (iii) transition elements occupied the troughs, (iv) the halogens occupied the ascending portions of the curve before the inert gases and (v) alkaline earth metals occupied the positions at about the mid points of the descending portions of the curve. On the basis of these observations he concluded that the atomic volumes (a physical property) of the elements are the periodic functions of their atomic masses.

(d) Mendeleev's Periodic Table :

Mendeleev's Periodic's Law

According to him the physical and chemical properties of the elements are the periodic functions of their atomic masses.

This table was divided into nine vertical columns called groups and seven horizontal rows called periods.

Periods	Number of Elements	Called as
(1) st n = 1	2	Very short period
(2) nd n = 2	8	Short period
(3) rd n = 3	8	Short period
(4) th n = 4	18	Long period
(5) th n = 5	18	Long period
(6) th n = 6	32	Very long period
(7) th n = 7	19	Incomplete period

The groups were numbered as I, II, III, IV, V, VI, VII, VIII and Zero group

Merits of Mendeleev's Periodic table:

- It has simplified and systematised the study of elements and their compounds.
- It has helped in predicting the discovery of new elements on the basis of the blank spaces given in its periodic table.

Demerits in Mendeleev's Periodic Table :

- Position of hydrogen is uncertain .It has been placed in IA and VIIA groups because of its resemblance with both the groups.
- No separate positions were given to isotopes.
- Anomalous positions of lanthanides and actinides in periodic table.
- Order of increasing atomic weights is not strictly followed in the arrangement of elements in the periodic table. For example Ar(39.94) is placed before K(39.08) and Te (127.6) is placed before I(126.9).
- Similar elements were placed in different groups e.g. Cu in IB and Hg in IIB and similarly the elements with different properties were placed in same groups e.g. alkali metals in IA and coinage metals in IB.
- It didn't explained the cause of periodicity.

(e) Long form of the Periodic Table or Moseley's Periodic Table :

Modern Periodic Law (Moseley's Periodic Law) :

Physical and chemical properties of the elements are the periodic functions of their atomic number. If the elements are arranged in order of their increasing atomic number, after a regular interval, elements with similar properties are repeated.

Periodicity :

The repetition of the properties of elements after regular intervals when the elements are arranged in the order of increasing atomic number is called periodicity.

Cause of Periodicity :

The periodic repetition of the properties of the elements is due to the recurrence of similar valence shell electronic configurations after certain regular intervals. For example, alkali metals have same valence shell electronic configuration ns^1 , therefore, have similar properties.

The modern periodic table consists of horizontal rows (periods) and vertical column (groups).

Periods :

There are seven periods numbered as 1, 2, 3, 4, 5, 6 and 7.

- Each period consists of a series of elements having same valence shell.
- Each period corresponds to a particular principal quantum number of the valence shell present in it.
- Each period starts with an alkali metal having outermost electronic configuration as ns^1 .
- Each period ends with a noble gas with outermost electronic configuration ns^2np^6 except helium having outermost electronic configuration as $1s^2$.
- Each period starts with the filling of new energy level.
- The number of elements in each period is twice the number of atomic orbitals available in energy level that is being filled.

Groups :

There are eighteen groups numbered as 1, 2, 3, 4, 5, 13, 14, 15, 16, 17, 18.

Group consists of a series of elements having similar valence shell electronic configuration.

S-Block Elements		p-Block Elements																		
1 IA	2 II A	d - Block Elements												13 III A	14 IV A	15 V A	16 VI A	17 VII A	18 VIII A	
1 H 1.007	2 He 4.002	3 Li 6.941	4 Be 9.012	5 B 10.811	6 C 12.011	7 N 14.006	8 O 15.999	9 F 18.998	10 Ne 20.179	11 Na 22.98	12 Mg 24.30	13 Al 26.981	14 Si 28.085	15 P 30.973	16 S 32.006	17 Cl 35.452	18 Ar 39.948			
19 K 39.08	20 Ca 40.078	21 Sc 44.958	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.938	26 Fe 55.84	27 Co 55.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.921	34 Se 78.96	35 Br 79.904	36 Kr 83.80			
37 Rb 85.46	38 Sr 87.62	39 Y 88.905	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc 98	44 Ru 101.07	45 Rh 102.905	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 132.29			
55 Cs 132.90	56 Ba 137.27	57 La* 138.905	72 Hf 178.49	73 Ta 180.947	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.666	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 207.980	84 Po 209	85 At 210	86 Rn 222			
87 Fr 223	88 Ra 226	89 Ac** 227	104 Rf 261.11	105 Ha 262.114	106 Sg 263.118	107 Bh 262.12	108 Hs 265	109 Mt 266	110 Uun 269				114 Uuq 257							
Inner - Transition Metals (f-Block elements)																				
*Lanthanides		58 Ce 140.115	59 Pr 140.907	60 Nd 144.24	61 Pm 145	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967					
**Actinides		90 Th 232.038	91 Pa 231	92 U 238.028	93 Np 237	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260					

Classification of the Elements :

It is based on the type of orbitals which receives the differentiating electron (i.e., last electron).

(a) s-block elements

When shells upto $(n - 1)$ are completely filled and the last electron enters the s-orbital of the outermost (n^{th}) shell, the elements of this class are called s-block elements.

Group 1 & 2 elements constitute the s-block. General electronic configuration is [inert gas] ns^{1-2} .
s-block elements lie on the extreme left of the periodic table.

(b) p-block elements

When shells upto $(n - 1)$ are completely filled and differentiating electron enters the p-orbital of the n^{th} orbit, elements of this class are called p-block elements.

Group 13 to 18 elements constitute the p-block. General electronic configuration is [inert gas] $ns^2 np^{1-6}$.
p-block elements lie on the extreme right of the periodic table. This block includes some metals, all nonmetals and metalloids. s-block and p-block elements are collectively called normal or representative elements.

(c) d-Block elements

When outermost (n^{th}) and penultimate shells ($n - 1$)th shells are incompletely filled and differentiating electron enters the $(n - 1)$ d orbitals (i.e., d-orbital of penultimate shell) then elements of this class are called d-block elements. Group 3 to 12 elements constitute the d-block. General electronic configuration is [inert gas] $(n - 1) d^{1-10} ns^{1-2}$ (except, palladium which has valence shell electron configuration $4d^{10} 5s^0$). All the transition elements are metals and most of them form coloured complexes or ions.

(d) f-Block elements

When n , $(n - 1)$ and $(n - 2)$ shells are incompletely filled and last electron enters into f-orbital of antepenultimate i.e., $(n - 2)$ th shell, elements of this class are called f-block elements. General electronic configuration is $(n - 2) f^{1-14} (n - 1) d^{0-1} ns^2$. All f-block elements belong to 3rd group.

The elements of f-blocks have been classified into two series. (1) 1st inner transition or 4 f-series, contains 14 elements ₅₈Ce to ₇₁Lu. Filling of electrons takes place in 4f subshell. (2). IIInd inner transition or 5 f-series, contains 14 elements ₉₀Th to ₁₀₃Lr. Filling of electrons takes place in 5f subshell.

Prediction of period, group and block :

- Period of an element corresponds to the principal quantum number of the valence shell.
- The block of an element corresponds to the type of subshell which receives the last electron.
- The group is predicted from the number of electrons in the valence shell or/and penultimate shell as follows.
 - (a) For s-block elements ; Group no. = the no. of valence electrons
 - (b) For p-block elements ; Group no. = $10 + \text{no. of valence electrons}$
 - (c) For d-block elements ; Group no. = no. of electrons in $(n - 1)$ d sub shell + no. of electrons in valence shell.

Metals and nonmetals :

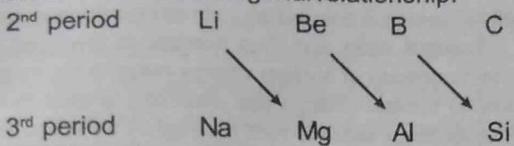
- ◆ The metals are characterised by their nature of readily giving up the electron(s) and from shining lustre. Metals comprises more than 78% of all known elements and appear on the left hand side of the periodic table. Metals are usually solids at room temperature (except mercury, gallium). They have high melting and boiling points and are good conductors of heat and electricity. Oxides of metals are generally basic in nature (some metals in their higher oxidation state form acid oxides e.g. CrO_3).
- ◆ Nonmetals do not lose electrons but take up electrons to form corresponding anions. Nonmetals are located at the top right hand side of the periodic table. Nonmetals are usually solids, liquids or gases at room temperature with low melting and boiling points. They are poor conductors of heat and electricity. Oxides of nonmetals are generally acidic in nature.

Metalloids (Semi metals) :

It can be understood from the periodic table that nonmetallic character increases as we move from left to right across a row. It has been found that some elements which lie at the border of metallic and nonmetallic behavior, possess the properties that are characteristic of both metals and nonmetals. These elements are called semi metals or metalloids. The metalloids comprise of the elements B, Si, Ge, As, Sb and Te.

Diagonal relationship :

Some elements of certain groups of 2nd period resemble much in properties with the elements of third period of next group i.e. elements of second and third period are diagonally related in properties. This phenomenon is known as diagonal relationship.



Diagonal relationship arises because of :

- (i) on descending a group, the atoms and ions increase in size. On moving from left to right in the periodic table, the size decreases. Thus on moving diagonally, the size remains nearly the same.
(Li = 1.23 Å & Mg = 1.36 Å ; Li⁺ = 0.76 Å & Mg²⁺ = 0.72 Å)
- (ii) it is sometimes suggested that the diagonal relationship arises because of diagonal similarity in electronegativity values.
(Li = 1.0 & Mg = 1.2 ; Be = 1.5 & Al = 1.5 ; B = 2.0 & Si = 1.8)

The periodicity of atomic properties :

(i) Effective nuclear charge :

The effective nuclear charge (Z_{eff}) is the charge actually felt by the valence electron. Z_{eff} is given by $Z_{\text{eff}} = Z - \sigma$, (where Z is the actual nuclear charge (atomic number of the element) and σ is the shielding (screening) constant). The value of σ i.e. shielding effect can be determined using the Slater's rules.

(ii) Atomic radius :

(A) Covalent radius : It is one-half of the distance between the centres of two nuclei (of like atoms) bonded by a single covalent bond. Covalent radius is generally used for nonmetals.

(B) Vander Waal's radius (Collision radius) : It is one-half of the internuclear distance between two adjacent atoms in two nearest neighbouring molecules of the substance in solid state.

(C) Metallic radius (Crystal radius) :

It is one-half of the distance between the nuclei of two adjacent metal atoms in the metallic crystal lattice.

◆ Thus, the covalent, vander Wall's and metallic radius magnitude wise follows the order,

$$r_{\text{covalent}} < r_{\text{crystal}} < r_{\text{vander Walls}}$$

Variation in a Period	Variation in a Group
In a period left to right :	In a group top to bottom :
Nuclear charge (Z) increases by one unit	Nuclear charge (Z) increases by more than one unit
Effective nuclear charge (Z_{eff}) also increases	Effective nuclear charge (Z_{eff}) almost remains constant because of increased screening effect of inner shells electrons.
But number of orbitals (n) remains constant	But number of orbitals (n) increases.
As a result, the electrons are pulled closer to the nucleus by the increased Z_{eff} . $r_n \propto \frac{1}{Z^2}$ Hence atomic radii decrease with increase in atomic number in a period from left to right.	The effect of increased number of atomic shells outweighs the effect of increased nuclear charge. As a result of this the size of atom increases from top to bottom in a given group.

The atomic radius of inert gas (zero group) is given largest in a period because it is represented as vander Waals's radius which is generally larger than the covalent radius. The vander Waal's radius of inert gases also increases from top to bottom in a group.

(iii) Ionic radius :

The effective distance from the centre of nucleus of the ion up to which it has an influence in the ionic bond is called ionic radius.

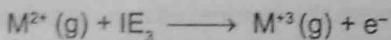
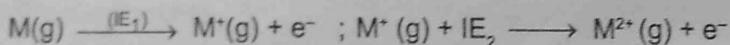
Cation	Anion
<p>It is formed by the loss of one or more electrons from the valence shell of an atom of an element.</p> <p>Cations are smaller than the parent atoms because,</p> <ul style="list-style-type: none"> (i) the whole of the outer shell of electrons is usually removed. (ii) in a cation, the number of positive charges on the nucleus is greater than number of orbital electrons leading to increased inward pull of remaining electrons causing contraction in size of the ion. 	<p>It is formed by the gain of one or more electrons in the valence shell of an atom of an element.</p> <p>Anions are larger than the parent atoms because</p> <ul style="list-style-type: none"> (i) anion is formed by gain of one or more electrons in the neutral atom and thus number of electrons increases but magnitude of nuclear charge remains the same. (ii) nuclear charge per electrons is thus reduced and the electrons cloud is held less tightly by the nucleus leading to the expansion of the outer shell. Thus size of anion is increased.

- ◆ The species containing the same number of electrons but differ in the magnitude of their nuclear charges are called as isoelectronic species. For example, N^{3-} , O^{2-} , F^- , Ne , Na^+ , Mg^{2+} and Al^{3+} are all isoelectronic species with same number of electrons (i.e 10) but different nuclear charges of +7, +8, +9, +10, +11, +12 and +13 respectively.

Within a series of isoelectronic species as the nuclear charge increases, the force of attraction by the nucleus on the electrons also increases. As a result, the ionic radii of isoelectronic species decrease with increases in the magnitude of nuclear charges.

(iv) Ionisation Energy :

Ionisation energy (IE) is defined as the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form a cation.



IE_1 , IE_2 & IE_3 are the Ist, IInd & IIIrd ionization energies to remove electron from a neutral atom, monovalent and divalent cations respectively. In general, $(IE)_1 < (IE)_2 < (IE)_3 < \dots$

◆ Factors Influencing Ionisation energy

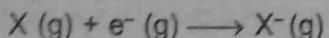
Variation in ionization energies in a period and group may or not be regular and can be influenced by the following factors.

- Size of the Atom :** Ionisation energy decreases with increase in atomic size.
- Nuclear Charge :** The ionisation energy increases with increase in the nuclear charge.
- Shielding or screening effect :** The electrons in the inner shells act as a screen or shield between the nucleus and the electrons in the outer most shell. This is called shielding effect. The larger the number of electrons in the inner shells, greater is the screening effect and smaller the force of attraction and thus ionization energy (IE) decreases.
- Penetration effect of the electron :** Penetration effect of the electrons follows the order s > p > d > f for, the same energy level. Higher the penetration of electron higher will be the ionisation energy.
- Electronic Configuration :** If an atom has exactly half-filled or completely filled orbitals, then such an arrangement has extra stability. The removal of an electron from such an atom requires more energy than expected. Metallic or electropositive character of elements increases as the value of ionisation energy decreases. The relative reactivity of the metals in gaseous phase increases with the decrease in ionisation energy.

The reducing power of elements in gaseous phase increases as the value of ionisation energy decreases. Amongst alkali metals, the lithium is strongest reducing agent in aqueous solution.

(v) Electron Gain Enthalpy :

The electron gain enthalpy $\Delta_{eg}H^\circ$, is the change in standard molar enthalpy when a neutral gaseous atom gains an electron to form an anion.



Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion. Electron gain may be either exothermic or endothermic depending on the elements.

When an electron is added to the atom and the energy is released, the electron gain enthalpy is negative and when energy is needed to add an electron to the atom, the electron gain enthalpy is positive.

The second electron gain enthalpy, the enthalpy change for the addition of a second electron to an initially neutral atom, invariably positive because the electron repulsion out weighs the nuclear attraction.

- Group 17 elements (halogens) have very high negative electron gain enthalpies (i.e. high electron affinity) because they can attain stable noble gas electronic configuration by picking up an electron.
- Across a period, with increase in atomic number, electron gain enthalpy becomes more negative because left to right across a period effective nuclear charge increases and consequently it will be easier to add an electron to a small atom.
- As we move in a group from top to bottom, electron gain enthalpy becomes less negative because the size of the atom increases and the added electron would be at larger distance from the nucleus.
- Noble gases have large positive electron gain enthalpies because the electron has to enter the next higher energy level leading to a very unstable electronic configuration.
- Negative electron gain enthalpy of O or F is less than S or Cl. This is due to the fact that when an electron is added to O or F, the added electron goes to the smaller $n = 2$ energy level and experiences significant repulsion from the other electrons present in this level. In S or Cl, the electron goes to the larger $n = 3$ energy level and consequently occupies a larger region of space leading to much less electron-electron repulsion.
- Electron gain enthalpies of alkaline earth metals are very less or positive because the extra electron is to be added to completely filled s-orbitals in their valence shells.
- Nitrogen has very low electron affinity because there is high electron repulsion when the incoming electron enters an orbital that is already half filled.
- (i) Electron affinity $\propto \frac{1}{\text{Atomic size}}$ (ii) Electron affinity \propto Effective nuclear charge (Z_{eff})
 (iii) Electron affinity $\propto \frac{1}{\text{Screening effect}}$. (iv) Stability of half filled and completely filled orbitals of a subshell is comparatively more and the addition of an extra electron to such a system is difficult and hence the electron affinity value decreases.

(vi) Electronegativity :

Electronegativity is a measure of the tendency of an element to attract shared electrons towards itself in a covalently bonded molecules.

The magnitude of electronegativity of an element depends upon its ionisation potential & electron affinity. Higher ionisation potential & electron affinity values indicate higher electronegativity value.

Pauling's scale : Linus Pauling developed a method for calculating relative electronegativities of most elements. According to Pauling

$$\Delta = X_A - X_B = 0.208 \sqrt{E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}}$$

E_{A-B} = Bond enthalpy/ Bond energy of A – B bond.

E_{A-A} = Bond energy of A – A bond

E_{B-B} = Bond energy of B – B bond

(All bond energies are in kcal / mol)

$$\Delta = X_A - X_B = 0.1017 \sqrt{E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}}$$

All bond energies are in kJ / mol.

Mulliken's scale : Electronegativity χ can be regarded as the average of the ionisation energy (IE) and the electron affinity (EA) of an atom (both expressed in electron volts).

$$\chi_M = \frac{IE + EA}{2}$$

Pauling's electronegativity χ_p is related to Mulliken's electronegativity χ_M as given below.

$$\chi_p = 1.35 (\chi_M)^{1/2} - 1.37$$

Mulliken's values were about 2.8 times larger than the Pauling's values.

(vii) Periodicity of Valence or Oxidation States :

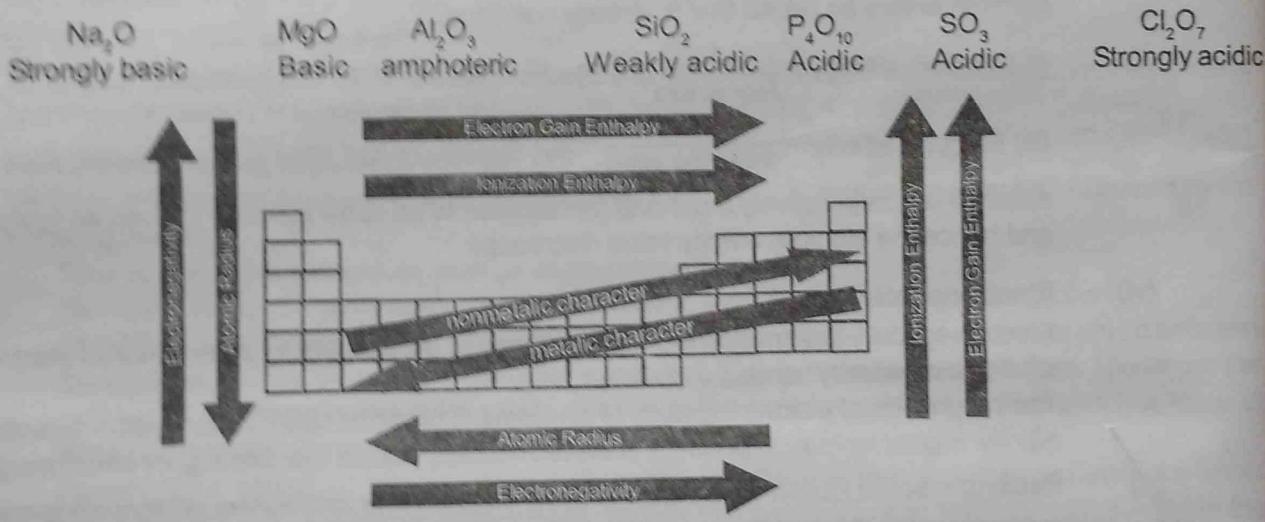
The valence of representative elements is usually (though not necessarily) equal to the number of electrons in the outermost orbitals and / or equal to eight minus the number of outermost electrons. Nowadays the term oxidation state is frequently used for valence.

There are many elements which exhibit variable valence. This is particularly characteristic of transition elements and actinoids.

(viii) Periodic Trends and Chemical Reactivity :

The ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (except noble gases which having completely filled shells have rather positive electron gain enthalpy values). This results in high chemical reactivity at the two extremes and the lowest in the centre. The loss and gain of electron can be related with the reducing and oxidizing behaviour of the elements respectively. However, it can also be directly related to the metallic and nonmetallic character of elements. Thus, the metallic character of an element, which is highest at the extremely left decreases and the nonmetallic character increases while moving from left to right across the period. The normal oxide formed by the element on extreme left is the most basic (e.g. Na_2O), whereas that formed by the element on extreme right is the acidic (e.g. Cl_2O_7). Oxides of elements in the centre are amphoteric (e.g. Al_2O_3 , As_2O_3) or neutral (e.g., CO , NO , N_2O).

- In a group, basic nature of oxides increases or acidic nature decreases. Oxides of the metals are generally basic and oxides of the nonmetals are acidic. The oxides of the metalloids are generally amphoteric in nature. The oxides of Be, Al, Zn, Sn, As, Pb and Sb are amphoteric.
- In a period the nature of the oxides varies from basic to acidic.



CHEMICAL BONDING

Chemical Bond :

The attractive force which holds various constituents such as atoms, ions etc., together in different chemical species is called a chemical bond.

In the formation of a chemical bond, only the electrons of the outermost shell of an atom are involved. In the process each atom attains a stable outer electronic configuration of inert gases.

Ionic or Electrovalent Bond :

The formation of an ionic compound would primarily depends upon :

- * The ease of formation of the positive and negative ions from the respective neutral atoms.
- * The arrangement of the positive and negative ions in the solid, that is the lattice of the crystalline compound.

Conditions for the formation of ionic compounds :

Electronegativity difference between two combining elements must be larger.

Ionization enthalpy ($\text{M(g)} \rightarrow \text{M}^+(g) + \text{e}^-$) of electropositive element must be low.

Negative value of electron gain enthalpy ($\text{X(g)} + \text{e}^- \rightarrow \text{X}^-(g)$) of electronegative element should be high.

Lattice enthalpy ($\text{M}^+(g) + \text{X}^-(g) \rightarrow \text{MX(s)}$) of an ionic solid must be high.

(i)
(ii)

Deter

Hydrat

Hydro

Gener
(a)

(b)

(c)

(D)

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

Lattice Enthalpy :

The lattice enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. The process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only. Factors associated with the crystal geometry have to be included.

Factors affecting lattice energy of an ionic compound :

i) Lattice energy $\propto \frac{1}{r_+ + r_-}$ where $(r_+ + r_-)$ = Inter-ionic Distance.

ii) Lattice energy $\propto Z_+ Z_-$

Z_+ \Rightarrow charge on cation in terms electronic charge.

Z_- \Rightarrow charge on anion in terms electronic charge.

Determination of lattice energy :**Born-Haber Cycle :**

It inter relates the various energy terms involved during formation of an ionic compound.

It is a thermochemical cycle based on the Hess's law of constant heat summation.

Hess's Law is the net enthalpy change of a chemical reaction or of any process always remain same whether the reaction takes place in one step or many steps.

Hydration :

All the simple salts dissolve in water, producing ions, and consequently the solution conduct electricity. Since Li^+ is very small, it is heavily hydrated. This makes radius of hydrated Li^+ ion large and hence it moves only slowly. In contrast, Cs^+ is the least hydrated because of its bigger size and thus the radius of the Cs^+ ion is smaller than the radius of hydrated Li^+ , and hence hydrated Cs^+ moves faster, and conducts electricity more readily.

Hydrolysis :

Hydrolysis means reaction with water molecules ultimately leading to breaking of O-H bond into H^+ and OH^- ions. While the term **Hydration** means the surrounding of polar molecule or ions by polar molecules of water.

In hydrolysis there is complex formation with water molecule or reaction with water molecule.

Hydrolysis in covalent compounds takes place generally by two mechanisms

(a) By Coordinate bond formation : Generally in halides of atoms having vacant d-orbitals.

(b) By H-bond formation : For example in Nitrogen trihalides

General properties of ionic compounds :

a) **Physical state :** At room temperature ionic compounds exist either in solid state or in solution phase but not in gaseous state.

b) **Isomorphism :** Simple ionic compounds do not show isomerism but isomorphism is their important characteristic. Crystals of different ionic compounds having similar crystal structures are known to be isomorphs to each other and the phenomenon is known as isomorphism.
e.g., $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ | $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

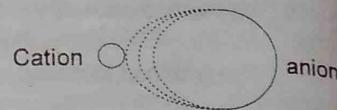
c) **Electrical conductivity :**
Ionic solids are almost non-conductors. However they conduct a very little amount of current due to crystal defects. All ionic solids are good conductors in molten state as well as in their aqueous solutions because their ions are free to move.

SOLUBILITY OF IONIC COMPOUNDS :

Soluble in polar solvents like water which have high dielectric constant

Covalent character in ionic compounds (Fajan's rule) :

When anion and cation approach each other, the valence shell of anion is pulled towards cation nucleus and thus shape of anion is deformed. This phenomenon of deformation of anion by a cation is known as polarization and the ability of cation to polarize a near by anion is called as polarizing power of cation.



Fajan's pointed out that greater is the polarization of anion in a molecule, more is covalent character in it.

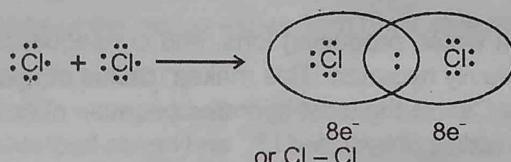
More distortion of anion, more will be polarization then covalent character increases.

Fajan's gives some rules which govern the covalent character in the ionic compounds, which are as follows:

- (i) Size of cation : Size of cation \propto 1 / polarisation.
- (ii) Size of anion : Size of anion \propto polarisation
- (iii) Charge on cation : Charge on cation \propto polarisation.
- (iv) Charge on anion : Charge on anion \propto polarisation.
- (v) Pseudo inert gas configuration of cation : Cation having pseudo inert gas configuration has more polarizing power than the cation that has inert gas configuration. Thus NaCl having inert gas configuration will be more ionic whereas CuCl having pseudo inert gas configuration will be more covalent in nature.

Covalent Bond :

It forms by sharing of valence electrons between atoms to form molecules e.g., formation of Cl_2 molecule :



Covalent bond between two Cl atoms

chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon). The dots represent electrons. Such structures are referred to as Lewis dot structures.

The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. The important conditions being that :

- (i) Each bond is formed as a result of sharing of an electron pair between the atoms.
- (ii) Each combining atom contributes at least one electron to the shared pair.
- (iii) The combining atoms attain the outer-shell noble gas configurations as a result of the sharing of electrons.

1.

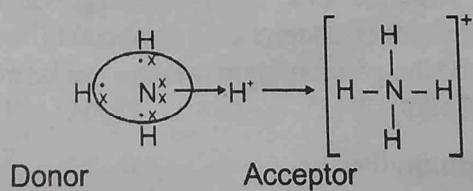
2.

3.

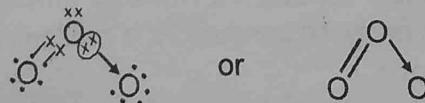
Coordinate Bond (Dative Bond):

The bond formed between two atom in which contribution of an electron pair is made by one of them while the sharing is done by both.

(i) NH_4^+ (ammonium ion)



(ii) O_3 (ozone)



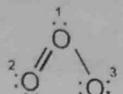
Other examples : H_2SO_4 , HNO_3 , H_3O^+ , N_2O , $[\text{Cu}(\text{NH}_3)_4]^{2+}$

Formal Charge :

The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as :

$$\text{Formal charge (F.C.)} \\ \text{On an atom in a Lewis structure} = \left[\text{Total number of valence electrons in the free atom} \right] - \left[\text{Total number of non bonding (lone pair) electrons} \right] - \left(\frac{1}{2} \right) \left[\text{Total number of bonding (shared) electrons} \right]$$

Let us consider the ozone molecule (O_3). The Lewis structure of O_3 , may be drawn as :

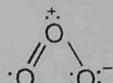


The atoms have been numbered as 1, 2 and 3. The formal charge on:

The central O atom marked 1 = $6 - 2 - \frac{1}{2}(6) = +1$; The terminal O atom marked 2 = $6 - 4 - \frac{1}{2}(4) = 0$

The terminal O atom marked 3 = $6 - 6 - \frac{1}{2}(2) = -1$

Hence, we represent O_3 along with the formal charges as follows:



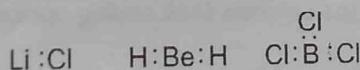
Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. Generally the lowest energy structure is the one with the smallest formal charges on the atoms.

Limitations of the Octet Rule :

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

1. The incomplete octet of the central atom

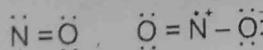
In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are $LiCl$, BeH_2 and BCl_3 .



Some other such compounds are $AlCl_3$ and BF_3 .

2. Odd-electron molecules

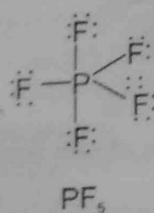
In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2 , the octet rule is not satisfied for all the atoms



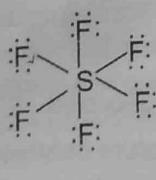
3. The expanded octet

Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

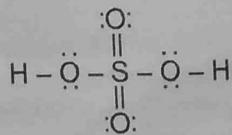
Some of the examples of such compounds are: PF_5 , SF_6 , H_2SO_4 and a number of coordination compounds.



10 electrons around the P atom



12 electrons around the S atom



12 electrons around the S atom

4. Other drawbacks of the octet theory

- (i) It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2 , KrF_2 , XeOF_2 etc.,
- (ii) This theory does not account for the shape of molecules.
- (iii) It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

Valence bond theory (VBT) :

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy, which is corresponding to minimum in the curve depicted in Fig. Conversely, 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

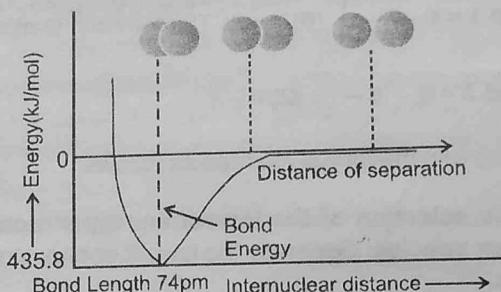
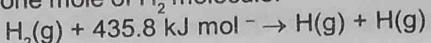


Figure : The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2 .

Orbital Overlap Concept

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present, in the valence shell having opposite spins.

Directional Properties of Bonds :

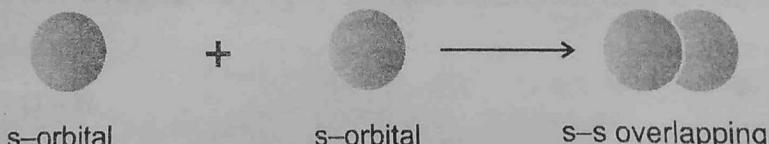
The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like CH_4 , NH_3 and H_2O , etc. in terms of overlap and hybridisation of atomic orbitals.

Types of Overlapping and Nature of Covalent Bonds

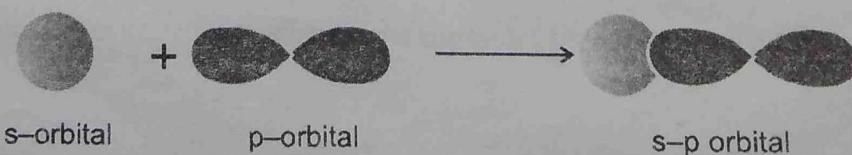
The covalent bond may be classified into two types depending upon the types of overlapping :

- (i) sigma (σ) bond, and (ii) pi (π) bond

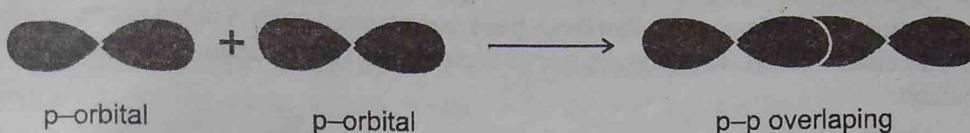
- (i) **Sigma (σ) bond :** This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.
 - s-s overlapping : In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below :



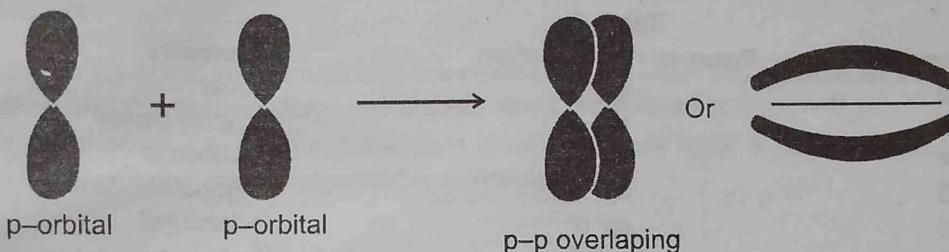
- s-p overlapping: This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.



- p-p overlapping : This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



- (ii) **$\pi(\pi)$ bond :** In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.



Strength of Sigma and pi Bonds :

Basically the strength of a bond depends upon the extent of overlapping- In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds)

Valence shell electron pair repulsion (VSEPR) theory :

The main postulates of VSEPR theory are as follows:

- The shape of a molecule depends upon the number of valence shell electron pairs [bonded or nonbonded] around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decreases in the order :

I lone pair (ℓp) - lone pair (ℓp) > lone pair (ℓp) - bond pair (bp) > bond pair (bp) - bond pair (bp)

Hybridisation :

Salient features of hybridisation : The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. ✓ The hybridised orbitals are always equivalent in energy and shape.
3. ✓ The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. ✓ These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement is obtained. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation :

- The orbitals present in the valence shell of the atom are hybridised.
- The orbitals undergoing hybridisation should have almost equal energy.
- Promotion of electron is not essential condition prior to hybridisation.

Compendium (Chemistry)

- (iv) It is the orbital that undergo hybridization and not the electrons. For example, for orbitals of nitrogen atom ($2s^2$ $2p_x^1$ $2p_y^1$ $2p_z^1$) belonging to valency shell when hybridize to form four hybrid orbitals , one of which has two electrons (as before) and other three have one electron each. It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

Determination of hybridisation of an atom in a molecule or ion:**Steric number rule (given by Gillespie) :**

Steric No. of an atom = number of atom bonded with that atom + number of lone pair(s) left on that atom.
Note : This rule is not applicable to molecules/ions which have odd e⁻ (ClO_2 , NO , NO_2), free radicals and compounds like B_2H_6 which involve 3 centre 2e⁻ bond (banana bond).

Table-3

Steric number	Types of Hybridisation	Geometry
2	sp	Linear
3	sp ²	Trigonal planar
4	sp ³	Tetrahedral
5	sp ³ d	Trigonal bipyramidal
6	sp ³ d ²	Octahedral
7	sp ³ d ³	Pentagonal bipyramidal

Hybridization Involving d-orbital :

Type of 'd' orbital involved
sp ³ d
sp ³ d ²
sp ³ d ³
dsp ²

dz²dx² - y² & dz²dx² - y², dz² & dxyd_{x²-y²}**Molecular Orbital Theory (MOT) :**

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

- (i) Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.
- (ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.
- (iii) An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule. **Thus an atomic orbital is monocentric while a molecular orbital is polycentric.**
- (iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular orbital** are formed.
- (v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- (vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital , the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.
- (vii) The molecular orbitals like the atomic orbitals are filled in accordance with the **Aufbau principle** obeying the **Pauli Exclusion principle** and the **Hund's Rule of Maximum Multiplicity**. But the filling order of these molecular orbitals is always **experimentally decided**, there is no rule like (n + l) rule in case of atomic orbitals.

CONDITIONS FOR THE COMBINATION OF ATOMIC ORBITALS :

1. The combining atomic orbitals must have the same or nearly the same energy.
2. The combining atomic orbitals must have the same symmetry about the molecular axis.
3. The combining atomic orbitals must overlap to the maximum extent.

ENERGY LEVEL DIAGRAM FOR MOLECULAR ORBITALS :

The energy levels of molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

The increasing order of energies of various molecular orbitals for Be_2 , B_2 , C_2 , N_2 etc., is :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

The important characteristic feature of this order is that the **energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.**

BOND ORDER

Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals i.e., Bond order (b.o.) = $\frac{1}{2}(N_b - N_a)$

A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b < N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable molecule.

NATURE OF THE BOND :

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively.

BOND-LENGTH :

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

MAGNETIC NATURE :

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field) e.g., N_2 molecule. However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O_2 molecule.

Dipole moment :

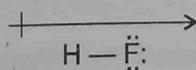
It is defined as the product of magnitude of the partial charge (δ^+ or δ^-) developed on any of the covalently bonded atoms and the distance between two atoms.

Dipole moment (μ) = Magnitude of charge (q) \times distance of separation (d)

Dipole moment is usually expressed in Debye units (D). The conversion factors are

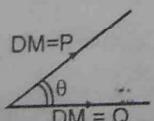
- $1 D = 3.33564 \times 10^{-30} \text{ Cm}$, where C is coulomb and m is meter.
- $1 \text{ Debye} = 1 \times 10^{-18} \text{ e.s.u. cm}$.

Further dipole moment is a vector quantity and is depicted by a small arrow with tail on the positive centre and head pointing towards the negative centre. For example the dipole moment of HF may be represented as



The shift in electron density is represented by crossed arrow (+→) above the Lewis structure to indicate the direction of the shift.

In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. i.e. a molecule will have a dipole moment if the summation of all of the individual moment vector is non-zero.

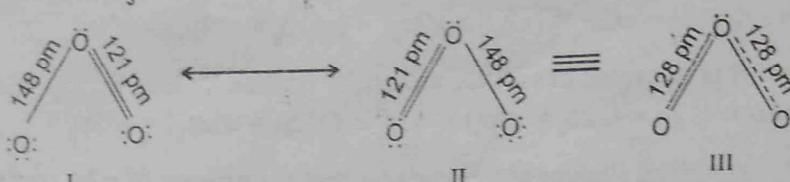


$$R = \sqrt{P^2 + Q^2 + 2PQ \cos \theta}, \text{ where } R \text{ is resultant dipole moment.}$$

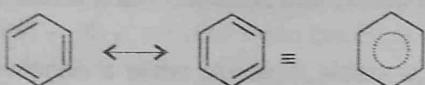
Resonance :

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

For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below:

Resonance in the O_3 molecule

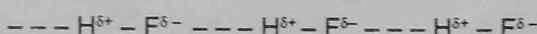
Resonance Hybrid : It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of covalence maxima for the atoms.



Resonance hybrid

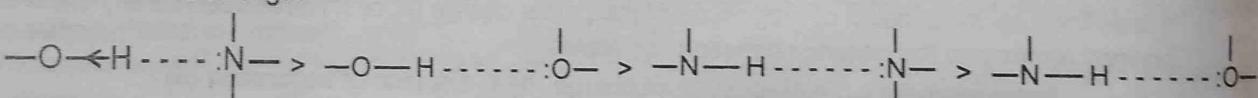
Hydrogen Bond :

Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are tied to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is called as hydrogen bond and is weaker than covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as given below:

**Conditions required for H-bond :**

- (i) Molecule should have more electronegative atom (F, O, N) linked to H-atom.
- (ii) Size of electronegative atom should be smaller.
- (iii) A lone pair should be present on electronegative atom.

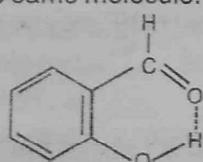
Order of H-bond strength

**TYPES OF H-BONDS :**

(A)

Intramolecular H-Bonding :

This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule i.e., it is formed when hydrogen atom is present in between the two highly electronegative (F, O, N) atoms within the same molecule.



o-hydroxy benzaldehyde

It has lower boiling point (i.e. more volatile) than its para-derivative (where association of molecules takes place using intermolecular H-bonding) because it exists as discrete molecules.

Necessary conditions for the formation of intramolecular hydrogen-bonding :

- (a) the ring formed as a result of hydrogen bonding should be planar.
- (b) a 5- or 6- membered ring should be formed.
- (c) interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

(B)

Intermolecular H-Bonding :

Exists between the negative and positive ends of different molecules of the same or different substances i.e., it is formed between two different molecules of the same or different compounds.

(a) by water molecules

✓ Due to polar nature of H_2O there is association of water molecules giving a liquid state of abnormally high boiling point.

(b) The hydrogen bonds in HF link the F atom of one molecule with the H-atom of another molecule, thus forming a zig-zag chain ($(HF)_n$) in both the solid and also in the liquid.

Some hydrogen bonding also occurs in the gas, which consists of a mixture of cyclic $(HF)_n$ polymers, dimeric $(HF)_2$, and monomeric HF.

Very strong hydrogen bonding occurs in the alkali metal hydrogen fluorides of formula $M[HF_2]$; in KHF_2 , for example, an X-ray diffraction study together with a neutrons diffraction study shows that there is a linear symmetrical anion having an over all, F-H-F distance of 2.26 \AA , which may be compared with the H-F bond length of 0.92 \AA in hydrogen fluoride monomer.

Intermolecular forces (Vander Waal's Forces) :

Intermolecular attractions hold two or more molecules together. These are weakest chemical forces and can be of following types.

- Ion-dipole attraction :
- Dipole-dipole attraction :
- Ion-induced dipole attraction :
- Dipole-induced dipole attraction :
- Instantaneous dipole- Instantaneous induced dipole attraction : (Dispersion force or London forces)

Strength of vander waal force \propto molecular mass.

van der Waal's force \propto boiling point.

Metallic bond :

Most metals crystallise in close-packed structures. The ability of metals to conduct electricity and heat must result from strong electron interactions among 8 to 12 nearest neighbours (which is also called coordination number). Bonding in metals is called metallic bonding. It results from the electrical attractions among positively charged metal ions and mobile, delocalised electrons belonging to the crystal as a whole.

Two models are considered to explain metallic bonding:

- Electron-sea model
- Band model

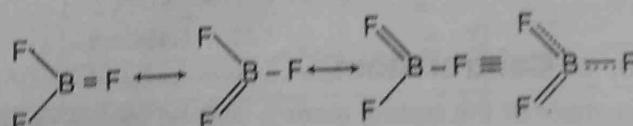
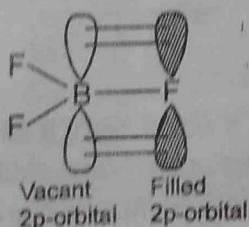
Some special bonding situations :

(a) Electron deficient bonding:

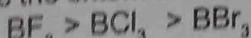
There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds. These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds (3c-2e) present in diborane B_2H_6 , $Al_2(CH_3)_6$, $BeH_2(s)$ and bridging metal carbonyls.

(b) Back Bonding :

Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair(generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length. For example, in BF_3 the boron atom completes its octet by accepting two 2p-electrons of fluorine into 2p¹empty orbital.



The extent of back bonding is much larger if the orbitals involved in the back bonding are of same size, for example the extent of back bonding in boron trihalides is as follows :



COORDINATION COMPOUNDS

The concept of co-ordination compounds arises from the complex formation tendency of transition elements.

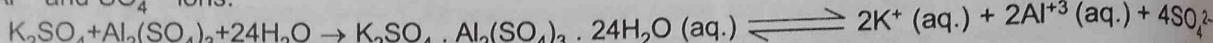
Addition Compounds :

They are formed by the combination of two or more stable compounds in stoichiometric ratio. These are

- (1) Double salts and (2) Coordination compounds

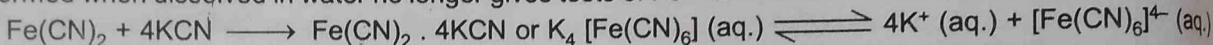
Double salts :

Those addition compounds which lose their identity in solutions are called double salts. For example, when K_2SO_4 solution is added to $Al_2(SO_4)_3$ solution, the species formed when dissolved in water gives tests of K^+ , Al^{3+} and SO_4^{2-} ions.



Coordination Compounds :

Those addition compounds which retain their identity (i.e. doesn't lose their identity) in solution are called coordination compounds. For example, when KCN solution is added to $Fe(CN)_2$ solution, the species formed when dissolved in water no longer gives tests of Fe^{2+} and CN^- .



Central Atom/Ion :

In a coordination entity—the atom/ion to which are bound a fixed number of ligands in a definite geometrical arrangement around it, is called the central atom or ion.

Ligands :

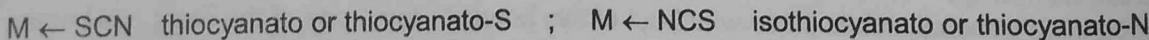
The neutral molecules, anions or cations which are directly linked with central metal atom or ion in the coordination entity are called ligands.

Chelate ligand :

Chelate ligand is a di or polydentate ligand which uses its two or more donor atoms to bind a single metal ion producing a ring. The complex formed is referred to as a chelate complex and the process of chelate formation is called chelation.

Ambidentate Ligand :

Ligands which can ligate through two different atoms present in it are called ambidentate ligands.



Coordination Number :

The coordination number of the central atom/ion is determined by the number of sigma bonds between the ligands and the central atom/ions i.e. the number of ligand donor atoms to which the metal is directly attached.

Oxidation number of Central Atom :

The oxidation number of the central atom is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. Metal oxidation number is represented by a Roman numeral in parentheses following the name of the coordination entity. For example oxidation number of iron in $[Fe(CN)_6]^{3-}$ is +3 and it is written as $Fe(III)$.

Denticity and Chelation :

Table : 1
Common Monodentate Ligands

Common Name	IUPAC Name	Formula
methyl isocyanide	methylisocyanide	CH ₃ N
triphenyl phosphine	triphenyl phosphine/triphenyl phosphane	PPh ₃
pyridine	pyridine	C ₆ H ₅ N (py)
ammonia	ammine	NH ₃
methyl amine	methylamine	MeNH ₂
water	aqua or aquo	H ₂ O
cacbonyl	carbonyl	CO
thiocarbonyl	thiocarbonyl	CS
nitrosyl	nitrosyl	NO
fluoro	fluoro or fluorido*	F ⁻
chloro	chloro or chlorido*	Cl ⁻
bromo	bromo or bromido*	Br ⁻
iodo	iodo or iodido*	I ⁻
cyno	cyanido or cyanido-C* (C-bonded)	CN ⁻
isocyno	isocyanido or cyanido-N* (N-bonded)	NC ⁻
thiocyno	thiocyanato-S (S-bonded)	SCN ⁻
isothiocyno	thiocyanato-N(N-bonded)	NCS ⁻
cyanato (cyanate)	cyanato-O (O-bonded)	OCN ⁻
isocyanato (isocyanate)	cyanato-N (N-bonded)	NCO ⁻
hydroxo	hydroxo or hydroxido*	OH ⁻
nitro	nitrito-N (N-bonded)	NO ₂ ⁻
nitrito	nitrito-O (O-bonded)	ONO ⁻
nitrate	nitrato	NO ₃ ⁻
amido	amido	NH ₂ ⁻
imido	imido	NH ⁻
nitride	nitrido	N ³⁻
azido	azido	N ₃ ⁻
hydride	hydrido	H ⁻
oxide	oxido	O ²⁻
peroxide	peroxido	O ₂ ²⁻
superoxide	superoxido	O ₂ ⁻
acetate	acetato	CH ₃ COO ⁻
sulphate	sulphato	SO ₄ ²⁻
thiosulphate	thiosulphato	S ₂ O ₃ ²⁻
sulphite	sulphito	SO ₃ ²⁻
hydrogen sulphite	hydrogensulphito	HSO ₃ ⁻
sulphide	sulphido or thio	S ²⁻
hydrogen sulphide	hydrogensulphido or mercapto	HS ⁻
thionitrito	thionitrito	(NOS) ⁻
nitrosylum	nitrosylum or nitrosonium	NO ⁺
nitronium	nitronium	NO ₂ ⁺

* The 2004 IUPAC draft recommends that anionic ligands will end with -ido.

Table : 2
Common Chelating Amines

Chelating Points	Common Name	IUPAC Name	Abbreviation	Formula
bidentate	ethylenediamine	1,2-ethanediamine/ ethane-1,2-diamine	en	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
bidentate	propanediamine	1,2-propanediamine	pn	$\text{NH}_2\text{CH}(\text{CH}_3)\text{NH}_2$
tridentate	diethylenetriamine	[N-(2-aminoethyl)-1,2-ethanediamine or diethylenetriamine]	dien	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
tetradeinate	triethylenetetraamine	[N,N'-bis-(2-aminoethyl)-1,2-ethanediamine or triethylenetetraamine]	trien	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
	triaminotriethylamine	[β,β',β"-tris(2-aminoethyl) amine.]	trien	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ $\quad \quad \quad $ $\quad \quad \quad \text{CH}_2\text{CH}_2\text{NH}_2$
pentadentate	tetraethylenepentaamine	1,4,7,10 pentaazatridecane or tetraethylenepentaamine		$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
hexadentate	ethylenediaminetetraacetate	1,2-ethanediyil (dinitrilo) tetraacetate or ethylenediaminetetraacetate	EDTA	

Table : 3
Common Multidentate (Chelating) Ligands

Common Name	IUPAC Name	Abbreviation	Formula	Structure
acetylacetone	2,4-pentanediono or acetylacetone	acac	$\text{CH}_3\text{COCHCOCH}_3^-$	
2,2'-bipyridine	2,2'-bipyridyl	bipy	$\text{C}_{10}\text{H}_8\text{N}_2$	
1,10-phenanthroline/ phenanthroline	1,10-diaminophenanthrene	phen,o-phen	$\text{C}_{12}\text{H}_8\text{N}_2$	
oxalato	oxalato	ox	$\text{C}_2\text{O}_4^{2-}$	
dialkyldithiocarbamato	dialkylcarbamodithioato	dtc	S_2CNR_2^-	
1,2-bis(diphenylphosphine)ethane	1,2-ethanediylibis (diphenylphosphine)	dppe	$\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$	
o-phenylenebis (dimethylarsine)	1,2-phenylenebis (dimethylarsene)	diars	$\text{C}_6\text{H}_4(\text{As}(\text{CH}_3)_2)_2$	
dimethylglyoximato	butanedionedioxime or dimethylglyoximato	DMG	$\text{HONC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{NO}^-$	
ethylenediaminetetraacetato	1,2-ethanediyil (dinitrilo)tetraacetato or ethylenediaminetetraacetato	EDTA	$(\text{OOCCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO})_2$	
pyrazolylborato	hydrotris- (pyrazo-1-yl)borato			

Homoleptic and heteroleptic complexes

Complexes in which a metal is bound to only one type of donor groups, e.g., $[\text{Cr}(\text{NH}_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one type of donor groups, e.g., $[\text{Co}(\text{NH}_3)_4\text{Br}_2]^+$, are known as heteroleptic.

Nomenclature of Coordination Compounds

Writing the formulas of Mononuclear Coordination Entities :

- (i) The central atom is placed first.
- (ii) The ligands are then placed in alphabetical order. The placement of a ligand in the list does not depend on its charge.
- (iii) Polydentate ligands are also placed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.
- (iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.
- (v) There should be no space between the ligands and the metal within a coordination sphere.
- (vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$ etc.
- (vii) The charge of the cation(s) is balanced by the charge of the anion(s).

Writing the name of Mononuclear Coordination Compounds :

- (i) Like simple salts the cation is named first in both positively and negatively charged coordination entities.
- (ii) The ligands are named in an alphabetical order (according to the name of ligand, not the prefix) before the name of the central atom/ion.
- (iii) Names of the anionic ligands end in -o and those of neutral ligands are the same except aqua for H_2O , ammine for NH_3 , carbonyl for CO, thiocarbonyl for CS and nitrosyl for NO. But names of cationic ligands end in -ium.
- (iv) Prefixes mono, di, tri, etc., are used to indicate the number of the one kind of ligands in the coordination entity. When the names of the ligands include a numerical prefix or are complicated or whenever the use of normal prefixes creates some confusion, it is set off in parentheses and the second set of prefixes is used.

2	di	bis	3	tri	tris
4	tetra	tetrakis	5	penta	pentakis
6	hexa	hexakis	7	hepta	heptakis

- (v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in the parentheses after the name of metal.
- (vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix - ate. For example, Co in a complex anion, $[\text{Co}(\text{SCN})_6]^{4-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions.

iron (Fe)	ferrate	lead (Pb)	plumbate
silver (Ag)	argentate	tin (Sn)	stannate
gold (Au)	aurate		

- (vii) The neutral complex molecule is named similar to that of the complex cation.

Werner's Theory :

According to Werner most elements exhibit two types of valencies : (a) Primary valency and (b) Secondary valency.

(a)

Primary valency :

This corresponds to oxidation state of the metal ion. This is also called principal, ionisable or ionic valency. It is satisfied by negative ions and its attachment with the central metal ion is shown by dotted lines.

(b) Secondary or auxiliary valency :

It is also termed as coordination number (usually abbreviated as CN) of the central metal ion. It is non-ionic or non-ionisable (i.e. coordinate covalent bond type). This is satisfied by either negative ions or neutral molecules having lone pair of electrons (e.g., H_2O , NH_3 etc.) or even sometimes by some positive groups. The ligands which satisfy the coordination number are directly attached to the metal atom or ion and shown by thick lines.

Every element tends to satisfy both its primary and secondary valencies. In order to meet this requirement a negative ion may often show a dual behaviour. This dual behaviour is represented by both thick and dotted lines.

The ions/groups bound by the secondary valencies have characteristic spatial arrangements corresponding to different coordination number. In the modern terminology, such spatial arrangements are called coordination polyhedra and various possibilities are

C.N. = 2

linear

C.N. = 3

Triangular

C.N. = 4

tetrahedral or square planar

C.N. = 6

octahedral.

Effective Atomic Number Rule given by Sidgwick :

Effective Atomic Number (EAN) = Atomic no. of central metal – Oxidation state of central metal + No. of electrons donated by ligands.

Bonding in coordination compounds :

Alfred-Werner described the bonding characteristic in coordination compounds. But this theory failed to explain certain basic questions like :

- Why only certain elements possess the remarkable property of forming compounds ?
- Why the bonds in coordination compounds have directional properties ?
- Why coordination compounds have the characteristic magnetic and optical properties ?

Valence bond theory :

The valence bond theory, VBT, was extended to coordination compounds by Linus Pauling in 1931. The formation of a complex involves reaction between a lewis base (ligand) and a lewis acid (metal or metal ion) with the formation of a coordinate-covalent (or dative) bonds between them. The model utilizes hybridisation of $(n-1)$ d, ns, np or ns, np, nd orbitals of metal atom or ion to yield a set of equivalent orbitals of definite geometry to account for the observed structures such as octahedral, square planar and tetrahedral, and magnetic properties of complexes. The number of unpaired electrons, measured by the magnetic moment of the compounds determines which d-orbitals are used.

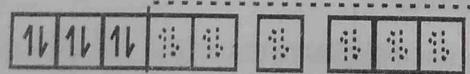
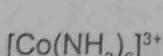
Table : 5

Coordiantion number of metal	Type of hybridisation	Shape of complex
4	sp^3	Tetrahedral
4	dsp^2	Square planer
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

It is to be noted that the type of hybridisation of metal and shape of complex involved can be predicted conveniently, if some characteristic of the complex like magnetic nature, geometry or whether exhibits isomerism or not, etc., be known.

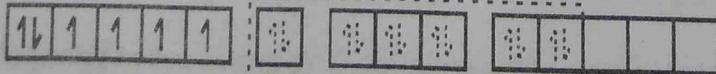
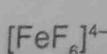
Coordination Number Six :

In the diamagnetic octahedral complex, $[\text{Co}(\text{NH}_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration represented as shown below.



d^2sp^3 hybrid orbital

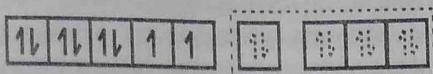
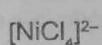
The complex $[\text{FeF}_6]^{4-}$ is paramagnetic and uses outer orbital (4d) in hybridisation (sp^3d^2) ; it is thus called as outer orbital or high spin or spin free complex. So,



sp^3d^2 hybrid orbitals

Coordination Number Four :

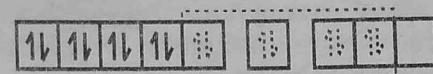
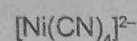
In the paramagnetic and tetrahedral complex $[\text{NiCl}_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in figure.

sp³ hybrid orbitals

Similarly complex $[\text{Ni}(\text{CO})_4]$ has tetrahedral geometry and is diamagnetic as it contains no unpaired electrons. The hybridisation scheme is as shown in figure.

sp³ hybrid orbitals

The hybridisation scheme for $[\text{Ni}(\text{CN})_4]^{2-}$ is as shown in figure.

dsp² hybrid orbitals

While the valence bond theory, to a large extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following **shortcomings**:

1. A number of assumptions are involved.
2. There is no quantitative interpretation of magnetic data.
3. It has nothing to say about the spectral (colour) properties of coordination compounds.
4. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
5. It does not make exact predictions regarding the tetrahedral and square-planar structures of 4-coordinate complexes.
6. It does not distinguish between strong and weak ligands.

Magnetic Properties of Coordination Compounds :

The number of unpaired electrons in any complex can be easily calculated from the configuration of the metal ion, its coordination number and the nature of the ligands involved (strong or weak from the spectrochemical series) and after that the magnetic moment of the complexes can be easily calculated using ;

$$\text{Magnetic Moment} = \sqrt{n(n+2)} \text{ Bohr Magnetons} ; n = \text{number of unpaired electrons}$$

For metal ions with upto three electrons in the d-orbitals like Ti^{3+} , (d^1) ; V^{3+} (d^2) ; Cr^{3+} (d^3) ; two vacant d-orbitals are easily available for octahedral hybridisation. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three 3d electrons are present, like in Cr^{2+} and Mn^{3+} (d^4) ; Mn^{2+} and Fe^{3+} (d^5) ; Fe^{2+} and Co^{3+} (d^6) ; the required two vacant orbitals for hybridisation is not directly available (as a consequence of Hund's rules). Thus, for d^4 , d^5 and d^6 cases, two vacant d-orbitals are only available for hybridisation as a result of pairing of 3d electrons which leaves two, one and zero unpaired electrons respectively.

Crystal Field Theory :

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five d orbitals is an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lost. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystals field.

(a) Crystal field splitting in octahedral coordination entities :

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal d orbital is directed towards the ligand than when it is away from the ligand.

Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals (axial orbitals) which point towards the axis along the direction of the ligand will experience more repulsion and will be raised in energy; and the d_{xy} , d_{yz} and d_{zx} orbitals (non-axial) orbitals which are directed between the axis will be lowered in energy relative to the average energy in the spherical crystal field. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_0 (the subscript 0 is for octahedral). Thus, the energy of the two e_g orbitals will increase by $(3/5)\Delta_0$ and that of the three t_{2g} will decrease by $(2/5)\Delta_0$.

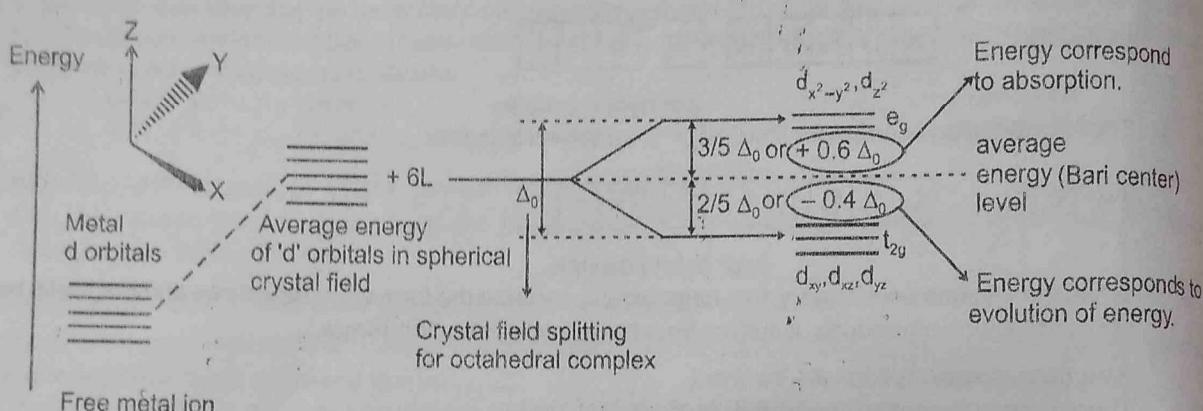


Figure showing crystal field splitting in octahedral complex.

The crystal field splitting, Δ_0 , depends upon the fields produced by the ligand and charge on the metal ion. Ligands can be arranged in a series in the orders of increasing field strength as given below :
 $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < NO_2^- < CN^- < CO$
Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands.

Calculation of Crystal Field stabilisation energy (CFSE)

Formula : CFSE = $[-0.4(n)t_{2g} + 0.6(n')e_g]\Delta_0 + *nP$.

where n & n' are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_0 crystal field splitting energy for octahedral complex. * n represents the number of extra electron pairs formed because of the ligands in comparison to normal degenerate configuration.

(b) Crystal field splitting in tetrahedral coordination entities :

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\Delta_0$.

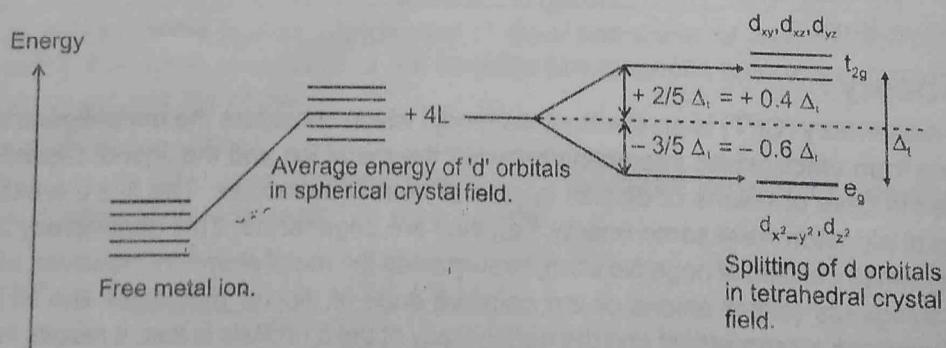


Figure showing crystal field splitting in tetrahedral complex.

COLOUR IN COORDINATION COMPOUNDS :

According to the crystal field theory the colour is due to the d-d transition of electron under the influence of ligands. We know that the colour of a substance is due to the absorption of light at a specific wavelength in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmission or reflection of the rest of the wavelengths. An object that absorbs all visible light appears black. The mechanism of light absorption in coordination compounds is that photons of appropriate energy can excite the coordination entity from its ground state to an excited state. Consider the Ti(III) ion in solution, that is $[Ti(H_2O)_6]^{3+}$. This is a violet colour octahedral complex, where in the ground state of the complex a single electron is present in t_{2g} level. The next higher state available for the transition is the empty e_g level. If the light corresponding to the energy of yellow-green is absorbed by the complex, it would excite the electron from t_{2g} level to e_g level. Consequently the complex appears violet in colour.

Limitations of crystal field theory

- (1) It considers only the metal ion d-orbitals and gives no consideration at all to other metal orbitals (such as s, p_x, p_y and p_z orbitals).
- (2) It is unable to account satisfactorily for the relative strengths of ligands. For example it gives no explanation as to why H₂O is a stronger ligand than OH⁻ in the spectrochemical series.
- (3) According to this theory, the bond between the metal and ligands are purely ionic. It gives no account on the partly covalent nature of the metal ligand bonds.
- (4) The CFT cannot account for the π -bonding in complexes.

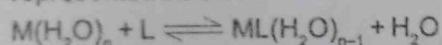
STABILITY OF COORDINATION COMPOUNDS :

The stability of a coordination compound $[ML_n]$ is measured in terms of the stability constant (equilibrium constant) given by the expression,

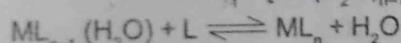
$$\beta_n = [ML_n]/[M(H_2O)_n][L]^n$$

for the overall reaction : $M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$

By convention, the water displaced is ignored, as its concentration remains essentially constant. The above overall reaction takes place in steps, with a stability (formation) constant, K₁, K₂, K₃, K_n for each step as represented below :



$$K_1 = [ML(H_2O)_{n-1}] / \{[M(H_2O)_n][L]\}$$



$$K_n = [ML_n] / \{[ML_{n-1}(H_2O)][L]\}$$



$$\beta_n = K_1 \times K_2 \times K_3 \times \dots \times K_n$$

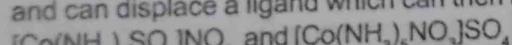
β_n , the stability constant, is related to thermodynamic stability when the system has reached equilibrium.

ISOMERISM :

(1) STRUCTURAL ISOMERISM :

(A) Ionisation isomerism :

This type of isomerism occurs when the counter ion in a coordination compound is itself a potential ligand and can displace a ligand which can then become the counter ion.



(B) Solvate / hydrate isomerism :

It occurs when water forms a part of the coordination entity or is outside it. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice.

Complex	Reaction with AgNO ₃	Reaction with conc. H ₂ SO ₄ (dehydrating agent)
[Cr(H ₂ O) ₆]Cl ₃	in the molar ratio of 3:1	No water molecule is lost or no reaction
[CrCl(H ₂ O) ₅]Cl ₂ .H ₂ O	in the molar ratio of 2:1	one mole of water is lost per mole of complex
[CrCl ₂ (H ₂ O) ₄]Cl.2H ₂ O	in the molar ratio of 1:1	two mole of water are lost per mole of complex

(C) Linkage isomerism :

In some ligands, like ambidentate ligands, there are two possible coordination sites. In such cases, linkage isomerism exist. e.g., NO₂ group can be bonded to metal ions through nitrogen ($-NO_2$) or through oxygen ($-ONO$). SCN too can be bonded through sulphur ($-SCN$) thiocyanate or through nitrogen ($-NCS$) isothiocyanate.

