PERIODIC PROPERTIS	
1	Periodic Table & Introduction of different blocks, Shielding Effect
2	Atomic, ionic size, Ionisation Energy
3	Electron Affinity, Electronegativity, Acidic basic strength, Hydration Energy

1.Long form of Periodic Table or Moseley's Periodic Table

i) Moseley (1909) studied the frequency of X-rays produced by the bombardment of a strong beam of electrons on a metal target.

ii)He found that the square root of the frequency of X-rays $\left(\sqrt{\nu}\right)$ is directly proportional to the total nuclear charge (Z) of metal. The relation between them was found to be

iii)

$$\sqrt{\nu} = a\ (Z - b)$$

where a and b are constants.

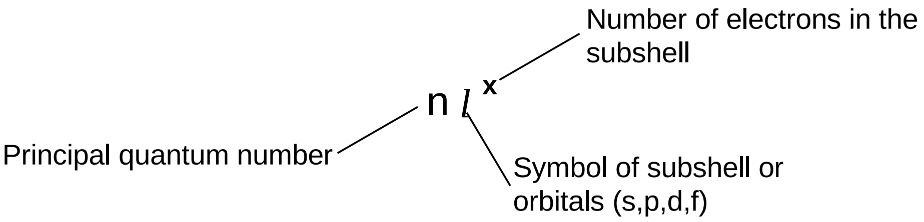
Nuclear charge of metal is equal to the atomic number.

Physical and chemical properties of elements are the periodic functions of their atomic number.

2. Long form of the Periodic Table and Electronic Configuration of elements

3. ELECTRONIC CONFIGURATION OF ELEMENTS

Electronic configuration is the distribution of electrons into different shells, subshells and orbitals of an atom.



$n\,l^{x}$

Number of electrons in the subshell

Principal quantum number

Symbol of subshell or orbitals (s,p,d,f)

(A) Each orbital can accommodate two electrons

(B) The number of electrons to be accomodated in a subshell is 2 × number of degenerate orbitals.

Subshell	Maximum number of electrons
s	2
p	6
d	10
f	14

(C) The maximum number of electron in each shell (K,L,M,N…) is given by $2n^2$. Where n is the principal quantum number.

(D) The maximum number of orbitals in a shell is given by n^2 where n is the principal quantum number.

Exceptional Configurations (Extra stability of half-filled and fully-filled sub shell) :

Some Exceptional electronic configuration :

${}_{24}$Cr: $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^1$

${}_{47}$Ag : $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 5s^1$

${}_{29}$Cu: $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^1$

${}_{42}$Mo: $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 4d^5, 4s^1$

${}_{24}$Cr → [Ar] $3d^5, 4s^1$ and not [Ar] $3d^4, 4s^2$

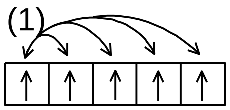
${}_{29}$Cu → [Ar] $3d^{10}\ 4s^1$ and not [Ar] $3d^9, 4s^2$

It has been found that there is extra stability associated with these electronic configurations. This stabilization is due to the following two factors

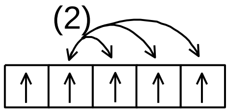
1. Symmetrical distribution of electron:

.

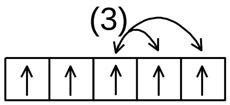
2. Exchange Energy:



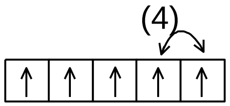
4-exchanges by electron 1



3-exchanges by electron 2



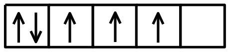
2-exchanges by electron 3

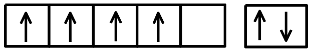


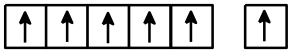
1-exchanges by electron 4

Total exchanges = 10

- **If n is the number of electron with parallel spins then can you calculate total number of possible exchanges?**

e.g.  Total exchanges possible are = 6

e.g. $_{24}Cr$:  Total exchanges possible are = 6



Total exchanges possible are = 10

The stabilation due to exchange energy will compensate for the energy required for excitation from 4s to 3d.

Electronic configuration of ions :

${}_{26}Fe \rightarrow 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^6, 4s^2$

& the configuration of ions would be

$Fe^{2+} \rightarrow 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^6$ & $Fe^{3+} \rightarrow 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5$

Similarly for copper

${}_{29}Cu \rightarrow 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^1$

& for its ions

$Cu^{+} \rightarrow 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}$ & $Cu^{2+} \rightarrow 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^9$

The anions are formed by adding electrons to the vacant orbital of lowest energy [follow (n +l) rule]

For example

$_9F \rightarrow 1s^2, 2s^2\ 2p^5$ & that of its ion $F^- \rightarrow 1s^2, 2s^2\ 2p^6$

Similarly for Chlorine $_{17}Cl \rightarrow 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^5$
& that of its ion $Cl^- \rightarrow 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6$

Applications of electronic configuration:

(1) Calculation of Magnetic Moment (μ) : $\Rightarrow \mu = \sqrt{n(n+2)}$ Bohr Magneton

Where n → no. of unpaired electrons & 1 BM

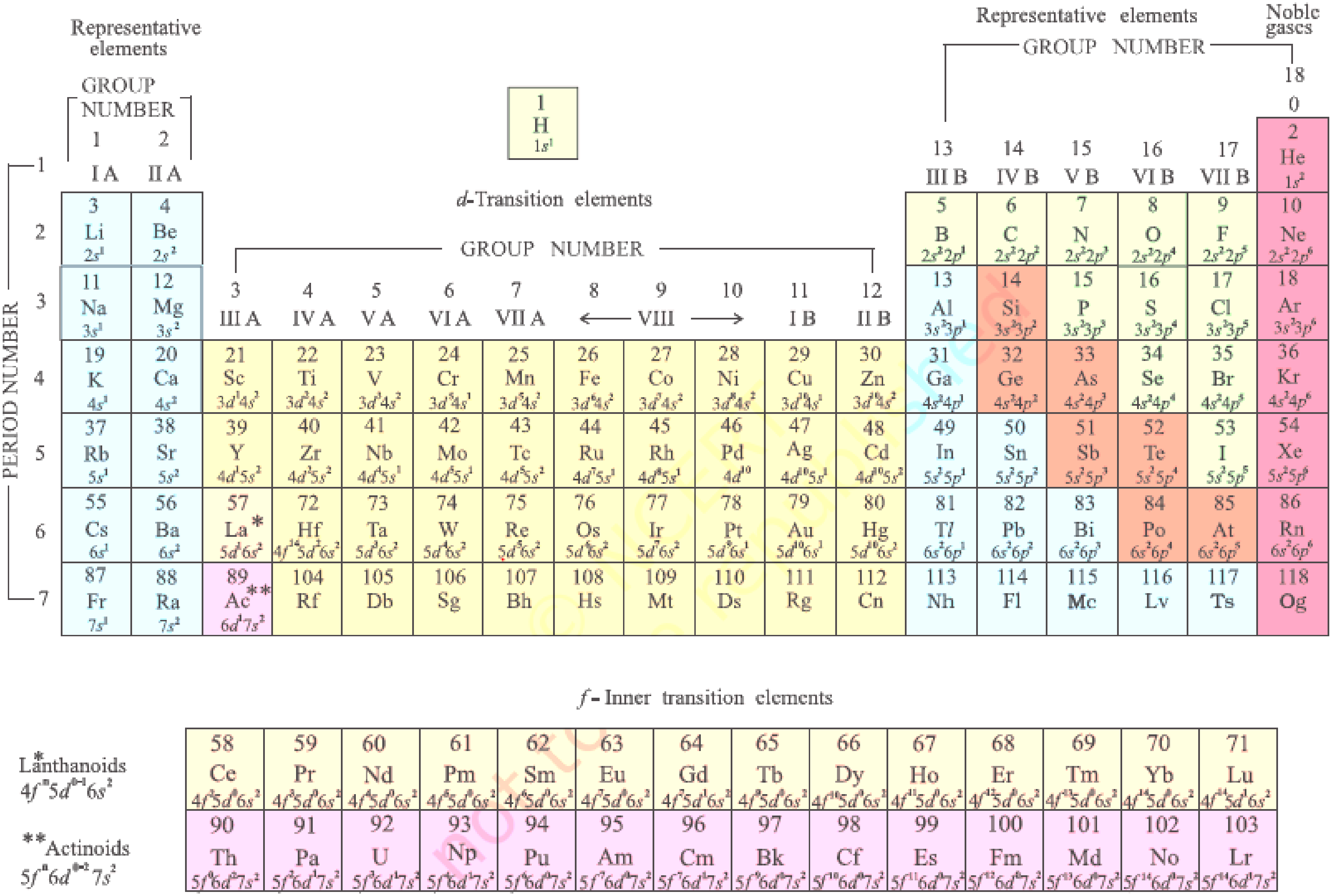
(Bohr Magneton) = $\dfrac{e.h}{4\pi m_e}$

When μ = 0 (Diamagnetic repelled, by magnetic field)

If $\mu \neq 0$, paramagnetic attracted by magnetic field.

(2) Colour: It has been observed that the species having unpaired e^- generally impart colour.

Electronic basis for the periodic classification



Representative elements — GROUP NUMBER 1, 2 (IA, IIA)

d-Transition elements — GROUP NUMBER 3–12

Representative elements — GROUP NUMBER 13–17

Noble gases — 18 (0)

PERIOD NUMBER

	1
	1 H $1s^1$

PERIOD NUMBER	1 IA	2 IIA	3 IIIA	4 IVA	5 VA	6 VIA	7 VIIA	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIB	14 IVB	15 VB	16 VIB	17 VIIB	18 0
1																		2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^1 6s^2$	72 Hf $4f^{14} 5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$	81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$	84 Po $6s^2 6p^4$	85 At $6s^2 6p^5$	86 Rn $6s^2 6p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^1 7s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

f - Inner transition elements

*Lanthanoids $4f^n 5d^{0-1} 6s^2$	58 Ce $4f^2 5d^0 6s^2$	59 Pr $4f^3 5d^0 6s^2$	60 Nd $4f^4 5d^0 6s^2$	61 Pm $4f^5 5d^0 6s^2$	62 Sm $4f^6 5d^0 6s^2$	63 Eu $4f^7 5d^0 6s^2$	64 Gd $4f^7 5d^1 6s^2$	65 Tb $4f^9 5d^0 6s^2$	66 Dy $4f^{10} 5d^0 6s^2$	67 Ho $4f^{11} 5d^0 6s^2$	68 Er $4f^{12} 5d^0 6s^2$	69 Tm $4f^{13} 5d^0 6s^2$	70 Yb $4f^{14} 5d^0 6s^2$	71 Lu $4f^{14} 5d^1 6s^2$
**Actinoids $5f^n 6d^{0-2} 7s^2$	90 Th $5f^0 6d^2 7s^2$	91 Pa $5f^2 6d^1 7s^2$	92 U $5f^3 6d^1 7s^2$	93 Np $5f^4 6d^1 7s^2$	94 Pu $5f^6 6d^0 7s^2$	95 Am $5f^7 6d^0 7s^2$	96 Cm $5f^7 6d^1 7s^2$	97 Bk $5f^9 6d^0 7s^2$	98 Cf $5f^{10} 6d^0 7s^2$	99 Es $5f^{11} 6d^0 7s^2$	100 Fm $5f^{12} 6d^0 7s^2$	101 Md $5f^{13} 6d^0 7s^2$	102 No $5f^{14} 6d^0 7s^2$	103 Lr $5f^{14} 6d^1 7s^2$

i) Inert gases

a) In the atoms of these elements, thes and p subshells of the outer most shell are completely filled. The outermost electronic configuration is ns^2np^6.

b)Helium is also inert gas but its electronic configuration is $1s^2$.

c) Because of stable configuration, these elements do not showchemical activity under normal conditions.

d) These are all gases under normal conditions and thus, termed as inert gases.

ii) Representative or Normal Elements

a) Outermost shell of these elements is incomplete. The number of electrons in the outermost shell is less than eight. The configuration of the outermost shell varies from ns^1 to ns^2np^5.

b) Inner shells are complete.

c) s and p-block elements except inert gases are called normal or representative elements. These consist of some metals, all non-metals and metalloids.

iii) Transition Elements

a) Last two shells of these elements namely outermost and penultimate shells are incomplete.

b) The last shell contains one or two electrons and the penultimate shell may contain more than eight up to eighteen electrons.

c) Their outermost electronic configuration is similar to d-block elements
i.e. $(n-1)d^{1-9}\ ns^{0\ \text{or}1\ \text{or}\ 2}$.

d) According to latest definition of transition elements those elements, which have partly filled d-orbitals in neutral state or in any stable oxidation state, are called transition elements. According to this definition***Zn, Cd and Hg (IIB group) are d-block elements but not transition elements because these elements have d^{10} configuration in neutral as well as in stable +2 oxidation state***.

e) Because of the extra stability, which is associated with empty, half-filled, and filled subshells, there are some apparent anomalies in electronic arrangements in the transition series. This empirical rule is illustrated by the chromium and copper configuration in the first d series of elements:

	Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
3d	1	2	3	5	5	6	7	8	10	10
4s	2	2	2	1	2	2	2	2	1	2

v) Inner Transition Elements

a) In these elements last three shells i.e. last, penultimate and pre-penultimate shells are incomplete.

b) There are two series of elements, (i) Lanthanides or rare-earths from Ce (58) to Lu (71) (ii) Actinides from Th (90) to Lr (103)

c) The last shell contains two electrons. Penultimate shell may contain eight or nine electrons and pre-penultimate shell contains more than 18 up to32 electrons.

d) Their outermost electronic configuration is similar to f-block element
i.e. $(n-2)f^{1-14}(n-1)s^2\ (n-1)p^6\ (n-1)d^{0-1}ns^2$

v) Elements of the seventh period after atomic number 93 (i.e. actinides) are synthetic elements and are called transuranium elements.

Periodic Properties

Shielding Effect

In a multielectron atom, **This decrease in the force of attraction exerted by the nucleus on the valency electrons due to the presence of electrons in the inner shells, is called screening effect or shielding effect.**
Due to screening effect the valency electron experiences less attraction towards nucleus. This brings decrease in the nuclear charge (Z) actually present on the nucleus.

The reduced nuclear charge is termed effective nuclear charge and is represented by Z^*. It is related to actual nuclear charge (Z) by the following formula:

$Z^* = (Z - \sigma)$, where σ is screening constant

The magnitude of 'σ' is determined by the **Slater's rules**.

S per electron of the orbit			
Electron in orbitals –	n	(n – 1)	(n – 2) or (n – 3), etc
(Shell) ®			
S or P orbital	0.35	0.85	1.00
d or f orbital	0.35	1.00	1.00

Effective Nuclear Charge

It is observed that magnitude of effective nuclear charge increases in a period when we move from left to right.

2nd Period	Li	Be	B	C	N	O	F	Ne
Z	3	4	5	6	7	8	9	10
σ	1.7	2.05	2.42	2.75	3.1	3.45	3.8	4.15
$Z^* = Z - \sigma$	1.3	1.95	2.6	3.25	3.9	4.55	5.2	5.85

In a subgroup of normal elements the magnitude of effective nuclear charge remains almost the same.

Alkali group	Li	Na	K	Rb	Cs
Z	3	11	19	37	55
σ	1.7	8.8	16.8	34.8	52.8
$Z^* = Z - \sigma$	1.3	2.2	2.2	2.2	2.2

Atomic Radius

The inter-nuclear distance between the two atoms can be measured by X – ray diffraction or spectroscopic studies.

v) **Covalent radius –:**

$$r_A = \frac{d_{A-A}}{2}$$

$$d_{A-A} = r_A + r_A$$

Metallic Radius:

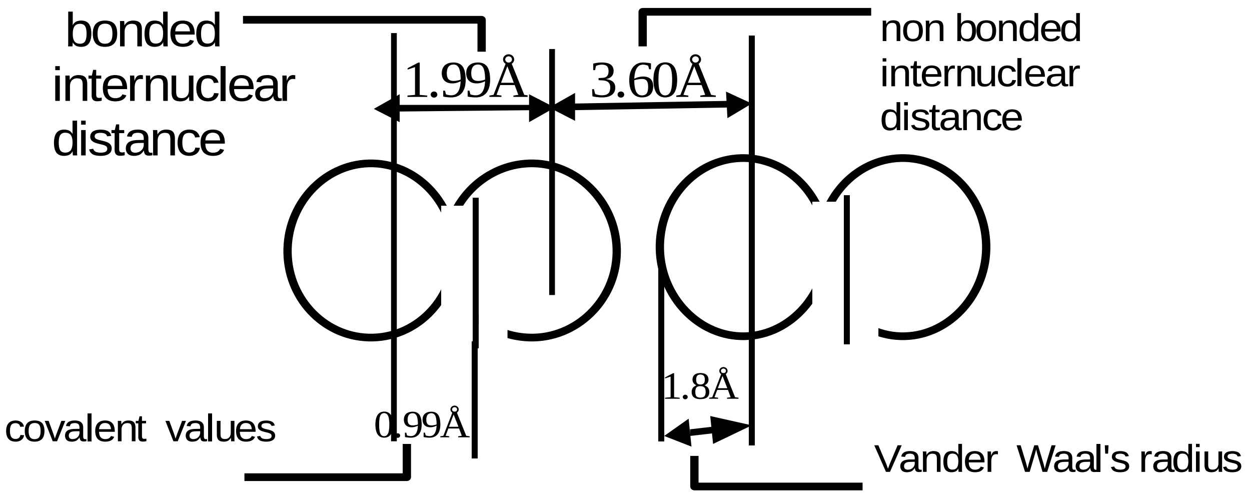
Metal atoms are assumed to be closely packed spheres in the metallic crystal. These metal atom spheres are considered to touch one another in the crystal. One half of the internuclear distance between the two closest metal atoms in the metallic crystal is called metallic radius.

Metallic radius > Covalent radius

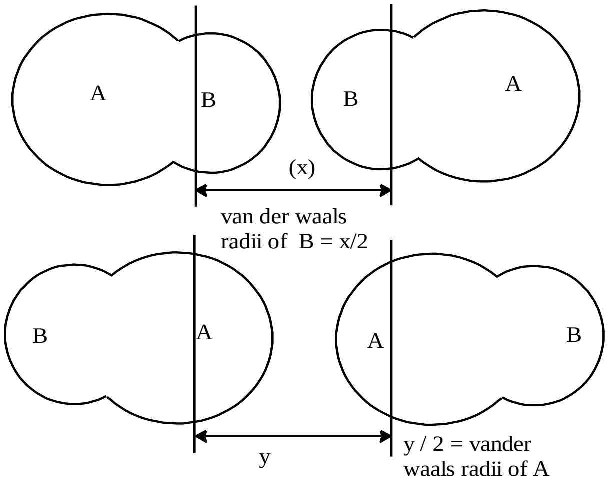
For example – Metallic radius and covalent radius of potassium are 2.3 Å and 2.03Å respectively.

Van der Waal's Radius or Collision radius

One half of the distance between the nuclei of two adjacent atoms belonging to two neighbouring molecules of a compound in the solid state is called Van der Waal's radius.



Vander Waal's radius > Metallic radius> Covalent radius



The Vander Waal's radius and Covalent radius of Chlorine atom are 1.80Å and 0.99Å respectively

Ionic Radius

i) Radius of a Cation: Radius of a cation is invariably smaller than that of the corresponding neutral atom

	Na	**Na^+**
Number of e^- =	11	10
Number of p =	11	11
	$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6$

ii) **Radius of an anion:** Radius of an anion is invariably bigger than that of the corresponding atom.

	Cl	**Cl^-**
Number of e^- =	17	18
Number of p =	17	17

iii) **Iso-electronic series:** A series of atoms, ions and molecules in which each species contains same number of electrons but different nuclear charge is called iso-electronic series

	N^{3-}	O^{2-}	F^{-}	Ne	Na^{+}	Mg^{2+}
Number of e^{-}	10	10	10	10	10	10
Number of p	7	8	9	10	11	12

$\longrightarrow$

a) Number of electrons is same.

b) Number of protons is increasing

c) So the effective nuclear charge is increasing and atomic size is decreasing. In an iso-electronic series atomic size decreases with the increase of charge.

Some of the examples of iso-electronic series are as under

i) $S^{2-}, Cl^{-}, K^{+}, Ca^{2+}, Sc^{3+}$

ii) SO_2, NO_3^{-}, CO_3^{2-}

iii) N_2, CO, CN^{-}

iv) NH_3, H_3O^{+}

Periodicity in atomic radius and ionic radius

1. For normal elements

a) In a period from left to right effective nuclear charge increases because the next electron fills in the same shell. So the atomic size decreases. For example the covalent radii of second period elements in Å are as follows –

Li	**Be**	**B**	**C**	**N**	**O**	**F**
1.23	0.89	0.80	0.77	0.74	0.73	0.72

b) In a group moving from top to bottom the number of shells increases. So the atomic size increases. Although the effective nuclear charge increases but its effect is negligible in comparison to the effect of increasing number of shells. For example the covalent radii of IA group elements in Å are as follows –

Li	**Na**	**K**	**Rb**	**Cs**
1.23	1.57	2.03	2.16	2.35

2. **For inert gases:** The atomic radius of inert gas (zero group) is shown largest in a period because of its Vander Waal's radius which is generally larger than the covalent radius. The Vander Waal's radius of inert gases also increases in moving from top to bottom in a group.

3. **For transition elements:** There are three series of transition elements –

3d – Sc (21) to Zn (30)
4d – Y (39) to Cd (48)
5d – La (57), Hf (72) to Hg (80)

a) From left to right in a period

i) The atomic size decreases due to the increase in effective nuclear charge.

ii) In transition elements, electrons are filled in the (n-1)d orbitals. These (n-1)d electrons screen the *ns* electrons from the nucleus. So the force of attraction between the *ns* electrons and the nucleus decreases.

This effect of (n-1)d electrons over *ns* electrons is called shielding effect or screening effect. The atomic size increases due to shielding effect and balance the decrease in size due to increase in nuclear charge to about 80%.

iii) Thus moving from left to right in a period, there is a very small decrease in size and it may be considered that size almost remains the same.

iv) In the first transition series the atomic size slightly decreases from Sc to Mn because effect of effective nuclear charge is stronger than the shielding effect. The atomic size from the Fe to Ni almost remains the same because both the effects balance each other. The atomic size from Cu to Zn slightly increases because shielding effect is more than effective nuclear charge due to d^{10} structure of Cu and Zn. The atomic radii of the elements of 3d transition series are as under.

Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
1.44	1.32	1.22	1.18	1.17	1.17	1.16	1.15	1.17	1.25

3. **Inner transition elements:** .

The atomic radii in Å are as under:

La	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**
1.88	1.82	1.83	1.82	1.81	1.80	2.04	1.80
Tb	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	
1.78	1.77	1.76	1.75	1.74	1.94	1.73	

There are two peaks one at Eu (63) and other at Yb (70). This is due to the difference in metallic bonding. Except Eu and Yb other lanthanides contribute three electrons in metallic bond formation. These two atoms contribute two electrons in the bond formation leaving behind half filled and completely filled $4f$-orbitals respectively.

As we move along the lanthanide series, there is a decrease in atomic as well as ionic radius. The decrease in size is regular in ions but not so regular in atoms. There is a significant drop in atomic size after III B group as we move from left to right in periods 6 & 7. This is called lanthanide contraction

Cause of Lanthanide contraction – In lanthanides the additional electron enters into (n-2)f orbital. The mutual shielding effect of (n-2)f electrons is very little because the shape of f-subshell is very much diffused. Thus the effective nuclear charge increases in comparison to the mutual shielding effect of (n-2) f electrons. The outer electrons are attracted more by the nucleus. Consequently the atomic and ionic radii decreases from La (57) to Lu (71).

This type of contraction also occurs in actinides. The jump in contraction between the consecutive elements in the actinides is greater than lanthanides. This is due to the lesser shielding of 5f-electronswhich are therefore pulled more strongly by the nucleus.

In a group

i) The atomic radius of elements increases moving from first transition series (3d) to second transition series (4d). This is due to the increase in number of shells with the increase in atomic number.

ii) The atomic radii of second (4d) and third (5d) transition series in a group is almost same except Y(39) and La (57)
In third transition series, there are fourteen lanthanides in between La (57) of III B and Hf (72) of IV B groups, so the atomic radius of Hf(72) decreases much due to lanthanide contraction in lanthanides. The difference in the nuclear charge in the elements of a group in first and second transition series is + 18 units while this difference in second and third transition series is + 32 units except Y (39)→ La(57). Due to the increase of + 32 units in the nuclear charge there is a sizable decrease in the atomic radius which balances the increase in size due to the increase in number of shells.
So in a group moving from second to third transition series, the atomic radii of the elements almost remain the same except IIIB. The difference is about 0.02Å.

Illustration 1: The radii of Ar is greater than the radii of chlorine

Solution: In chlorine, the radii means the atomic or covalent radii which is actually half the intermolecular distance between 2 atoms whereas in Argon the radii means the Vander Waal's radii as Argon is not a diatomic molecule. Vander Waal's radiiis actually half the distance between adjacent molecule. So Vander Waal's radii being larger than atomic radii, Argon,has got a larger radii than chlorine.

Illustration 2: ***Beryllium(Be) and Aluminium(Al) are placed in different periods and groups but they show the similar properties.***

Solution: On moving across a period the charge on the ions increases and the size decreases, causing the polarising power to increase. On moving down a group the size increases and polarising power decreases. On moving diagonally i.e., from Be to Al these two effects partly cancel each other and so there is no marked change in properties.

5.7 Ionisation potential or Ionisation Energy

i) The amount of energy required to remove the most loosely bound electron of the outermost shell (i.e. the outermost electron) from one mole of an isolated gaseous atom of an element in its ground state to produce a cation is known as ionisation energy of that element.

$$A_{(g)} + I_1 \rightarrow A_{(g)}^{+} + e^{-}$$

$$A^{+}_{(g)} + I_2 \rightarrow A_{(g)}^{2+} + e^{-}$$

$$A_{(g)}^{2+} + I_3 \rightarrow A_{(g)}^{3+} + e^{-}$$

$$I_1 < I_2 < I_3$$

1. **Factors affecting ionisation potential**

i) ***Atomic radius:***

$$\text{Ionisation potential} \, \alpha \, \frac{1}{\text{Atomic radius}}$$

ii) ***Effective nuclear charge:***

Ionisation potential α Effective nuclear charge (Z_{eff})

iii) ***Penetration effect of orbitals:***

The order of energy required to remove electron from s,p,d-and f-orbitals of a shell is s>p>d>f because the distance of the electron from the nucleus increases.

iv) ***Shielding or screening effect:***

Ionisation potential $\alpha \frac{1}{\text{Shielding effe}}$

iv) Stability of half-filled and fully-filled orbitals:

For example

a) Removal of electron is comparatively difficult from the half filled configuration of N (Z=7, $Is^2 2s^2\, 2p_x^1 p_y^1 p_z^1$).

b) The ionisation potential of inert gases is very high due to most stable s^2p^6 electronic configurations.

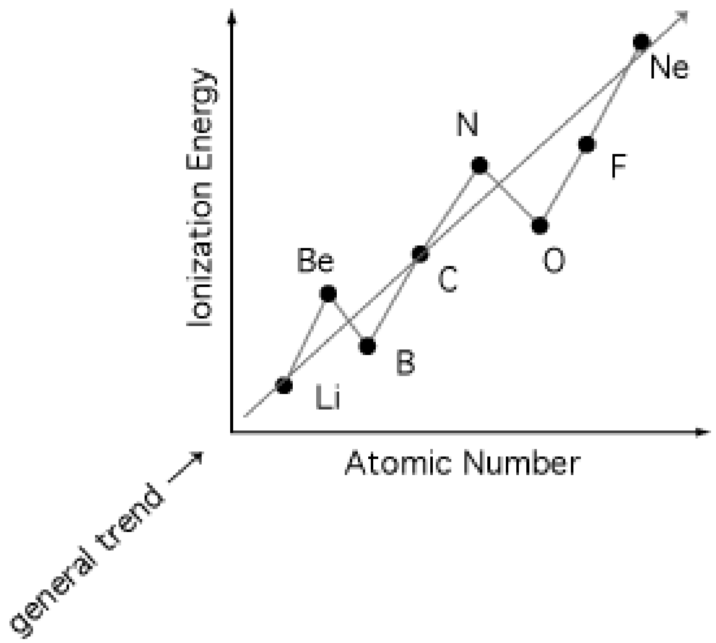
2. **Periodicity in ionisation potential**

i) **For normal elements:** On moving from left to right in a period, value of ionisation potential of elements increases because effective nuclear charge also increases.

Exceptions

a) The value of ionization energy of Be($1s^22s^2$) is more than B ($1s^22s^2p^1{}_x$) because the penetration power of 2s-electrons of Be is more than the $2p_{x-}$ electrons of B.

b) Ionization energy N($Is^22s^22p^1{}_xp_y{}^1pz^1$) >O $Is^2 2s^2 2p_x^2 p_y^1 p_z^1$



Thus P>S, As>Se.

But the value of I.P. of Sb (VA) &Te (VIA) and Bi (VA) &Po(VIA) are according to general rule i.e.

Sb (VA) <Te (VIA)

Bi (VA) < Po (VIA)

On moving from top to bottom in a group the value of I.P. decreases because the atomic size increases.

Exceptions

a) In group IIIA the ionization potential of Al (13) is equal to the ionization potential of Ga(31). Before Ga (31) the electrons are filled in 3d – orbitals of ten transition elements. These 3d orbital electrons do not completely shield the 4p electron. So the increase of +18 units in nuclear charge results in the greater increase of effective nuclear charge. Due to increase in nuclear charge the I.P. increases which counter balance the decrease in I.P. due to the increase in number of shells.

b) The values of I.P. of Tl (81) and Pb (82) of sixth period is more than the I.P. values of In (49) and Sn (50) of same groups in period fifth. This is because of the electrons are filled in 4f-orbitals before Tl (81) and Pb (82) which do not completely shield the outer electrons. Thus increase in + 32 units in nuclear charge results in the increase of ionisation potential values.

ii) ***For transition elements:*** On moving from left to right in a transition series

a) As the atomic number increases the effective nuclear charge also increases. Hence the I.P. increases.

b) The shielding effect of (n-1)d electrons over ns electrons increases with the addition of electron in (n-1)d orbitals. Hence the I.P. decreases.

c) The increased values of I.P. due to the increase of effective nuclear charge almost balances the decreased value of I.P. due to increase in shielding effect. There is a very small increase in the values of I.P. or it may be said that I.P. almost remains the same.

d) In first transition series from Sc to Cr the value of I.P. increases because effect of increase in effective nuclear charge is more than the shielding effect I.P. values of Fe, Co, Ni and Cu are almost same. Due to $d^{10}s^2$ configuration of Zn, the first I.P. increases.

On moving from top to bottom in a group in transition series

a) In a group on moving from first to second transition series, the values of I.P. decreases because atomic size increases.

b) In moving from second to third transition series the value of I.P. somewhat increases except IIIB group [Y(39) → La(57)]. This is because of 14 electrons are filled in $4f$-orbitals of lanthanides which do not shield the 5d electrons effectively. Thus the increase in +32 units in nuclear charge results in the increase of I.P., on moving from left to right this effect decreases and becomes negligible in the later part.

3. Applications of ionisation potential

i) Metallic or electropositive character of elements increases as the value of ionisation potential decreases. So in a group moving from top to bottom metallic or electropositive character increases because I.P. value decreases. In a period moving from left to right the values of I.P. increases so metallic or electropositive character decreases. Non-metallic character increases.

ii) The relative reactivity of the metals increases with the decrease in I.P. values. The I.P. values of IA and IIA metals are comparatively low. So they are comparatively more reactive. The I.P. values of inert gases are very high. So they are almost unreactive.

In a group moving from top to bottom the reactivity of metal atoms increases because their I.P. value decreases.

iii) The reducing power of elements increases as the values of I.P. decreases because tendency to lose the electron increases. The reducing power increases going down a group because the I.P. value decreases. Li is exception in IA group. The reducing power of Li is highest in its own group. The order of reducing Power of IA elements is as under

Li > Cs >Rb> K > Na

iv) Determination of oxidation state or valency electrons of an element –

a) If the difference of two consecutive I.P.'s of an element is 16 eV or more, the lower oxidation state is stable. For e.g. the difference of first and second I.P. of Na is 42.4 eV, which is, more than 16 eV. So Na^+ will be stable. It can also be explained from its electronic configuration

Na (11) = $1s^2 2s^2 2p^6 3s^1$

$Na^+ = 1s^2 2s^2 2p^6$

Neutral Na atom has the tendency to acquire the stable s^2p^6 configuration by the loss of one electron. Due to s^2p^6 configuration of Na^+, the further separation of electron is difficult. So IA group metals form mono-positive ions.

b) If the difference of two consecutive I.P.s. of an element is 11.0 eV or less, the higher oxidation state is stable. For e.g. the difference of first and second I.P. of Mg is 7.4 eV which is less than 11.0 eV. So Mg^{2+} will be stable. It can also be explained on the basis of its electronic configuration.
The electronic configuration of Mg^{2+} is stable s^2p^6 configuration
$Mg^{2+} = 1s^22s^22p^6$
So IIA group elements form dipositive ions.

c) The difference of first and third I.P. of Al is 12.8 eVwhich is more than 11eV. Therefore first oxidation state of Al i.e. Al^+ must be stable. In gaseous state Al^+ is stable. This is due to the proportionate distribution of lattice energy and the difference of second and third I.P.s 9.6eV<11 eV.

Illustration 3: ***The first I.P. of nitrogen is greater than oxygen while the reverse is true for their second I.P. values.***

Solution: The first I.P corresponds to the removal of first electron. Since nitrogen is already half filled,So more energy is required to remove the electron. But once the electron is removed from oxygen it gains half-filled stability and therefore the 2nd I.P. becomes high.

Illustration 4: ***The ionisation energy of the coinage metals fall in the order Cu $>$ Ag $<$ Au.***

Solution: In all the 3 cases an s-electron in the unpaired state is to be removed. In the case of Cu a 4s electron is to be removed which is closer to the nucleus than the 5s electron of Ag. So I.P. decreases from Cu to Ag. However from Ag to Au the 14 f electrons are added which provide very poor shielding effect. The nuclear charge is thus enhanced and therefore the outer electron of Au is more tightly held and so the IP is high.

Electron affinity

i) The amount of energy released when an electron is added to the outermost shell of one mole of an isolated gaseous atom in its lower energy state.

ii) Electron affinity just defined is actually first electron affinity since it corresponds to the addition of one electron only. In the process of adding further electron, the second electron will be added to gaseous anion against the electrostatic repulsion between the electron being added and the gaseous anion. Sometimes energy instead of being released is supplied for the addition of an electron to an anion.

$$A_{(g)} + e^- \rightarrow A^-_{(g)} + E_1$$

$$A^-_{(g)} + e^- + \text{Energy supplied} \rightarrow A^{2-}_{(g)}$$

1. **Factors affecting the magnitude of electron affinity**

i) ***Atomic size:***

$$\text{Electron affinity } \alpha \frac{1}{\text{Atomic size}}$$

ii) ***Effective nuclear charge:***

Electron affinity α Effective nuclear charge (Z_{eff})

iii) ***Screening or Shielding effect:***

$$\text{Electron affinity } \alpha \frac{1}{\text{Shielding eff}}$$

iv) ***Stability of half filled and completely filled orbitals:***

.

2. **Periodicity in electron affinity**

i) In general electron affinity value increases in moving from left to right in a period because effective nuclear charge increases.

Exceptions

a) The electron affinity value of alkaline earth metals of IIA group is zero.

b) Electron affinity value of alkali metals of IA group is also approximately zero because these elements have the tendency of losing the electron instead of gaining the electron.

c) Electron affinity values of nitrogen and phosphorous (VA) are lesser than the electron affinity values of carbon and silicon respectively. It is due to the comparatively stable half filled configuration (np^3) of nitrogen and phosphorus and the tendency to acquire the stable np^3 configuration by the gain of one electron in carbon and silicon (np^2).

d) The theoretical value of the electron affinity of zero group inert gas elements is zero due to stable s^2p^6 configuration.

ii) In a group moving from top to bottom the electron affinity value of elements decreases because the atomic size increases

Exceptions

a) Electron affinity values of second period elements are smaller than the electron affinity values of third period elements. This unexpected behavior can be explained by the very much high value of charge densities, of second period elements due to much smaller size. The electron being added experiences comparatively more repulsion and the electron affinity value decreases.

b) The electron affinity of fluorine (Second period) is less than the electron affinity of chlorine (third period). 2p-orbitals in fluorine are much more compact than 3p- orbitals of chlorine. So the electron being added in 2p-orbitals experiences comparatively more repulsion and the electron affinity value decreases.

Illustration 5: Electron affinity of SF_5 is among the highest known but that of SF_6 is quite modest.

Solution: Sulfur in SF_6 is saturated in terms of maximum covalency and maximum co-ordination number and so it has very little tendency to attract electron. In SF_5 which is actually a free radical so it has got a very strong tendency to attract an electron to fulfill its covalency and co-ordination number. Therefore the electron affinity of SF_5 is high.

Electronegativity

It may be defined as the tendency of an atom to attract shared pair of electrons towards itself in a covalently bonded molecules.

1. Electronegativity scale: **Some arbitrary scales for the quantitative measurement of electronegativities are as under**

2.

i) ***Pauling's scale:***

$0.208\sqrt{\Delta_{AB}} = x_A - x_B$ if $x_A > x_B$ or $\Delta_{AB} = 23.06\ (x_A - x_B)^2$

$\Delta_{AB} = E_{A\text{-}B(\text{experimental})} - E_{A\text{-}B(\text{theoretical})}$

where $E_{A\text{-}B}$ is the energy of A-B bond. In a purely covalent molecule, AB, the experimental and theoretical values of bond energy A-B are equal. $\Delta_{AB} = 0$

or $0 = 23.06\ (x_A - x_B)^2$ or $x_A = x_B$

In an ionic molecule AB, $E_{A\text{-}B(\text{experimental})}$ is more than $E_{A\text{-}B(\text{Theoretical})}$.

Pauling assumed the electronegativity value of fluorine 4 and calculated the electronegativity values of other elements from this value.

ii)Mulliken's electronegativity:

$$\text{Electro-negativity} = \frac{\text{Electron affinity} + \text{Ionisation potential}}{2}$$

$$= \frac{\text{Electron affinity} + \text{Ionisation potential}}{5.6} \quad \text{(on pauling scale)}$$

When both are expressed in electron volt

3. Factors affecting the magnitude of electronegativity

4.

i) Electronegativity $\alpha \frac{1}{\text{Atomic radius}}$

iii) Electronegativity α Effective nuclear charge (Z_{eff})

iii) The electronegativity value increases as the oxidation state (i.e. the number of positive charge) of the atom increases.

iv) ***Hybridisation state of an atom in a molecule:***

Hybridisation states	sp^3	sp^2	sp
s-Character	25%	33.33%	50%
Electronegativity	2.48	2.75	3.25

$$\longrightarrow$$

s-character is increasing So the electronegativity value is increasing

4. Periodicity in Electronegativity

i) In a period moving from left to right, the electronegativity increases due to the increase in effective nuclear charge.

ii) In a period the electronegativity value of IA alkali metal is minimum and that of VIIA halogen is maximum.

iii) In a group moving from top to bottom, the electronegativity decreases because atomic radius increases.

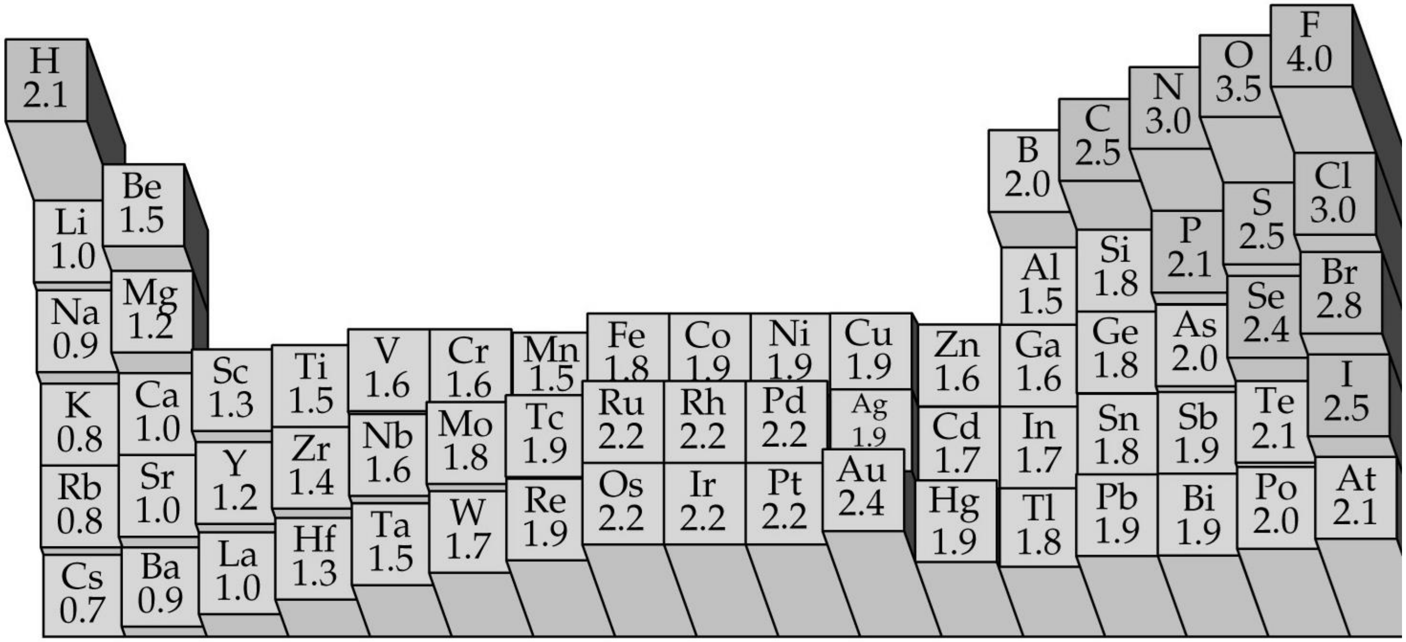
iv) Theelectronegativity value of F is maximum and that of Cs is minimum in the periodic table.

v) The electronegativity of Cs(55) should be more than Fr(87) but it is less. This is due to the increase of +32 units in nuclear charge of Fr which makes the effective nuclear charge comparatively high.

vi) On moving from second to third transition series in a group [except Y(39) → La (57)] electronegativity increases due to the increase of +18 units in nuclear charge.

Viii) The variation of electronegativity along any period or row of the periodic table may be understood with reference to the following table:

Electronegativity values of some elements in Pauling scale:



5. Applications of electronegativity

i) ***Partial ionic character in covalent Bond:***

The ionic character of a covalent bond increases as the electronegativity difference of bonded atoms increases. According to Haney and Smith if the electronegativity difference of bonded atoms is Δx then percentage ionic character of the bond $= 16\Delta x + 3.5\Delta x^2$

If the value of Δx is 2.1 then ionic character percentage is about 50. For example the order of ionic character in H–X bond is as follows–

H–F>H–Cl>H–Br>H–I

.

ii) ***Bond strength:*** If the electronegativity difference of covalently bonded atoms (Δx) increases, the bond energy of the covalent

bond also increases. For example – the order of the H–X bond strength is –
H – F > H – Cl> H – Br > H – I

As the bond strength is decreasing the acid strength is increasing. So order of increasing acid strength is
HF <HCl<HBr< HI

iii) ***Acidic and basic nature of oxides of normal elements in a period:***

Na_2O MgO SiO_2 P_2O_5 SO_3 Cl_2O_7

$$\xrightarrow{\hspace{10cm}}$$

The value of $x_O - x_E$ is decreasing

Basic nature is decreasing Acidic nature is increasing

iv) ***Metallic and non metallic properties of elements:***

The metallic character decreases as the electronegativity of the element increases.

v) ***Basic nature of the hydroxides of elements:***

A hydroxide MOH of an element M may ionize in two ways in water.

$$M{-}O{-}H + H_2O \rightleftharpoons MO^- + H_3O^+ \quad \ldots(1)$$

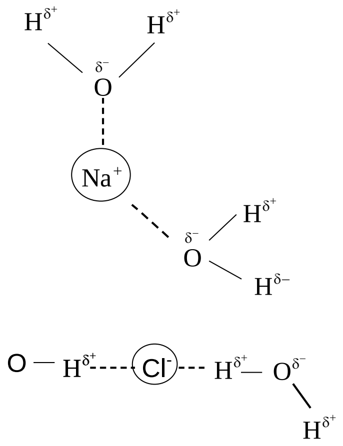
$$M{-}O{-}H + H_2O \rightleftharpoons MOH_2^+ + OH^- \quad \ldots(2)$$

If the ionisation is according to eqn(1) then it is acidic. It is possible when ionic character of O–H bonds is more than the ionic character of M-O bond i.e. $(x_O - x_H) > (x_O - x_M)$ where x_O, x_H and x_M are the electronegativities of oxygen, hydrogen and element respectively.

If the ionisation is according to eqn. (2) then it is basic. This is only possible when ionic character of O –H bond is less than M–O bond i.e. $(x_O - x_H) < (x_O - x_M)$

Hydration Energy

When a gaseous cation or gaseous anion interacts with water hydrated cation or hydrated anion is produced and in this process (called hydration process), the energy released is called as hydration energy



NaCl added in water (Polar solvent)

$$M^+_{(g)} + H_2O_{(l)} \rightarrow \underset{\text{Hydrated cation}}{M^+_{(aq)}} + \text{Hydration energy}$$

$$X^-_{(g)} + H_2O_{(l)} \rightarrow \underset{\text{Hydrated anion}}{X^-_{(aq)}} + \text{Hydration energy}$$

Hydration energy is the enthalpy change that accompanies when one mole of the gaseous ion is dissolved in water.

For example, reaction of the hydration of Li ion is shown as:

$Li^+(g) + nH_2O \longrightarrow [Li(H_2O)_n]^+(aq)$; $\Delta H = -806$ kJ mol^{-1}.

The process by which polar water molecules clings (sticks) to Na^+ and Cl^- is called hydration. Ions are converted to hydrated form.

- **Hydration energies (heat of hydration) of some ions: (KJ/mol)**

H^+1091	Be^{2+}2494	F^-515
Li^+531	Mg^{2+}1954	Cl^-381
Na^+ 422	Ca^{2+}1577	Br^-347
K^+339	Sr^{2+}1443	I^-305
Rb^+ 319	Ba^{2+}1352	
Cs^+280		

Factors affecting Hydration energy :

1. ***Size of gaseous ion:*** As the size of gaseous ion will increase the hydration energy will decrease. This is because more concentrated charge means more hydration energy.
2. ***Charge on ion:*** As the charge increases there would be more attraction for water molecules & hence hydration energy will increase, provided size does not increase significantly.

$$Hydration\ enegy\ \alpha \frac{charge\ on\ the\ ion}{size\ of\ \ the\ ion}$$

BOOST YOUR LEARNING

1 The correct order of relative stability of half filled and completely filled shell is

(a) $p^3 > d^5 < d^{10} < p^6$ (b) $d^5 > p^3 < d^{10} < p^6$

(c) $d^5 < p^3 < d^{10} < p^6$ (d) $p^3 > d^{10} < d^5 < p^6$

(c) Completely filled and half filled p – subshell are more stable than d – subshell.

2 K^+, Ar , Ca^{2+} and S^{2-} have
(a) same electronic configuration and atomic value
(b) different electronic configuration but same I.P.
(c) same electronic configuration but different atomic value
(d) none of the above

(c) All have different number of charge but same 18 electrons

3 Ionization potential values of ‘d’ – block elements as compared to I.P. value of ‘f’ block elements are
(a) higher (b) lower (c) equal (d) all of these

(a) Removal of electron is easier in f – block elements due to more shielding

4 An element having electronic configuration (Ar) $3d^2$ $4s^2$ belongs to
(a) s – block elements (b) p – block elements
(c) d – block elements (d) f – block elements

(c) The last electron enters in 3d

5 Which of the following does not involve covalent bond?
(a) PH_3 (b) CsF (c) HCl (d) H_2S

(b)CsF is the ionic compound

6 Which has minimum ionic radius?
(a) N^{3-} (b) K^+ (c) Na^+ (d) F^-

(c) Cations are smaller than anions and Na^+ is smaller than K^+ as it has only 2 shells

7 Identify the least stable ion amongst the following

(a) Li^- (b) Be^- (c) B^- (d) C^-

(b) Addition of the electron Be− is unfavorable since it is having its 2s filled. As a result, Bewill be least stable.

8 In which of the following there is a drop in I.P.

(a) Be →B (b) O → N (c) Si → C (d) Na → Ne

(a) Greater amount of energies is required to remove an electron from filled 2s orbital (stable) of Be as compared with B where the electron to be removed from $2p^1$ orbital.

9 The IP_1, IP_2, IP_3, IP_4 and IP_5 of an element are 7.1, 14 .3, 34.5, 46.8, 162.2 eV respectively. The element is likely to be

(a) Na (b) Si (c) F (d) Ca

(b) ***The jump in IP values exist in IP_5 and thus, removal of 5th electron occurs from inner shell. Thus element contains 4 electrons in its valence shell.***

10 In which of the following process energy is liberated?

(a) $Cl \rightarrow Cl^+ + e^-$ (b) $HCl \rightarrow H^+ + Cl^-$ (c) $Cl + e \rightarrow Cl^-$ (d) $O^- + e \rightarrow O^{2-}$

(c) ***1st electron affinity is energy releasing process***

11 Which is the most acidic oxide?
(a) Cl_2O (b) Cl_2O_3 (c) Cl_2O_5 (d) Cl_2O_7

(d) Higher the oxidation state of the central atom higher is the Lewis acidic character.

12 The outermost electronic configuration of the most electronegative element is
(a) $ns^2\ np^3$ (b) $ns^2\ np^4$ (c) $ns^2\ np^5$ (d) $ns^2\ np^6$
(c)

13 The first ionization potential in electron volts of nitrogen and oxygen atoms are respectively given by
(a) 14.6, 13.6 (b) 13.6, 14.6 (c) 13.6, 13.6 (d) 14.6, 14.6
(a) Half filled orbital has higher stability.

14 The electronic configuration of element ‘A’ is $1s^2\ 2s^2\ 2p^6\ 3s^2$ while of the element ‘B’ is $1s^2\ 2s^2\ 2p^5$. The formula of the compound containing A and B will be:

(a) AB (b) A_2B (c) AB_2 (d) A_2B_6

(c) A will lose two electrons and two B will gain two electrons (one each) to gets their octet complete.

15 An element is having the electronic configuration ns^2np^5, a very high jump in I.E. values is associated with

(a) $IP_1 \rightarrow IP_2$ (b) $IP_2 \rightarrow IP_3$ (c) $IP_3 \rightarrow IP_4$ (d) $IP_4 \rightarrow IP_5$

(b) From IP_2 to IP_3 electrons will be ejected from half filled p (stable) orbitals.

16 Which transition involves maximum amount of energy

(a) $X^{-}_{(g)} \rightarrow X_{(g)} + e$ (b) $X^{-}_{(g)} \rightarrow X^{+} + 2e$

(c) $X^{+}_{(g)} \rightarrow X^{2+}_{(g)} + 2e$ (d) $X^{2+}_{(g)} \rightarrow X^{3+}_{(g)} + e$

(d) High amount of energy would be necessary to put to eject one electron from dipositive gaseous ion.

17 Ionization potential of Li^{+} is

(a) Lesser than He (b) Greater than He

(c) Greater than He^{2+} (d) Equal to He

(b) High amount of energy always would be necessary to remove an electron from a cation.

18 Oxidation states of Nitrogen varies from

(a) -3 to + 5 (b) +3 to – 5 (c) -1 to – 5 (d) – 3 to – 5

(a) ***Nitrogen is having compounds from hydride (NH_3) to oxide (N_2O_5).***

CHEMICAL BONDING :	
1	Ionic Bond, Lattice energy, Hydration, lattice & Solubilty, Octet Theory
2	Valance bond theory, Sigma& Pi bond, Lone pair, Coordinate bond
3	VSEPR Theory & Hybridisation
4	Fajan’s Rule amd Dipole Moment
5	Bond length, Energy and Bond Angle
6	MOT and Hydrogen Bond

Ionic Bond or Electrovalent Bond

$$\dot{K}(1s^2 2s^2 2p^6 3s^2 3p^6 4s^1) \xrightarrow[1\,\text{electron}]{\text{loses}} \overset{+}{K}(1s^2 2s^2 2p^6 3s^2 3p^6)$$

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot \quad (1s^2 2s^2 2p^6 3s^2 3p^5) \xrightarrow[1\ \text{electron}]{\text{gains}} Cl^- \underset{(\text{Ar configuration})}{(1s^2 2s^2 2p^6 3s^2 3p^6)}$$

i) ***Ionization energy:*** Lower the value of ionization energy of an atom, greater will be the ease of formation of the cation from it.

ii) ***Electron affinity:*** Higher the electron affinity of an atom, greater the ease of formation of the anion from it.

Lattice Energy

When one mole of an ionic solid is formed from its constituent gaseous ions, the energy released is called the lattice energy.

Energetics of Formation of Ionic Substances:.

$$\mathrm{Na_{(s)}} \xrightarrow[+S]{\text{Sublimation}} \mathrm{Na_{(g)}} \xrightarrow[+I]{} \mathrm{Na^{+}_{(g)}} + e^{-}$$

$$\frac{1}{2}\mathrm{Cl_{2(g)}} \xrightarrow[+1/2D^{*}]{\text{Dissociation}} \mathrm{Cl_{(g)}} \xrightarrow[+E_{A}]{\text{Addition of } e^{-}} \mathrm{Cl^{-}_{(g)}}$$

$$\mathrm{Na^{+}_{(g)}} + \mathrm{Cl^{-}_{(g)}} \xrightarrow[+U]{\text{Crystal formation}} \mathrm{NaCl_{(S)}}$$

Where S = heat of sublimation of sodium metal
I = ionization energy of sodium
D = heat of dissociation of molecular chlorine
E_a = electron affinity of chlorine, and
U = lattice energy of sodium chloride

The amount of heat liberated in the overall reaction is the heat of formation of sodium chloride. From the above

$$\Delta H_f = S + I + \frac{1}{2}D - E_a - U$$

More the negative value of the heat of formation, greater would be the stability of the ionic compound produced.

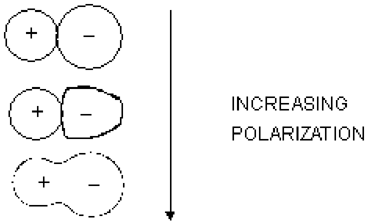
Thus on the basis of the above equation, formation of an ionic compound is favoured by

a) low ionization energy (I) of the metal.
b) high electron affinity (E_A) of the other element.
c) higher lattice energy (U) of the resulting compound.

Fajan’s Rules

It is generally assumed that covalent and ionic bonds are entirely distinct but this is probably not a totally valid assumption. Bonds intermediate between ionic and covalent do occur through a process of **deformation or polarization.**

(1) **Small cation** _



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(2) **Large anion** _ The large anion has **polarizability. Effect of anion size upon covalent character**

Compound	Anion	Anion radius Å	Melting point °C
CaF_2	F^-	1.36	1392
$CaCl_2$	Cl^-	1.81	772
$CaBr_2$	Br^-	1.95	730

Effect of cationic size upon covalent character

Cation	Cation radius Å	m.p. of anhydrous chlorides, °C
Be^{2+}	0.31	405
Mg^{2+}	0.65	702
Ca^{2+}	0.99	772
Sr^{2+}	1.33	870
Ba^{2+}	1.35	960

(3) **Large charge on either of the ions**

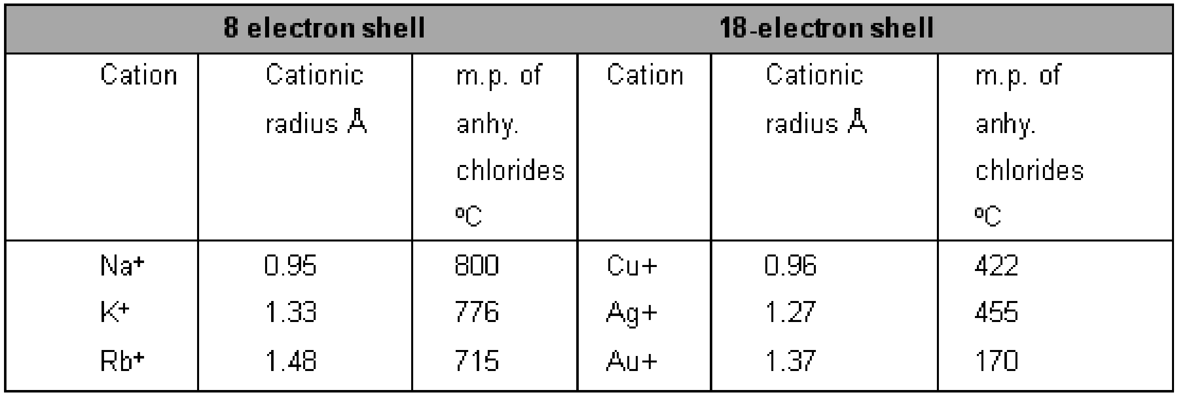
Effect of cationic charge upon covalent character

Cation	Cationic radius Å	m.p. of anhydrous chlorides °C
Na^{+}	0.95	800
Mg^{2+}	0.65	712
Al^{3+}	0.50	sublimes

(4) **Cation with non-inert gas atom structure _**

if the charge and size are kept nearly constant, cations with 18-electron structure cause greater anion deformation than those with 8-electron arrangements. It is shown in table by the comparison of the melting points of anhydrous chlorides of IA and IB group of periodic table.

Effect of 8 and 18 electronic shell upon the covalent character



8 electron shell			18-electron shell		
Cation	Cationic radius Å	m.p. of anhy. chlorides °C	Cation	Cationic radius Å	m.p. of anhy. chlorides °C
Na^+	0.95	800	Cu+	0.96	422
K^+	1.33	776	Ag+	1.27	455
Rb^+	1.48	715	Au+	1.37	170

$NaCl < Na_2S < Na_3P$

$BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$

$$\xrightarrow[\text{increasing covalent character}]{CaF_2 < CaCl_2 < CaBr_2 < CaI_2}$$

$$\xrightarrow[\substack{\text{Covalent character increases as the} \\ \text{size of the halide ion increases}}]{AlF_3 \qquad AlCl_3 \qquad AlBr_3 \qquad AlI_3}$$

Illustration 4: ***The decomposition temperature of Li_2CO_3 is less than that of Na_2CO_3. Explain.***

Solution: As Li^+ ion is smaller than Na^+ ion, thus small cation (Li^+) will favour more covalent character in Li_2CO_3 and hence it has lower decomposition temperature than that of Na_2CO_3.

Applications of Fajan's Rule

(1) **Melting point**

According to Fajan's Rule

$$\text{Covalent character} \propto \text{Polarization of anion} \propto \text{Ionic potential}$$

$$= \frac{\text{Charge of cation}}{\text{Radius of cation}}$$

$$\text{Melting point of compound} \propto \text{Ionic character}$$

$$\propto \frac{1}{\text{Covalent character}}$$

(2) **Diagonal relationship**

$$\begin{array}{llll} \text{Li} & \text{Be} & \text{B} & \text{C} \\ \text{Na}^{+} & \text{Mg}^{+2} & \text{Al}^{+3} & \text{Si}^{+4} \end{array}$$

diagonal relationship then two elements of similar polarizing power may result, e.g., polarizing power of Be_{2+} and Al_{3+} is almost similar as their ionic potential (ϕ) are also almost similar [ϕ of $Be_{2+} = 6.48$ and $\phi$of $Al_{3+} = 6.0$]. Such elements will form bonds of a similar type in the corresponding compounds. This explains almost identical chemical and physical properties of the above mentioned pairs of elements.

(3) **Non- polar character and colour**

The increase in nonpolar character of inorganic salts is manifested in the appearance or enhancement of colour. Thus:

Colour deepening tendency $\propto$ polarization of anion $\propto$ size of anion

(i) The oxides of colourless cations are usually white but the corresponding sulphides are likely to be deeply coloured if the cation is one which has a tendency to polarize anions.

(ii) With a few exceptions, the white metal sulphides are only those of alkali and alkaline earth metals.

In a series of halides of ions such as Ag^+, the fluorides and chlorides are colourless ions is usually an indication of an appreciable amount of nonpolar character or some other unusual structural feature.

An appreciable amount of polarization leads to intense absorption bands.

(4) **Chemical reactions_ Stability of metal carbonates**

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$$MCO_3 \longrightarrow MO + CO_2$$

$K_2CO_3 > CaCO_3 > CuCO_3$.

Further, the effect of d electrons is also evident. Cd_{2+} and Pb_{2+} are approximately of the same size as Ca_{2+} but both $CdCO_3$ and $PbCO_3$ decompose at approximately 350°C.

(5) **Acidic, Basic and Amphoteric character of oxides**

$$\text{Ionic potential } (\phi) = \frac{\text{Charge on metal ion}}{\text{Radius of metal ion}}$$

If $\sqrt{\varnothing} < 2.2$ metal oxide is basic e.g., MnO, CrO, Na_2O, MgO etc.

If $\sqrt{\varnothing} = 2.2$ to 3.2 metal oxide is amphoteric e.g., MnO_2, CrO_2 etc.

If $\sqrt{\varnothing} > 3.2$ metal oxide is acidic e.g., MnO_3, CrO_3, Mn_2O_7 etc.

(6) **Solubility**

Solubility of salts in polar solvents like water is affected by polarization. The example of silver halides may be considered in which there is polarizing cation and increasing polarizable anions.

Silver fluoride is quite ionic and soluble in water.
Less ionic silver chloride is soluble only after complexation with ammonia.
silver bromide and silver iodide are insoluble even with the addition of ammonia.
Increasing covalence from fluoride to iodide is expected and decreases solubility in water is observed.
However, many other factors are involved in solubility in addition to covalence.

Factors affecting Hydration (solvation) energy

(a) Size of ions-

: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, $F^- > Cl^- > Br^- > I^-$, $Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2}$

In transition series (d-Block) size of ions are almost same due to balancing of shielding effect and nuclear attraction force, therefore their hydration energy is almost constant.
Transition metal ion can form strong bond with water due to presence of vacant d-orbital so they contain high solvation energy.

(b) Charge on ions _ As the charge on ions increases, attraction between ions and dipole (H_2O) increases so hydration energy increases.

(c) Dielectric constant of solvent – As the DEC increases force of attraction between ions decreases so solvent with high DEC is responsible for solubility of compound.

Solubility of compounds

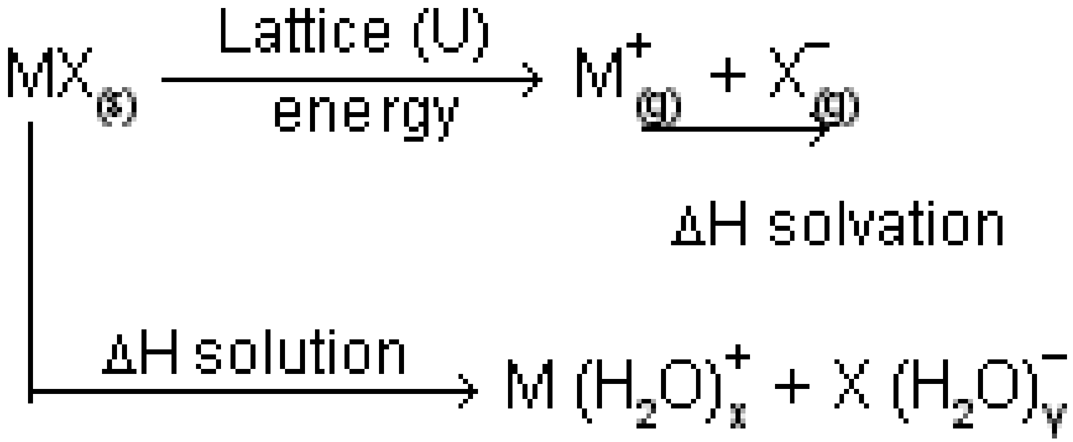
Solubility of different compounds in solvents depends upon many factors. It is very complicated property because many factors control this property simultaneously for example

(a) Nature of solute
(b) Nature of solvent
(c) Temperature of reaction
(d) Pressure
(e) Lattice energy
(f) Solvation energy etc.

When any solute dissolves in solvent to give the saturated solution, heat evolved or absorbed to the surroundings is known as heat of solution.

Whether the heat of solution is positive or negative depends on the nature of solute and solvent. When any solid are dissolved in water enthalpy of over all reaction is depends upon strength of two energies, that is

(i) Energy required breaking down one mole ionic crystal lattice into their respective ions known as lattice energy.



(ii) Energy liberated when the ions are solvated or hydrated by solvent there is process of neutralisation, known as solvation energy or hydration energy. This energy actually takes into account of both solvent. Solvent interaction (energy required to make a hole in water) and solvent solute interaction. These two are combined together because experimentally they are hard to separate. Energy change involved in dissolution of a salt represented by born haber cycle.

(a) Size of ions – As the size of ions decreases their is compact packing of atoms so system is stable with high lattice energy for example LiF contains high lattice energy.

(b) Charge on ions – As the charge on ions increases, their is high attraction between ions so stability increases which increases lattice energy for example $Al_2O_3 > MgCl_2 > NaCl$.

(c) Bond character _ Ionic compounds have high lattice energy than covalent compound due to more stability.

Factors affecting solubility of ionic compounds

Solubility of compounds mainly control by solvation energy and lattice energy with the support of some minor factor like DEC of solvent, hydrogen bonding etc but it is very difficult to set a trend in periodic table for solubility of different compounds because both solvation-energy and lattice energy decreases with increase in size, thing is which decreases more with respect to other, actually this decides the solubility of compound.

Generally, ionic substances dissolve more readily in solvents composed of molecules containing electrostatic dipoles.

Solids are usually crystalline in nature. In the crystal lattice the ions are arranged in a symmetrical fashion and are held in their relative positions by strong electrostatic forces resulting from the charge upon the ions. To breakdown the arrangement of ions in the crystal, these forces must be overcome. Thus, for a substance to be readily soluble, more energy must be provided for the separation of the ions from the crystal than was liberated in building up the ionic lattice. In other words, the energy of solvation must be of greater magnitude than the lattice energy. (The interaction that takes place when a substance is introduced into a solvent is called **solvation** and the energy change involved in this process is known as the **solvation energy**).

Thus, both the solvation energy and the lattice energy affect solubility of ionic compounds but in an opposite manner. The important factors affecting solubility of ionic compounds are discussed below.

1. Nature of solvents. As the DEC of solvents increases solubility of ionic compounds increases because it weakens the force of attraction between ions. Force of attraction between ions given by formula

$$F = \frac{q^+ q^-}{4\pi\varepsilon r} \text{ or } F \propto \frac{1}{\varepsilon}$$

DEC of water is very high (81), it is the best solvent for ionic compounds. Hydrogen peroxide has higher DEC (92) than water but it not used as a solvent for ionic compounds because it undergo decomposition at room temperature so work as powerful oxidising agent.

$H_2O_2 \quad H_2O + [O]$

Nonpolar solvents like benzene, ether and CCl_4 fail to solvate the ions so these are not use to dissolve ionic compounds.

2. Size of ions. Both lattice energy and solvation energy depends upon size of ions on following manner

$$U = K\frac{1}{r^+ + r^-},\ S = K\frac{1}{r^+} + \frac{1}{r^-}$$

where r^+ and r^- are radii of cation and anion. It is clear from the above relations that decrease in the size of the ions affect the two energies in a similar manner. However, the two energies are influenced to different extents and the predominating energy affects the solubility to different extents.

In case of compounds containing large anions e.g., I^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-} etc., the solubility will decrease with increase of cationic size. For example, in case of sulphates of alkaline earth metals, the decrease in solvation energy is more rapid than the decrease in lattice energy with the increase in the size of cation. The solubility of alkaline earth metal sulphates decreases in the following order :

$MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

Similarly, the solubility of alkali metal iodides decrease in the following order :

$LiI > NaI > KI > RbI > CsI$

In case of compounds containing small anions e.g., F—, the decrease in lattice energy is more rapid than the decrease in solvation energy with increasing size of the cation. Thus the solubility of the fluorides of alkali metals increase as the size of cation increases as given below :

$CsF > RbF > KF > NaF > LiF$

Solubility of II group carbonates in H_2O

$BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 >$ BaCO3 (Large size anion)

$BeF_2 > BaF_2 > SrF_2 > CaF_2 > MgF_2$

(Small size anion but exceptionally high solubility of BeF_2 due to high hydration energy of Be^{+2})

$Ba(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$ (Small size anion)

Solubility in water

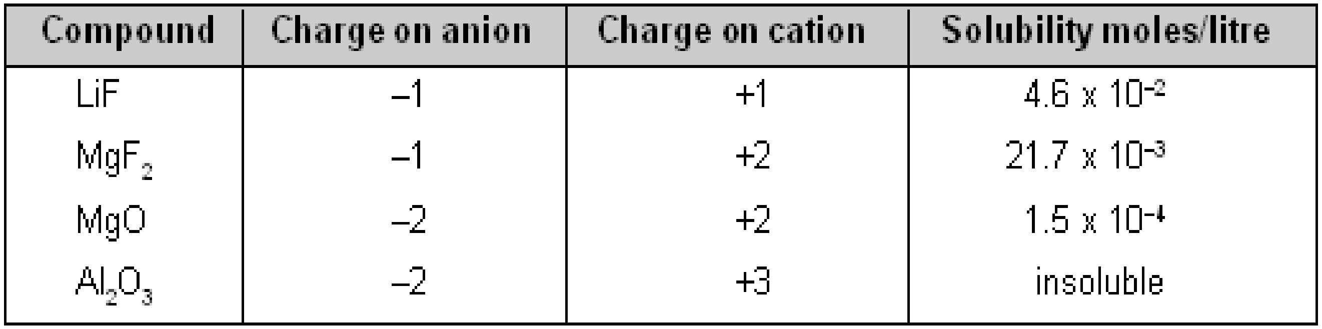
$LiI > LiBr > LiCl > LiF$

$CaI_2 > CaBr_2 > CaCl_2 > CaF_2$

(Due to decrease in lattice energy by increase in size)

3. Ionic Charge. With the increasing ionic charge, the lattice energy increases much more rapidly than the solvation energy. Thus, solubility of ionic compounds decreases very sharply as the ionic charge increases.

Effect of Ionic charge on Solubility



Compound	Charge on anion	Charge on cation	Solubility moles/litre
LiF	–1	+1	4.6×10^{-2}
MgF_2	–1	+2	21.7×10^{-3}
MgO	–2	+2	1.5×10^{-4}
Al_2O_3	–2	+3	insoluble

4. Polarization of Anions. Large anions are more polarizable than small anions (Fajan's Rule). Polarization of anion increases covalent character in the molecule, hence decreases solubility in water. This explains the order of solubility of silver halides in water as given below:

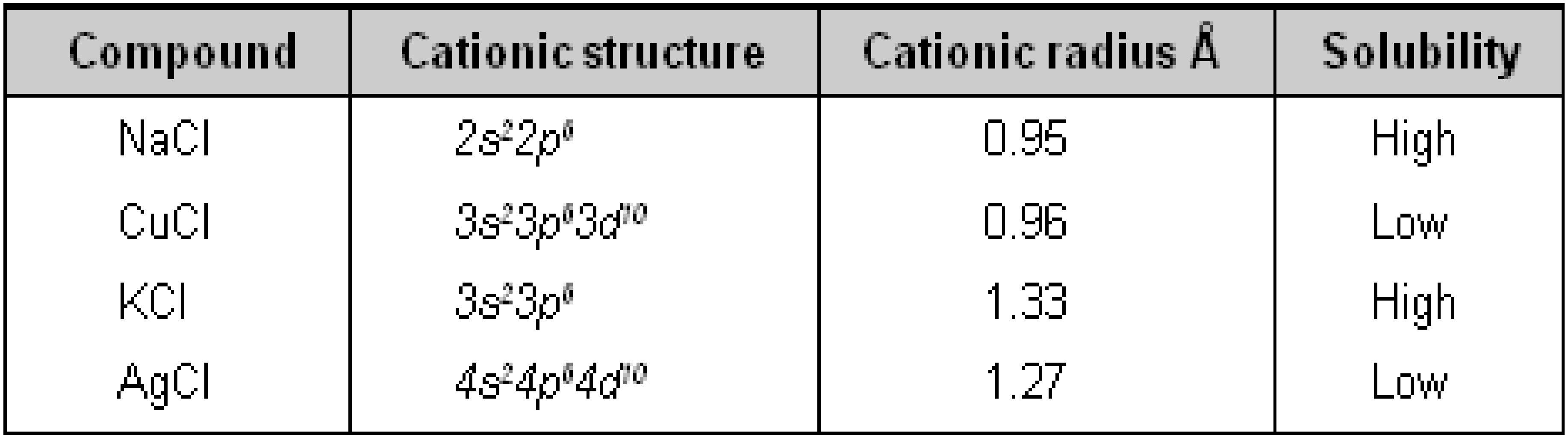
AgF > AgCl > AgBr > AgI

Cations with 18-electrons structure polarize anions more than those with 8-electron arrangements. Polarization of anion decreases the solubility. This explains the following order of solubility

KCl > AgCl

NaCl > CuCl

Compound Cationic structure Cationic radius Å Solubility



Compound	Cationic structure	Cationic radius Å	Solubility
NaCl	$2s^2 2p^6$	0.95	High
CuCl	$3s^2 3p^6 3d^{10}$	0.96	Low
KCl	$3s^2 3p^6$	1.33	High
AgCl	$4s^2 4p^6 4d^{10}$	1.27	Low

5. Effect of Temperature. Formation of a solution may be exothermic or endothermic process and may be represented as follows:
Exothermic: Solute + Solve Solution + Heat ....(1)
Endothermic: Solute + Solvent + Heat Solution ....(2)
The addition of heat (i.e., a rise in temperature) in equation (2) causes more of the solute to dissolve. This is the case with most of the solid-

liquid solutions, where the solubility increases with rise in temperature. In equation (1) the solubility decreases with the rise in temperature. For example,
the solubilities of KNO_3, $NaNO_3$, KCl, NH_4Cl etc. increases with the rise in temperature

whereas that of Na_2SO_4 decreases with the rise in temperature.

6. Hydrogen bonding. It is very minor factor which control solubility of compounds. In the system where solute and solvent particles shows association with H-Bonding are more soluble than other combination. For example NH_3 is more soluble in H_2O than PH_3, ROH are more soluble in H_2O than RSH due to association. In case of ROH & ROR their solubility in water is almost same because both show H-Bonding with H_2O. Diols and triols are much more soluble than mono hydroxy derivatives because they form more effective hydrogen bonding.

ODD ELECTRON BOND

It has been observed that almost all the compounds of non-transition elements contain aneven number of bonding electrons. Very few exceptions like NO, NO_2 etc. possess odd numberof bonding electrons. Such type of compounds are called Odd Molecules. The odd moleculesare classified into following two categories

1.<u>One electron bond molecules and ions:</u>

H_2^+ ion is an example in which one electron bond is formed. H_2^+ ion is considered to be resonance hybrid of the two resonating structures (i) and (ii) i) $^+H \bullet H$ ii) $H \bullet H^+$

H_2^+ ion has its bond energy equal to 61 kcal/mol. These two forms are of equal stability. H_2 molecules has its bond energy equal to 109 kcal/mol. Internuclear distance between the H-atoms in H_2^+ is 1.06Å and in H_2 molecule it is 0.74Å.

Other examples having 1 electron bond are Li_2^+, Na_2^+, K_2^+ ions and B_2H_6 (diborone) molecule.

6. <u>Three electron bond molecules and ions:</u>

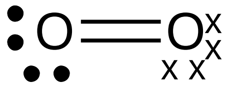
Examples of some molecules and ions are given below.

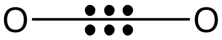
He_2^+ ion: This ion is represented as a resonance hybrid of (a) and (b)

$$He_{x}^{x}\bullet He^{+} \longleftrightarrow {}^{+}He \bullet {}_{x}^{x}He$$

Resonance between the two forms (a) and (b) leads to the formation of a three-electron bond between He and He^+. It is only one electron that plays part in resonance. Thus, 1- and 3-electron bonds have approximately the same energy. The binding energy of He_2^+ is 58 kcal/mol.

O_2 molecule: Normal VBT structure for O_2 molecules

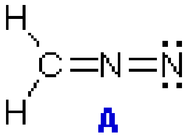


This structure however, does not represent the paramagnetic property of O_2 molecule. It is therefore assumed that two O-atoms in O_2 molecule are linked by a normal covalent bond and two 3-electron bonds. Thus O_2molecule is 

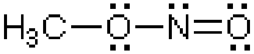
Properties of Odd-electron Bonds

- One and three electron bonds are approximately half as strong as an ordinary electron pair bond (normal covalent bond)
- Such bonds are not stable if the electronegativity difference between the atoms involved is large. Formation of 1-electron bond generally occurs between like atoms while its formation between unlike atoms is rare.
- Molecules containing a 3-electron bond in addition to an electron pair bond sometimes shows a tendency to dimerise. Since the three electron bond is half as strong as an electron pair bond, the energy of dimer will be close to that of two monomeric molecules.

Formal Charges



A



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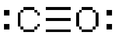

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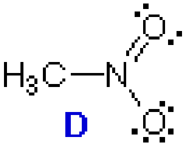

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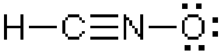
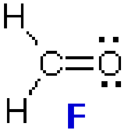
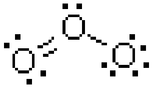


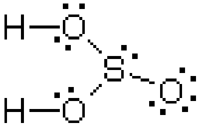
E



F



G



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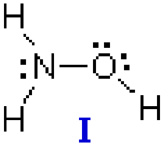

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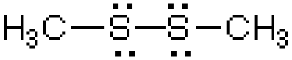

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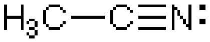


K

7. VALENCE BOND THEORY

According to this theory proposed by Heitler and London and developed by Linus Pauling and Slater.

- For the formation of a covalent bond, a half – filled atomic orbital of one atom overlaps with the half – filled atomic orbitals of another atom. These atomic orbitals belong to the outermost shell of the atoms.
- A covalent bond is formed by the overlapping of atomic orbitals having electrons with opposite spins.
- The atomic orbitals containing paired electrons do not participate in the processes of overlapping. These electrons are called non – bonding electrons.
- Due to the directional nature of most of the orbitals, overlapping is possible only when orbitals are properly oriented.

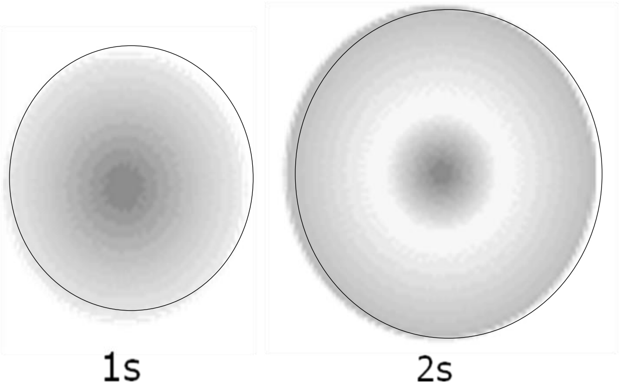
SHAPES AND SIZE OF ORBITALS

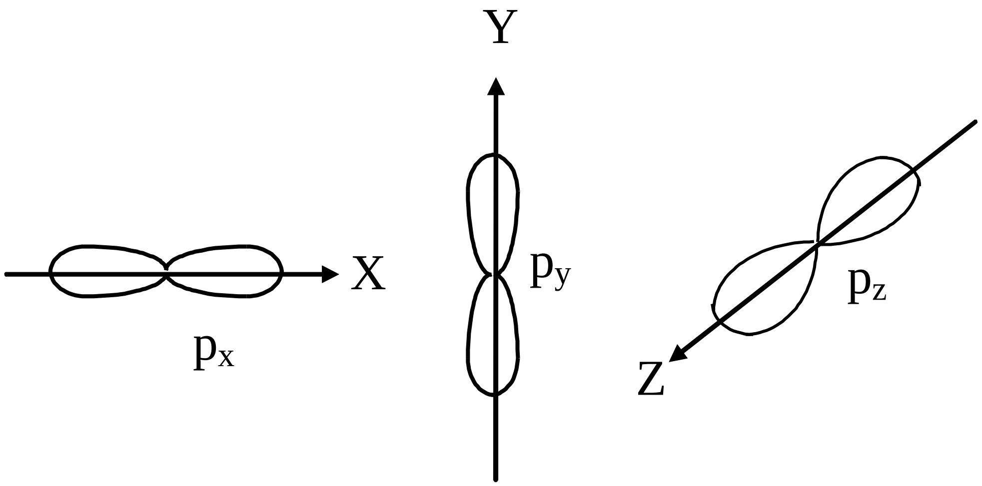
- An orbital is the region of space around the nucleus within which the probability of finding an electron of given energy is maximum (B > 90%). The shape of this region (electron cloud) gives the shape of the orbital. It is basically determined by the azimuthal quantum number ℓ, while the orientation of orbital depends on the magnetic quantum number (m). Let us now see the shapes of orbitals in the various subshells

s–orbitals:

These orbitals are spherical and symmetrical about the nucleus. The probability of finding the electron is maximum near the nucleus and keeps on decreasing as the distance from the nucleus increases. There is vacant space between two successive s–orbitals known as radial node. But there is no radial node for 1s orbital since it is starting from the nucleus.

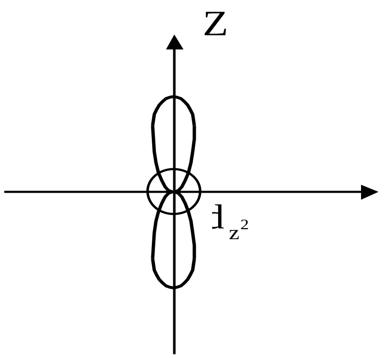
- The size of the orbital depends upon the value of principal quantum number (n). Greater the value of n, larger is the size of the orbital. Therefore, 2s– orbital is larger than 1s orbital but both of them are non-directional and spherically symmetrical in shape.



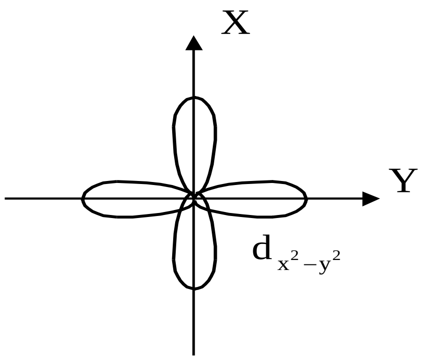


- ***<u>p–orbitals</u> (ℓ =1):*** The probability of finding the p–electron is maximum in two lobes on the opposite sides of the nucleus. This gives rise to a dumb–bell shape for the p–orbital. For p–orbital $l = 1$. Hence, m = –1, 0, +1. Thus, p–orbital have three different orientations. . The two lobes of p–orbitals are separated by a nodal plane, where the probability of finding electron is zero.

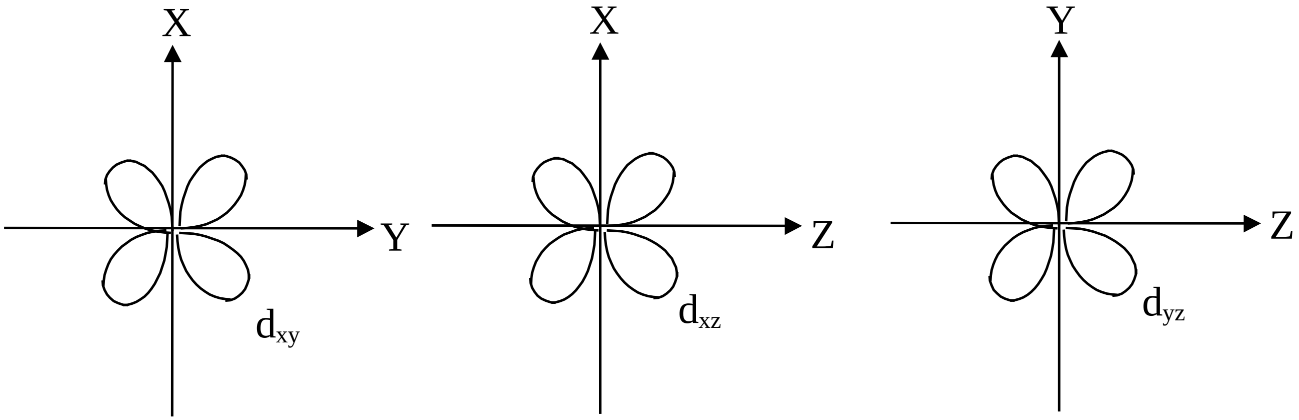
- ***d–orbitals* (ℓ=2):** For d–orbitals, l =2. Hence m= – 2,–1,0,+1,+2. Thus there are 5 d orbitals. They have relatively complex geometry. Out of the five orbitals, the three (d_{xy}, d_{yz},d_{zx}) project in between the axis and the other two d_{z^2} and $d_{x^2-y^2}$ lie along the axis.



Dough–nut shape or Baby soother shape



Clover leaf shape



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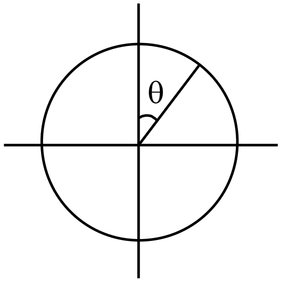
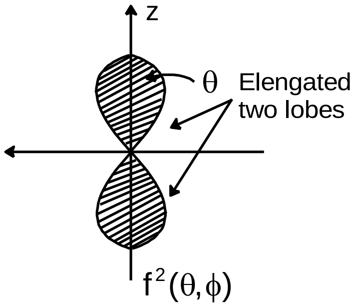
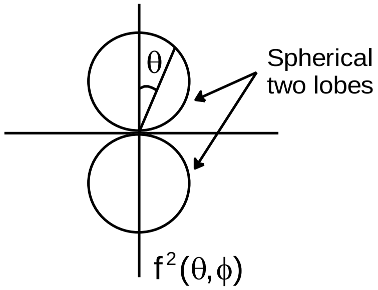


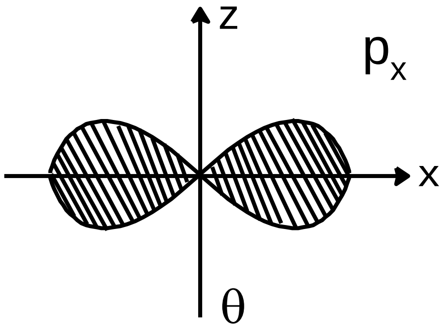




Angular nodes (Nodal Planes):

Total no. of angular nodes for any orbital = ℓ

For s orbital there will be no angular node.

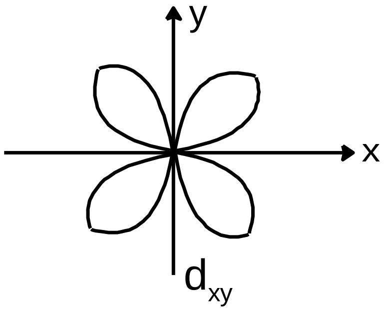


For p_x orbital, $\ell = 1 \Rightarrow$ no. of angular nodal = 1 (yz plane)

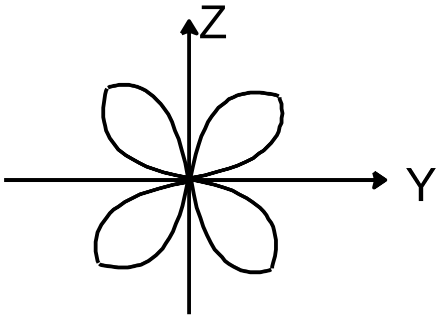
For p_y orbital, nodal plane (xz plane)

For p_z orbital, nodal plane (xy plane)

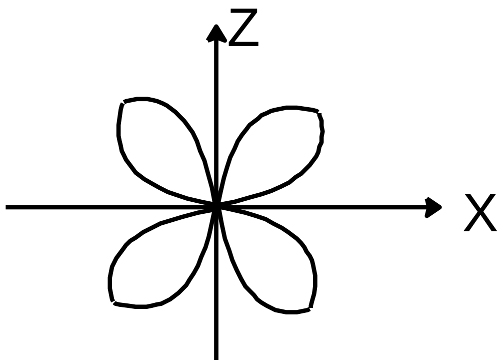
For d_{xy} orbital, ℓ = 2 therefore 2 nodal planes, nodal planes: xz & yz planes

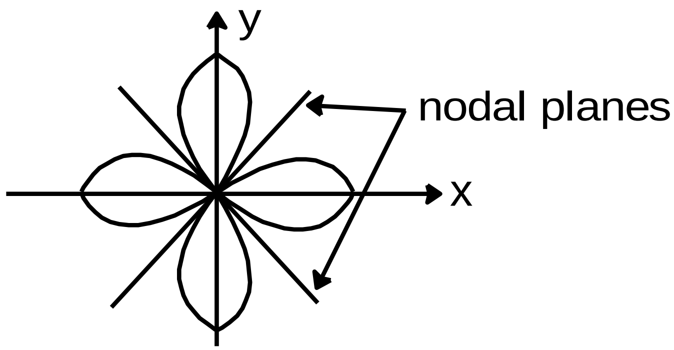


For d_{yz} orbital : xy & xz planes are nodal planes.



For d_{zx} orbital : xy & yz planes are nodal planes.





$d_{x^2-y^2}$

- Can you guess where will be the two angular nodes for d_{z2} located ?

- no. of radial nodes = n - ℓ - 1
  no. of angular nodes = l
  total no. of nodes = n - l- 1 + l
  = (n – 1)

Sigma and Pi Bonding

When two hydrogen atoms form a bond, their atomic orbitals overlap to produce a greater density of electron cloud along the line connecting the two nuclei. In the simplified representations of the formation of H_2O and NH_3 molecules, the O—H and N—H bonds are also formed in a similar manner, the bonding electron cloud having its maximum density on the lines connecting the two nuclei. Such bonds are called sigma bonds (σ-bond).

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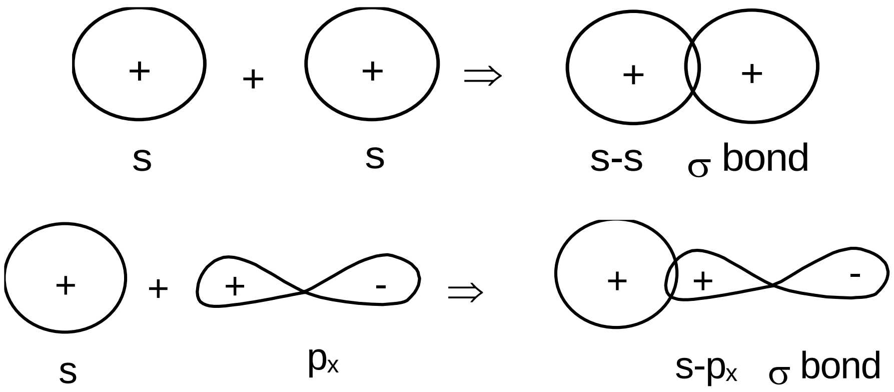
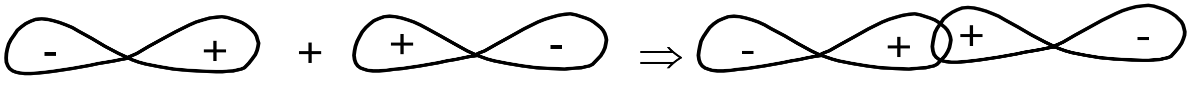
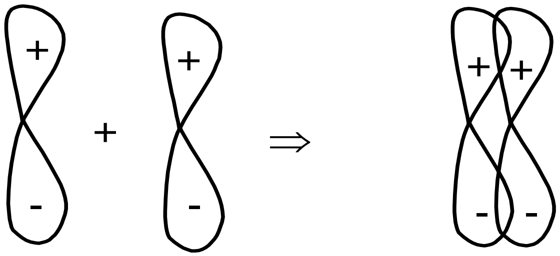




p_x + p_x ⇒ p_x–p_x σ - bond



p_π - p_π bond

Limitation of Valance Bond Theory

Limitation1:

When the bonding scheme of certain polyatomic molecules is discussed, our simple valence bond theory fails to accurately describe what is going on.

Methane is one of these molecules where we must expand upon our valence bond theory. The 2s orbital is filled with two electrons and the $2p_y$ orbital has no electrons for use in bonding. This leaves only the $2p_x$ and the$2p_z$ orbitals as the orbitals that can participate in bonding. We know however, that in CH_4, four hydrogen atoms must make four bonds with the central carbon atom.

Limitation 2:

Another one of the shortcomings of the Valence Bond Theory is the inability to predict molecular geometries.

If we take a look at the bonding orbitals of H_2O, only two of the p orbitals of sulphur bond with a 1s orbital from H. The molecular geometry predicted by these two bonding orbitals is 90^{o}. This is obviously incorrect because the valence bond theory does not take into account the lone pair electrons on the central O atom. The two lone pair electrons create a angle of 104.5^{o} between the two hydrogen atoms.

8. VSEPR THEORY

In 1957 Gillespie and Nyhom gave this theory to predict and explain molecular shapes and bond angles more exactly.:

Lone pair - lone pair > lone pair – bond pair > bond pair – bond pair

- The magnitude of repulsions between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms.
- Double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond.

8.1 Geometry of Molecules

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as

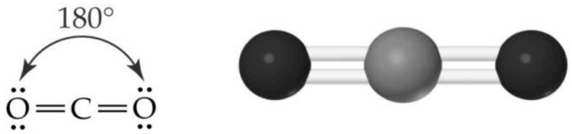
(i) Molecules in which the central atom has no lone pair and

(ii) Molecules in which the central atom has one or more lone pairs.

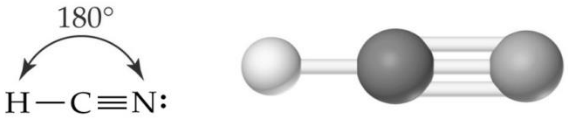
Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry	Example
2	0	2	 Linear	$O{=}C{=}O$
3	0	3	 Trigonal planar	
2	1		 Bent	

Two Charge Clouds: .

A CO_2 molecule is linear, with a bond angle of 180°.



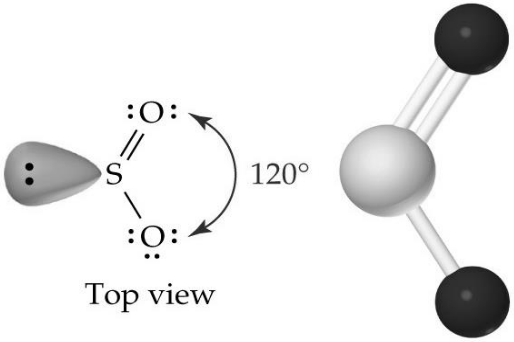
An HCN molecule is linear, with a bond angle of 180°.



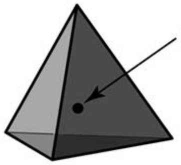
Three Charge Clouds:

A form
trigona
angles

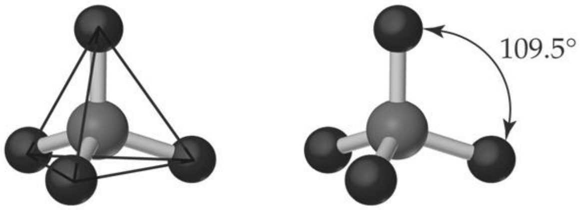
An SO_2 molecule is bent with a bond angle of approximately 120°.



Four Charge Clouds:

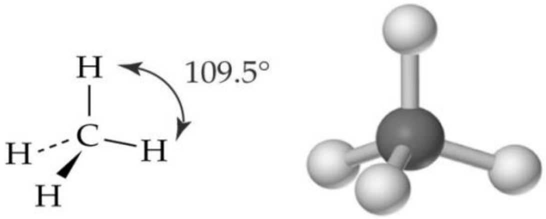


A regular tetrahedron

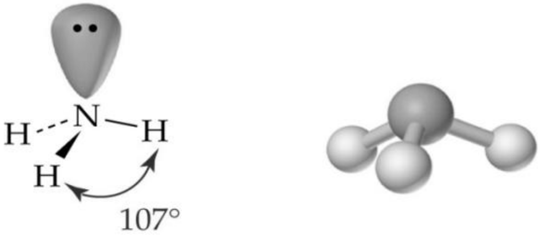


A tetrahedral molecule

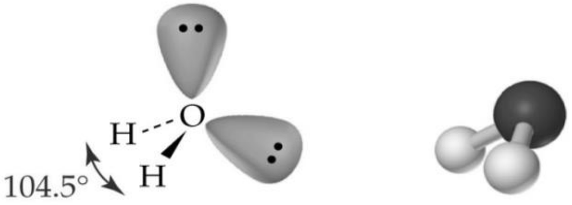
A methane molecule is tetrahedral, with bond angles of 109.5°.

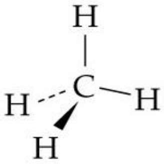
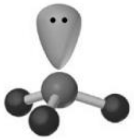
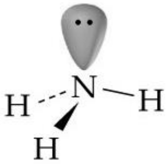
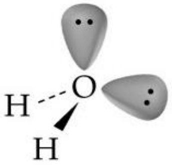


An ammonia molecule is trigonal pyramidal, with bond angles of 107°.

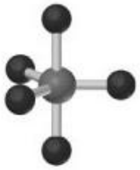
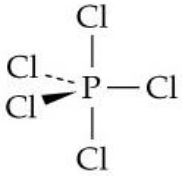
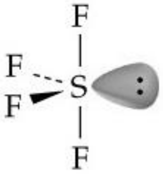
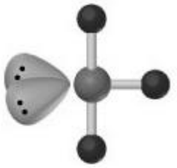
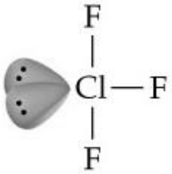
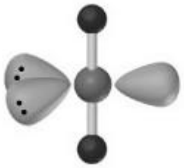
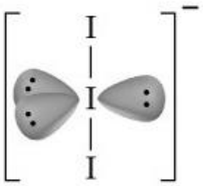


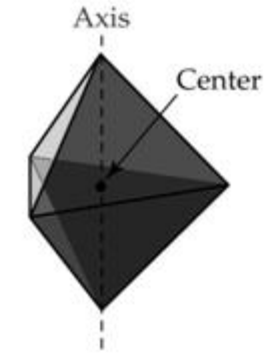
A water molecule is bent, with a bond angle of 104.5°.



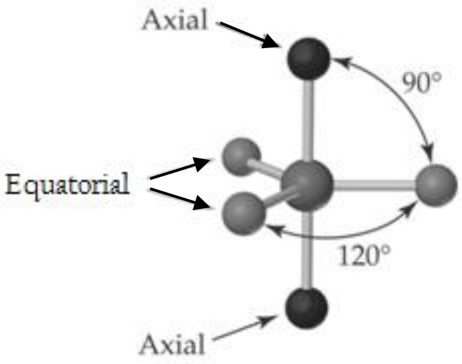
4	0	4		Tetrahedral	
3	1			Trigonal pyramidal	
2	2			Bent	

Five Charge Clouds:

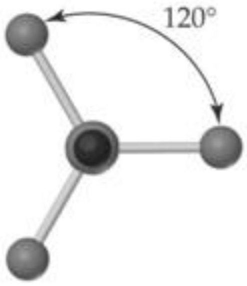
5	0	5		Trigonal bipyramidal	
4	1			Seesaw	
3	2			T-shaped	
2	3			Linear	



A trigonal bipyramid

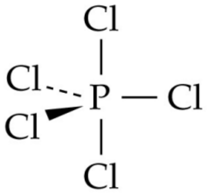


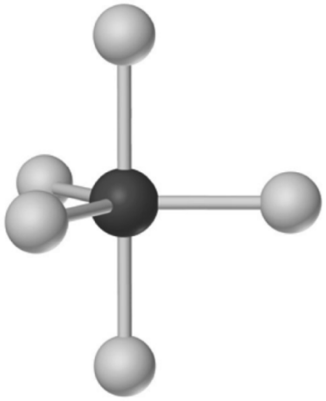
Side view



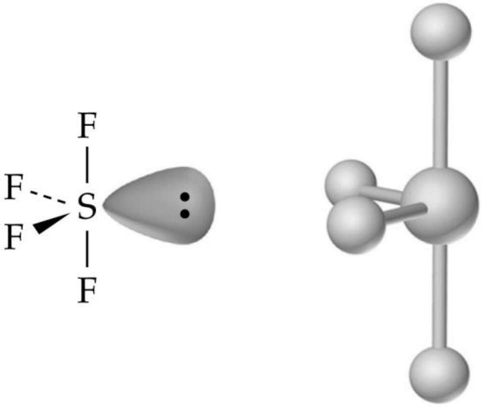
Top view

A PCl_5 molecule is trigonal bipyramidal.

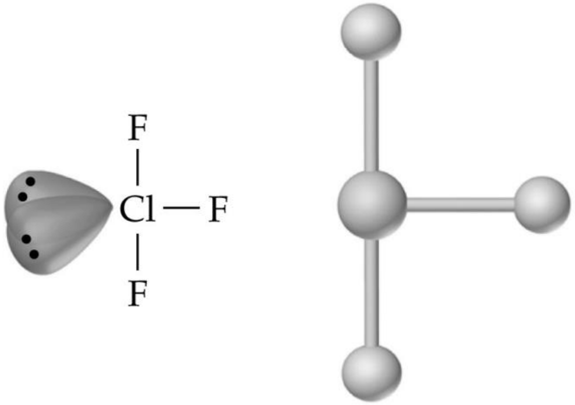




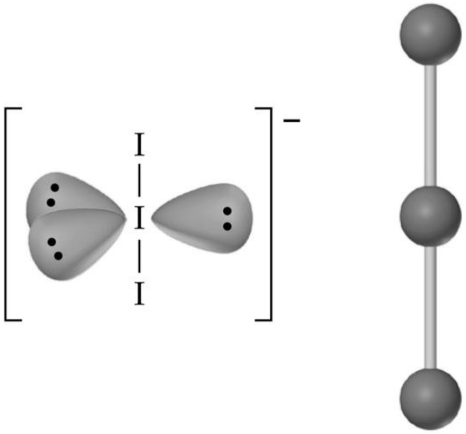
An SF_4 molecule is shaped like a seesaw (turn 90° to see it).



A ClF_3 molecule is T-shaped (turn 90° to see it).

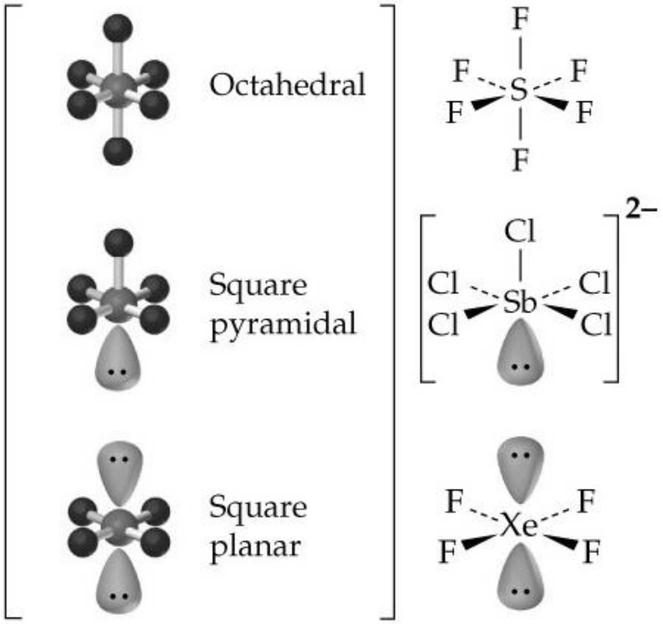


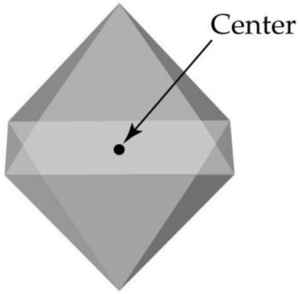
An I_3^- ion is linear.



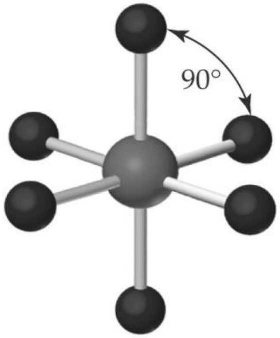
Six Charge Clouds:

6	0	6	Octahedral
5	1		Square pyramidal
4	2		Square planar

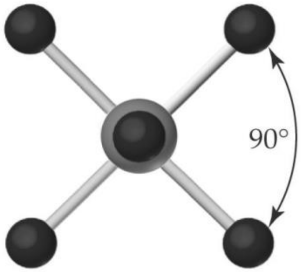




A regular
octahedron

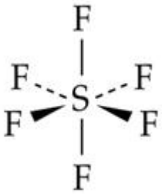


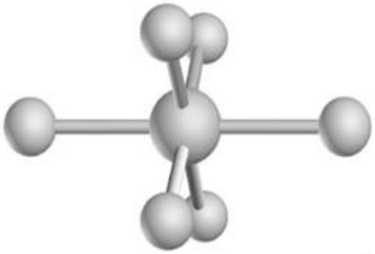
Side view



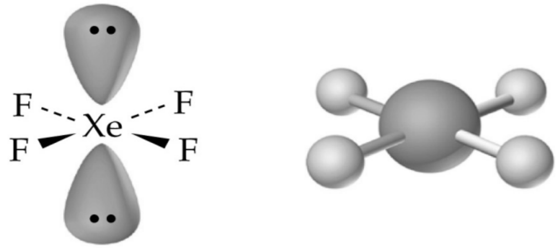
Top view

An SF_6 molecule is octahedral.

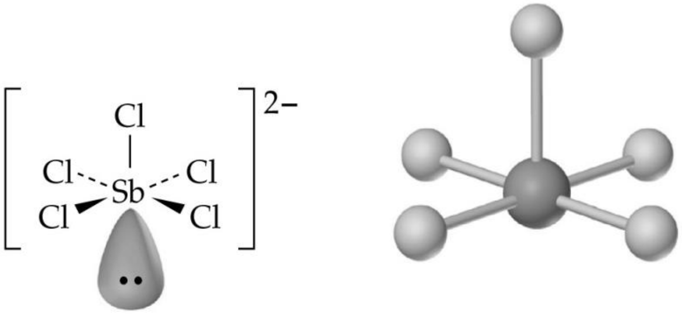




An XeF_4 molecule has a square planar shape.



An $SbCl_5^{2-}$ ion has a square pyramidal shape.



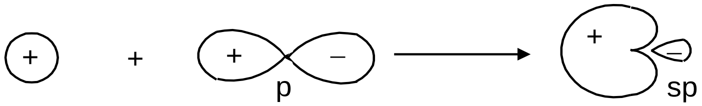
SF_6 has six bond pairs in the outer shell and is a regular octahedron with bond angles of exactly 90°.

In BrF_5, the Br also has six outer pairs of electrons, made up of five bond pairs and one lone pair. The lone pair reduces the bond angles to 84°30’.

9.HYBRIDIZATION

- The intermixing of two or more pure atomic orbitals of an atom with almost same energy to give same number of identical and degenerate new type of orbitals is known as hybridization.
- The new orbitals formed are also known as hybrid orbitals. The intermixing or hybridization of atomic orbitals is a mathematical concept based on quantum mechanics.
- During this process, the wavefunctions, Ψ of atomic orbitals of same atom are combined to give new wavefunctions corresponding to hybrid orbitals.

Hybrid Orbitals



Method of Predicting the hybridization state

The hybrid state of the central atom in simple covalent molecule or polyatomic ion can be predicted by using the generalized formula as described below:

Simple Molecule	Polyatomic Anion	Poyatomic Cation
$X = \frac{1}{2}[V + G]$	$X = \frac{1}{2}[V + G + a]$	$X = \frac{1}{2}[V + G - c]$

In the above formulae,

V = Number of monovalent atoms or groups attached to the central atom

G = Number of outer shell electrons in ground state of the central atom

a = Magnitude of charge on anion

c = Magnitude of charge on cation

X	**2**	**3**	**4**	**5**	**6**	**7**
Hybrid state	sp	sp^2	Sp^3	sp^3d	sp^3d^2	sp^3d^3

For Example:

PF_5	**$COCl_2$**	**NH_4^+**	**ClO_4^-**
$X = \frac{1}{2}[5+5]$	$X = \frac{1}{2}[2+4]$	$X = \frac{1}{2}[4+5-1]$	$X = \frac{1}{2}[0+7+1]$
= 5	= 3	= 4	= 4
Hybrid state of P is sp^3d	Hybrid state of C is sp^2	Hybrid state of N is sp^3	Hybrid state of Cl is sp^3
NO_3^-	IF_5	CO_2	XeF_4
$X = \frac{1}{2}[0+5+1]$	$X = \frac{1}{2}[5+7]$	$X = \frac{1}{2}[0+4]$	$X = \frac{1}{2}[4+8]$
= 3	= 6	= 2	= 6
sp^2	sp^3d^2	sp	sp^3d^2
PCl_6^-	PH_3	SF_3^+	SF_4
$X = \frac{1}{2}[6+5+1]$	$X = \frac{1}{2}[3+5]$	$X = \frac{1}{2}[3+6-1]$	$X = \frac{1}{2}[4+6]$
= 6	= 4	= 4	= 5
Hybrid state	Hybrid state	Hybrid state	Hybrid state
sp^3d^2	sp^3	sp^3	sp^3d

HYBRIDISATION AND SHAPE OF DIFFERENT MOLECULES:

Types of Molecule / Ion	**No. of bond pairs**	**No. of lone pairs**	**Hybrid Orbitals**	**Shape of Molecule/ Ion**	**Examples**
AX_2	2	0	sp	Linear	$BeCl_2$, $HgCl_2$
	2	1	sp^2	bent (V-shape)	$SnCl_2$, $PbCl_2$
	2	2	sp^3	bent (V-shape)	H_2O, OF_2
	2	3	sp^3d	Linear	I_3^-, XeF_2
AX_3	3	0	sp^2	Trigonal planar	BF_3, BCl_3

	3	1	sp^3	Pyramidal	NH_3, H_3O^+
	3	2	sp^3d	T-shape	ClF_3, BrF_3
AX_4	4	0	sp^3	Tetrahedral	CH_4, NH_4^+
	4	1	sp^3d	Distorted tetrahedral (See Saw)	SF_4
	4	2	sp^3d^2	Square planar	XeF_4
AX_5	5	0	sp^3d	Trigonalbipyramidal	PCl_5
	5	1	sp^3d^2	Square pyramidal	IF_5
AX_6	6	0	sp^3d^2	Octahedral	SF_6

	6	1	sp^3d^3	Distorted Octahedral	XeF_6
AX_7	7	0	sp^3d^3	Pentagonal bipyramidal	IF_7

BONDING PARAMETERS

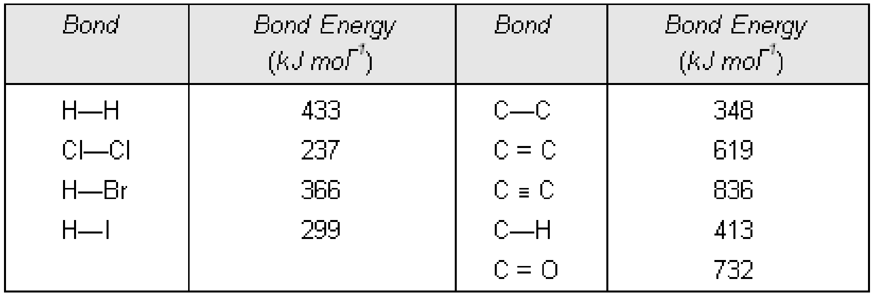
Bond Energy

1. Size of the participating atoms:

Larger the size of the atoms involved in bond formation, lesser is the extent of overlapping and consequently, smaller is the value of bond energy.

For example, bond energy of Cl—Cl bond is 237 kJmol^{-1} whereas that of H—H bond is 433 kJmol^{-1}.

2. Multiplicity of bonds:



Bond	Bond Energy (kJ mol^{-1})	Bond	Bond Energy (kJ mol^{-1})
H—H	433	C—C	348
Cl—Cl	237	C = C	619
H—Br	366	C ≡ C	836
H—I	299	C—H	413
		C = O	732

3. Number of lone pairs of electrons:

Greater the number of lone pair of electrons present on the bonded atoms, greater is the repulsive interactions between them and smaller is the bond energy

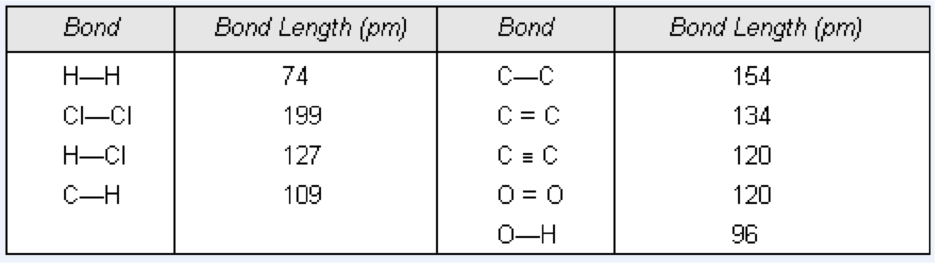
BOND LENGTH

Bond length is usually expressed in Angstrom units (Å) or Pico meters (pm) and it can be determined experimentally by X-ray diffraction and other spectroscopic techniques.

1. <u>Bond length increases with the increase in the size of the atoms:</u>

Bond length between hydrogen and chlorine atoms in HCl molecule is 127 pm whereas bond length between carbon and chlorine atoms is C—Cl bond 177 pm.

7. <u>Bond length decreases with the multiplicity of bonds:</u>



Bond	*Bond Length (pm)*	*Bond*	*Bond Length (pm)*
H—H	74	C—C	154
Cl—Cl	199	C = C	134
H—Cl	127	C ≡ C	120
C—H	109	O = O	120
		O—H	96

BOND ANGLE

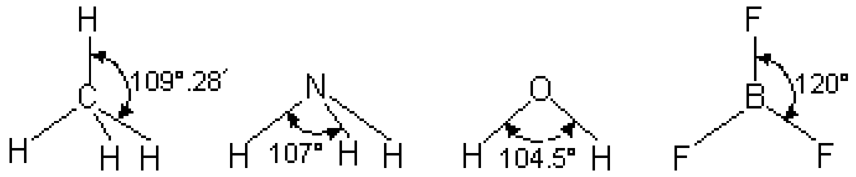


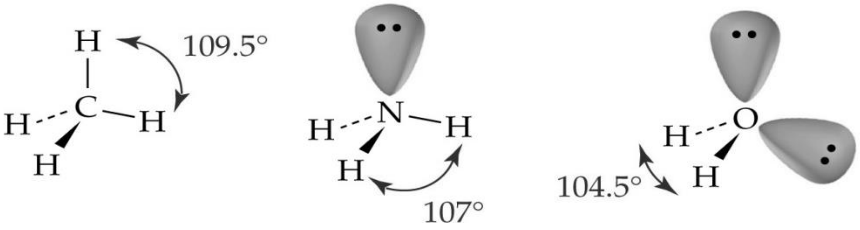
Figure. Bond angles in CH_4, NH_3, H_2O and BF_3.

Following factors can affect bond angle:

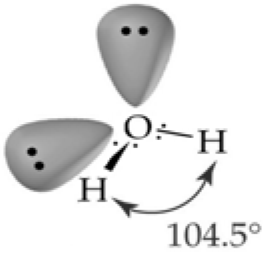
1.Hybridisation of central atom:

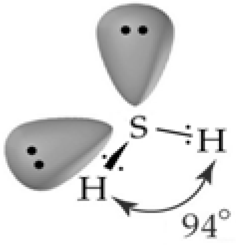
sp	180°
sp^2	120°
sp^3	109.5°
sp^3*d*	90°, 120°, 180°
sp^3*d*^{2}	90°, 180°
sp^3*d*^{3}	72°, 90°, 144°, 180°

2. Presence of lone pair: lp─bp repulsion is more than bp─bp

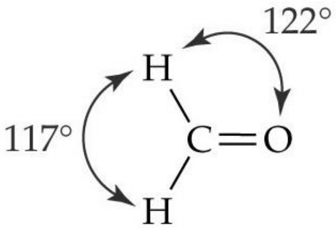


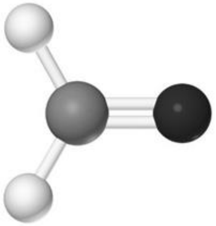
3. Electronegativity of central atom: Due to more electronegativity of central atom bond pair get shifted toward it and distance between them decrease thus further *bp*–*bp*repulsion increases.





4. Multiple bonds: Due to more electron density for double bond than that of single bond, repulsion due to double bond is more than single bond.





Resonance

Resonance can occur when the canonical structures

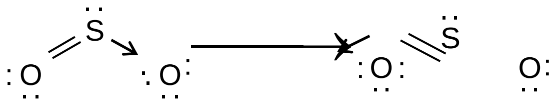
(i) have the constituent atoms in the same relative positions;
(ii) have nearly the same energy;
(iii) have the same number of unpaired electrons (to allow for continuous change from one type of bond to another);
(iv) differ in the distribution of electrons around the constituent atoms;
(v) (molecules or ions) are planar.

Resonance Energy

***The difference in energy between the actual observed energy of the resonance hybrid and the most stable of the contributing structures is called resonance energy*.**

OTHER EXAMPLES OF RESONANCE

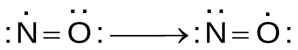
(i) Sulphur dioxide SO_2



(ii) Nitrous oxide (dinitrogen oxide), N_2O

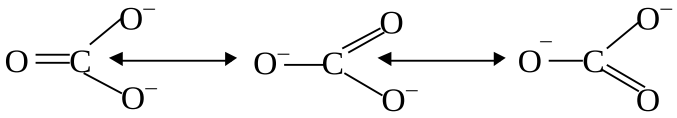
$N = N = O \longleftrightarrow N \equiv N \rightarrow O$

(iii) Nitric oxide, NO

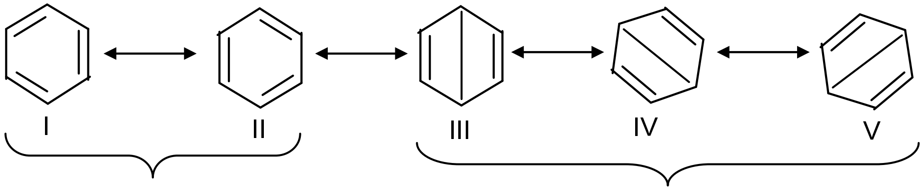


$:\dot{N} = \ddot{O}: \longrightarrow :\ddot{N} = \dot{O}:$

(iv) Carbonate ion, co_3^- (planar, triangular)



(v) Benzene, C_6H_6. It is a resonance hybrid of the following structures (hexagonal, planar).

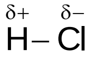


Kekule Structures **Dewar Structures**

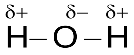
C–C bond length is 1.54 Å; C=C bond length is 1.34 Å. In benzene, all the
C–C bonds are identical in length, 1.39 Å, i.e., intermediate between those of single and double bonds. Note that shortening of bond length and therefore increased stability is an indication of the existence of resonance [Decrease in dipole moment also indicates resonance]. Resonance energy of benzene is 152 kJ/mol.

Polar Covalent Bond

.



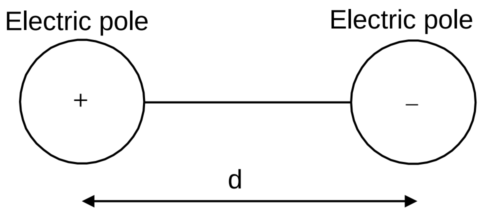
$\overset{\delta+}{H}-\overset{\delta-}{Cl}$



$\overset{\delta+}{H}-\overset{\delta-}{O}-\overset{\delta+}{H}$

Molecules like HCl, H_2O, NH_3 i.e. molecules of the type H – X having two polar ends (positive and negative) are known as polar molecules. The extent of polar character or the degree of polarity in a compound is given by it's dipole moment

which is defined as the product of the net positive or negative charge and the distance of separation of the charges i.e. the bond length. The symbol of dipole moment is μ. It is vector quantity and is defined as the product of the magnitude of charge on any of the atom and the distance between the atoms.



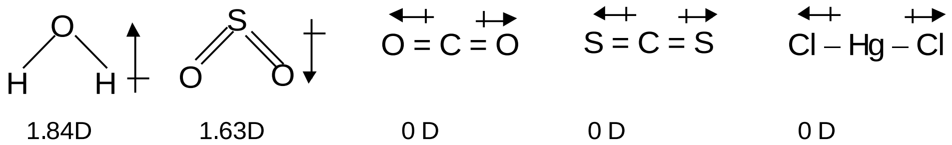
$$\mu = q \times d$$

The unit of dipole moment is Debye (D)

$$\mathbf{1D = 3.33 \times 10^{-30}\ Cm = 10^{-18} esu\ cm}$$

Dipole moment is indicated by an arrow having a symbol (+⟶) pointing towards the negative end. Dipole moment has both magnitude and direction and therefore it is a vector quantity.

Examples of Covalent compounds having diapole moment:

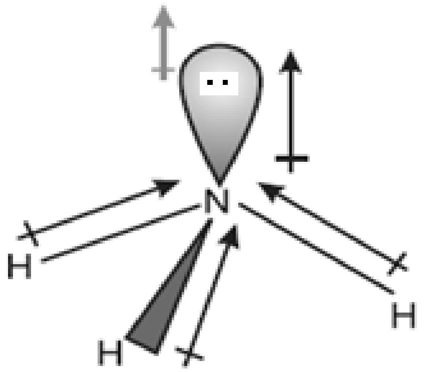


Let us study an interesting case of NH_3 and NF_3 molecule.

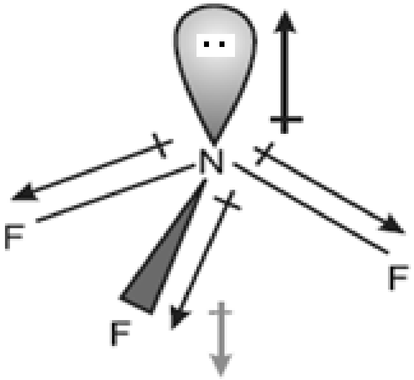
Both the molecules have pyramidal shape with a lone pair of electrons on nitrogen atom.

Although fluorine is more electronegative than nitrogen, the resultant dipole moment of NH_3(4.90 × 10^{-30} Cm) is greater than that of NF_3 (0.8 × 10^{-30} Cm).

This is because, in case of NH_3 the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N – H bonds, whereas in NF_3 the orbital dipole is in the direction opposite to the resultant dipole moment of the three N–F bonds.



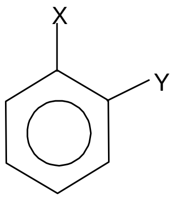
Resultant dipole moment in $NH_3 = 4.90 \times 10^{-30}$ C m



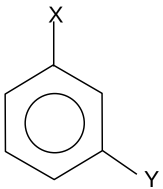
Resultant dipole moment in $NF_3 = 0.80 \times 10^{-30}$ C m

The dipole moments of the aromatic compounds present a very good illustration of dipole moment.

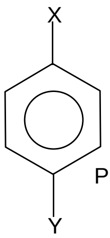
Suppose we have three isomers of o-nitrophenol, m-nitrophenol and p-nitrophenol. We have also the e.g. o-aminophenol, m-aminophenol and p-aminophenol.



Ortho



Meta



Para

$$\mu_{ortho} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 60^\circ}$$

$$\mu_{meta} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 120^\circ}$$

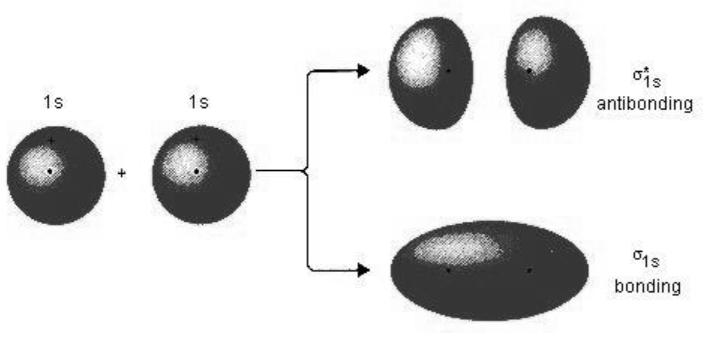
$$\mu_{para} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 180^\circ}$$

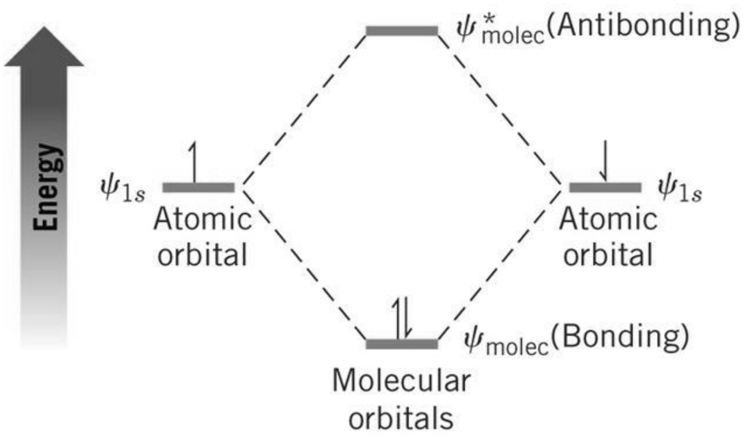
Percentage Ionic Character

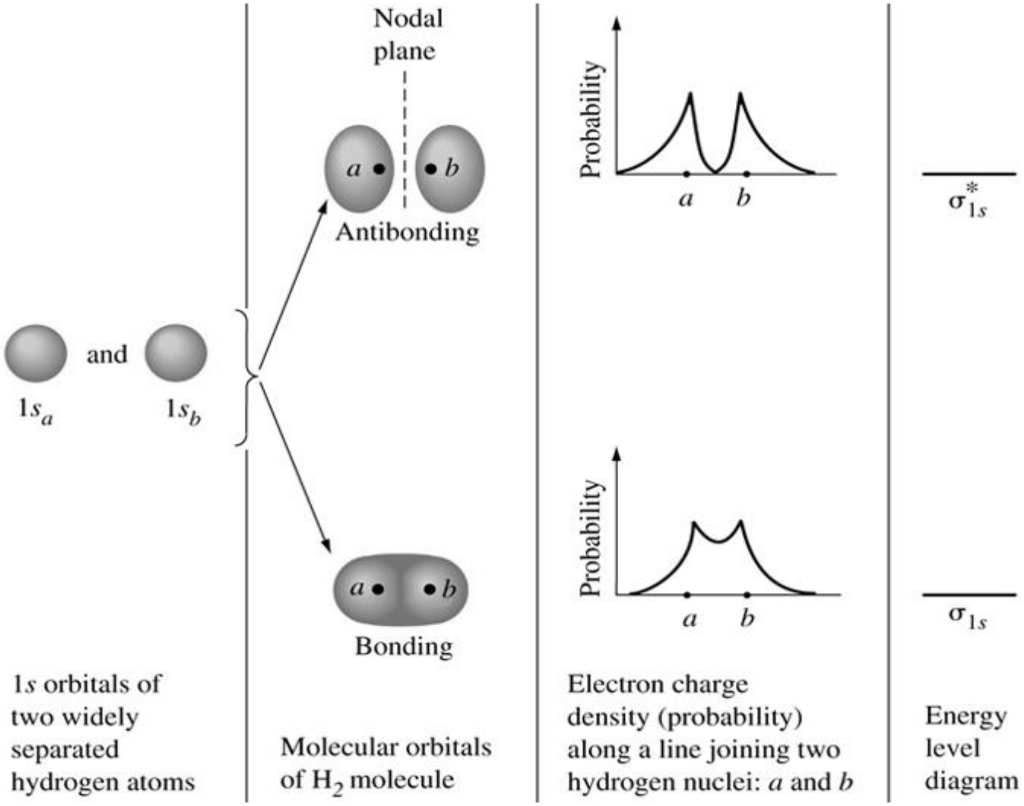
The measured dipole moment of a substance may be used to calculate the percentage ionic character of a covalent bond in simple molecules.

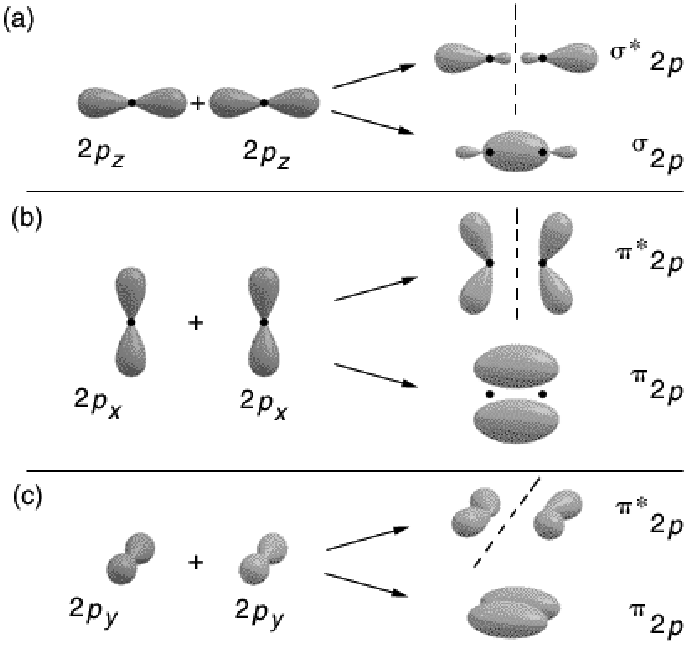
$$\text{Percent ionic character} = \frac{\text{Observed dipole moment}}{\text{Calculated dipole moment assuming 100\% ionic bond}} \times 100$$

14.MOLECULAR ORBITAL THEORY



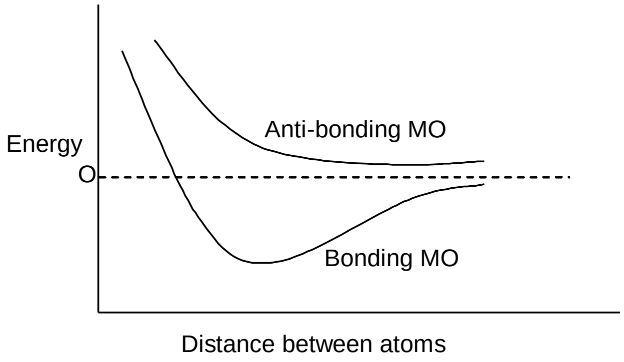

Energy
ψ^*_{molec}(Antibonding)
ψ_{1s}
Atomic orbital
ψ_{1s}
Atomic orbital
ψ_{molec}(Bonding)
Molecular orbitals


Nodal plane
a
b
Antibonding
and
$1s_a$
$1s_b$
a
b
Bonding
Probability
a
b
Probability
a
b
σ^*_{1s}
σ_{1s}
1s orbitals of two widely separated hydrogen atoms
Molecular orbitals of H_2 molecule
Electron charge density (probability) along a line joining two hydrogen nuclei: a and b
Energy level diagram



The number of molecular orbitals produced must always be equal to the number of atomic orbitals involved. Electron density is increased for the bonding MO's in the inter-nuclear region but decreased for the anti-bonding MO's, Shielding of the nuclei by increased electron density in bonding MO's reduces inter nuclei repulsion and thus stabilizes the molecule whereas lower electron

density even as compared to the individual atom in anti-bonding MO's increases the repulsion and destabilizes the system.



In denotion of MO's,σ indicates head on overlap and π represents side ways overlap of orbitals. In simple homo-nuclear diatomic molecules the order of MO's based on increasing energy is

$$\sigma_{1s}\sigma^{*}_{1s}\sigma_{2s}\sigma^{*}_{2s}\sigma_{2p_x}\begin{Bmatrix}\pi_{2p_y}\\ \pi_{2p_z}\end{Bmatrix}\begin{Bmatrix}\pi^{*}_{2p_y}\\ \pi^{*}_{2p_z}\end{Bmatrix}\sigma^{*}_{2p_x}$$

This order is true except B_2, C_2& N_2. For them $\pi 2p_y$ and $\pi 2p_z$ are probably lower than $\sigma 2p_x$.

(DUE TO SP MIXING)

Bond order = $\frac{\text{no. of } e^{-}\text{s occupying bonding MO's} - \text{no. of } e^{-}\text{s occupying anti-bonding MO's}}{2}$

MO Electronic Configuration of Some Molecules

Molecule or ion	Total no. of electrons	MO configuration	Bond order	Magnetic behaviour
H_2	2	$(\sigma\,1s)^2$	1	Diamagnetic
H_2^+	1	$(\sigma\,1s)^1$	0.5	Paramagnetic
H_2^-	3	$(\sigma\,1s)^2, (\sigma^*1s)^1$	0.5	Paramagnetic
He_2	4	$(\sigma\,1s)^2, (\sigma^*1s)^2$	0	Diamagnetic
N_2	14	$KK(\sigma\,2s)^2\,(\sigma^*2s)^2\,(\sigma\,2p_x)^2\,(\pi\,2p_y)^2\,(\pi\,2p_z)^2$	3	Diamagnetic
O_2	16	$KK(\sigma\,2s)^2(\sigma^*2s)^2(\sigma\,2p_x)^2\,(\pi\,2p_y)^2(\pi\,2p_z)^2\;(\pi^*2p_y)^1(\pi^*2p_z)^1$	2	Paramagnetic
O_2^+	15	Remove one electron from π^*2p_z from O_2	2.5	Paramagnetic
O_2^{2+}	14	Same as that of N_2	3	Diamagnetic
O_2^-	17	$KK(\sigma\,2s)^2\,(\sigma^*2s)^2(\sigma\,2p_x)^2(\pi\,2p_y)^2(\pi\,2p_z)^2(\pi^*2p_y)^2(\pi^*2p_z)^1$	1.5	Paramagnetic
O_2^{2-}	18	$KK(\sigma\,2s)^2\,(\sigma^*2s)^2(\sigma\,2p_x)^2\;(\pi\,2p_y)^2(\pi\,2p_z)^2(\pi^*2p_y)^2(\pi^*2p_z)^2$	1	Diamagnetic
F_2	18	Same as above	1	Diamagnetic
Ne_2	20	18 as above and $(\sigma^*2p_x)^2$	0	Diamagnetic
CO	14	Same as in N_2	3	Diamagnetic
NO	15	Same as in O_2^+	2.5	Paramagnetic
NO^+	14	Same as in N_2	3	Diamagnetic
NO^{2+}	13	$K(\sigma\,2s)^2(\sigma^*2s)^2(\sigma\,2p_x)^2(\pi\,(2p_y)^2(\pi\,2p_z)^1$	2.5	Paramagnetic
NO^-	16	Same as in O_2	2	Paramagnetic
CN	13	Same as in NO^{2+}	2.5	Paramagnetic
CN^-	14	Same as in N_2	3	Diamagnetic

SP MIXING : Intermixing of orbital

The 2*s* and 2*p* energy levels of O and F are very far apart. The combination of the 2*s* orbitals from the two atoms form a sigma bonding and sigma antibonding orbitals in a way very similar to the case of the hydrogen molecules, because the 2*p* orbitals have little to do with the 2*s* orbitals.

On the other hand, the three 2*p* orbitals of each O (or F) atom can form one sigma and two pi bonds and their corresponding antibonding molecular orbitals. The interaction of the 2*p* orbitals for the sigma bond is stronger, and the levels of sigma and anti sigma bonds are farther apart than those of pi and anti pi bonds.

Atomic energy levels E in kJ mol^{-1}
of second group elements

Element	E_{2s}	E_{2p}	$E_{2p}-E_{2s}$
Li	-521		
Be	-897		

B	-1350	-801	549
C	-1871	-1022	849
N	-2470	-1274	1196
O	-3116	-1524	1592
F	-3879	-1795	2084
Ne	-4680	-2084	2596

Recently, the study of the energies of electrons in molecules revealed that the relative energy levels of molecular orbitals of Li_2 to N_2 are different from those of O_2 and F_2. The explanation for the difference comes from the consideration of hybrid atomic orbitals. Because the 2*s* energy levels and 2*p* energy levels for Li to N are relatively close, the 2*s* orbitals are influenced by the 2*p* orbitals. This influence makes the bonding orbitals stronger than, and the antibonding orbitals weaker than those formed by pure 2*s* orbitals. This process is called ***s p* mixing**

Due to *s p* mixing, the σ_{2p} orbital is weakened, and the $\sigma^*_{2p}$is also affected. These effects cause the relative order to change.

HYDROGEN BOND

$$A^{\delta-} \text{———} H^{\delta+} \cdots\cdots\cdots : B$$

Generally hydrogen bond is formed with only F, O and N atoms. Sometimes less electronegative atoms such as Cl, S etc., also take part in the formation of hydrogen bond. Hydrogen bond is denoted by dotted lines (...........). It can be defined as :

The attractive force that binds a hydrogen atom, which is already covalently attached with strongly electronegative atom of gain element is known as hydrogen bond. The bond energy of hydrogen bond is 3--10 kcal/mole.

Types of Hydrogen Bonding

Three types of hydrogen bonding exist :

(i) Intermolecular hydrogen bonding
(ii) Intramolecular hydrogen bonding
(iii) π-Hydrogen bonding

(i) Intermolecular hydrogen bonding

(a) Homo-intermolecular hydrogen bonding.

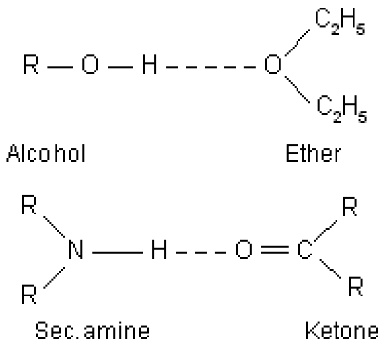
molecules e.g., association in alcohol, association in water.

It is also termed as self-association.

It refers to the association of two or more identical in NH_3, association in HF etc.

(b) Hetero-intermolecular hydrogen bonding.

It refers to the association of two different species.

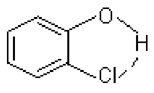


results in the increase in melting point and boiling point of the compound.

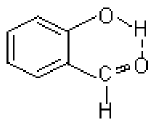
(iii) Intramolecular hydrogen bonding.

hydrogen bonding two groups of the same molecule link through hydrogen bond, forming a stable five or six membered ring structure

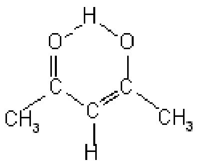
e.g., salicylaldehyde, o-chlorophenol, acetylacetone, ethylacetoacetate etc.



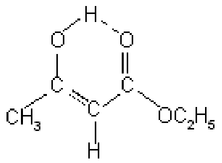
O – Chlorophenol



Salicylaldehyde

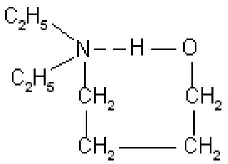


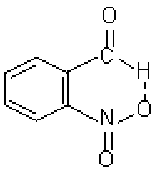
Acetylacetone

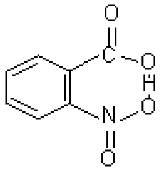


Ethyl acetoacetate

This intramolecular hydrogen bonding was first called chelation (after the Greek word "Chela" meaning, claw)

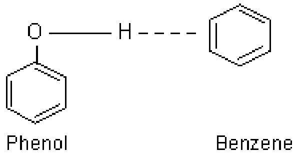

Amino alcohol

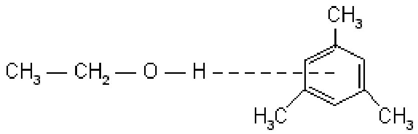

o - Nitrobenzaldehyde


o - Nitrobenzoic acid

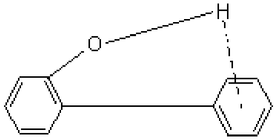
(iii) π-Hydrogen bonding.

(a) **Intermolecular π-hydrogen bonding.** It occurs between two or more molecules of the same or different compounds. For example,

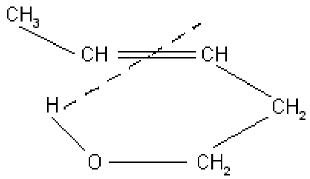




(b) **Intramolecular π-hydrogen bonding.**



o – Phenylphenol



3 – Penten – 1 – ol

Properties of Hydrogen Bond

Bond energy of hydrogen bond is in the range of 3-10 kcal/mole. Thus hydrogen bond is a weaker bond than a covalent bond (bond energy of a covalent bond is 50-100 kcal/mole).

But it is stronger than Van der Waal's forces (1 kcal/mol).

In the formation of hydrogen bond electron pair is not shared. In this respect it is different from the covalent bond.

Effect of Hydrogen Bonding on Physical Properties of the Molecules

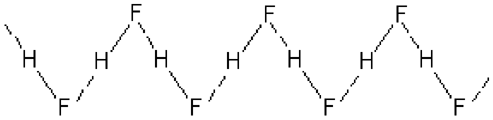
(1) Physical States

i) **H_2O and H_2S.**

Oxygen is more electronegative than sulphur. There is a considerable hydrogen bonding in H_2O while in H_2S the same is absent.

H_2O exists as liquid.

(ii) **HF and HCl.** In HF, molecules are associated through hydrogen bonding and it is a liquid at ordinary temperature.



Hydrogen fluoride

In HCl, due to less electronegativity of chlorine atom and its large size, hydrogen bond does not exist hence molecules of HCl are not associated as in HF. Therefore, HCl is a gas at ordinary temperature.

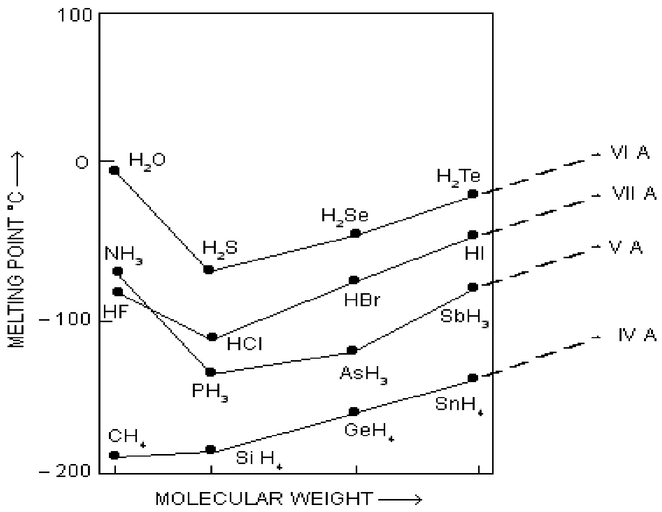
Bp. HF>HI>HBr>HCl

(2) Melting Points and Boiling Points

(i) M.P. and B.P. of Hydrides of Oxygen, Fluorine and Nitrogen

The melting point and boiling point of CH_4, SiH_4, GeH_4, and SnH_4 decrease with decreasing molecular weights.

But in case of VA, VIA and VIIA groups the melting point and boiling point of H_2O, NH_3 and HF are exceptionally high than the hydrides of other members of their groups.



(a)

(a) Melting point curves of hydrides of IV, V, VI and VII group elements.

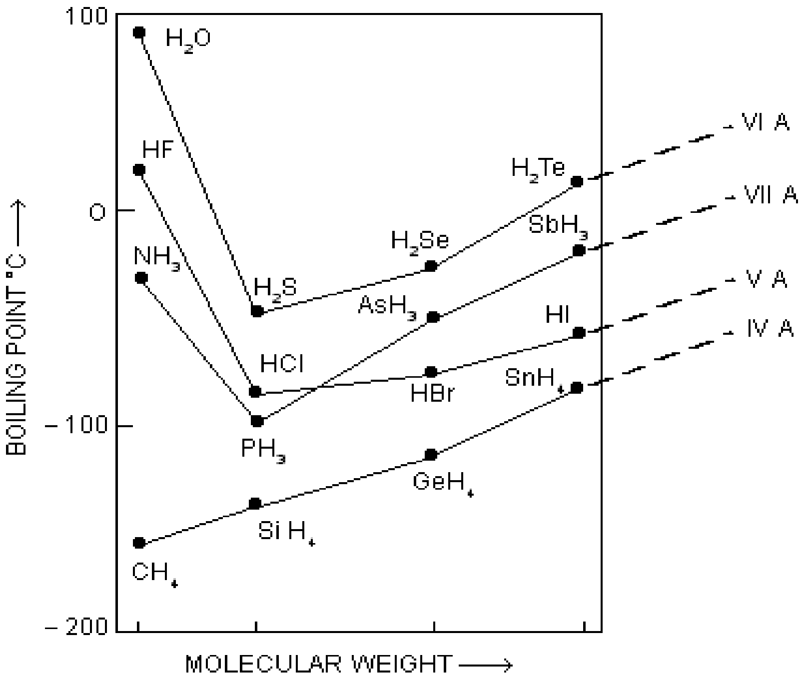
The melting point and boiling point of the hydrides of the elements of IVA, VA, VIA and VIIA groups can be represented as below :

IVA $CH_4 < SiH_4 < GeH_4 <$ SnH4

VA $NH_3 > PH_3 < AsH_3 < SbH_3$

VIA $H_2O > H_2S < H_2Se < H_2Te$

VIIA $HF > HCl < HBr < HI$

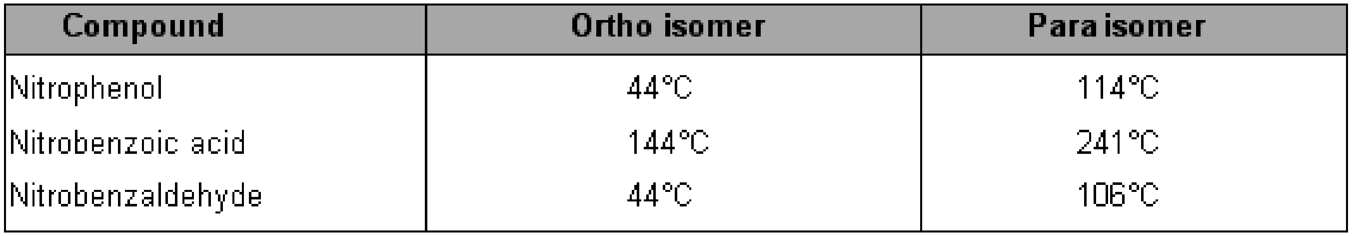


(b)

(b) Boiling Point curves of hydrides of IV, V VI and VII group elements.

(ii) Melting point of ortho- nitrophenol and para- nitrophenol

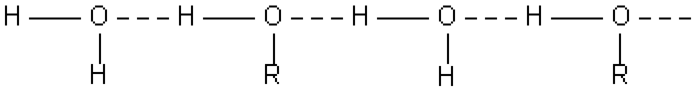
Intramolecular hydrogen bonds do not involve molecular association



Compound	Ortho isomer	Para isomer
Nitrophenol	44°C	114°C
Nitrobenzoic acid	144°C	241°C
Nitrobenzaldehyde	44°C	106°C

(3) Solubility. Alcohols, glycol, glycerol and sugars are soluble in water due to the formation of hydrogen bond with water molecules.

Dimethylether, $(CH_3)_2O$, is miscible in water as it can form hydrogen bond with water molecule but dimethyl sulphide, $(CH_3)_2S$, is immiscible as it cannot form hydrogen bond with water molecules since the electronegativity of sulphur is less.



$$H-\underset{H}{\underset{|}{O}}---H-\underset{R}{\underset{|}{O}}---H-\underset{H}{\underset{|}{O}}---H-\underset{R}{\underset{|}{O}}---$$

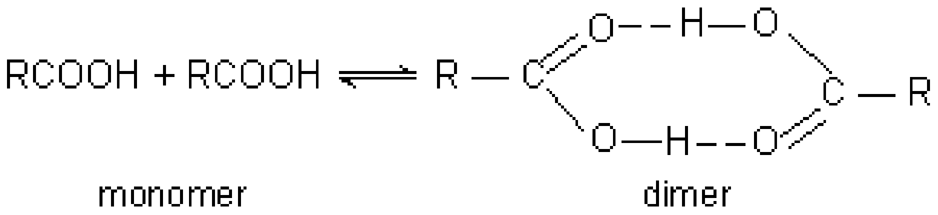
(4) Viscosity.

Viscosity increases with the extent of hydrogen bonding in molecules. The viscosity of water is 10.05 millipoise, methanol 6 millipoise and dimethyl ether 2.3 millipoise.

Since both H_2O and CH_3OH are hydrogen bonded the viscosities are high, but when there is substitution of second methyl group to produce the non-hydrogen-bonded dimethyl-ether, $(CH_3)_2O$, the viscosity drops to a low value. Polyhydroxy alcohols such as ethylene glycol, $CH_2OH.CH_2OH$ and glycerol, $CH_2OH.CHOH.CH_2OH$ which have extensive hydrogen bonding exhibit much higher viscosities.

(5) Molecular weights.

The association of two or more molecules by intermolecular hydrogen bonding affect the apparent molecular weight. In case of carboxylic acids (RCOOH) it is observed that the apparent molecular weights are

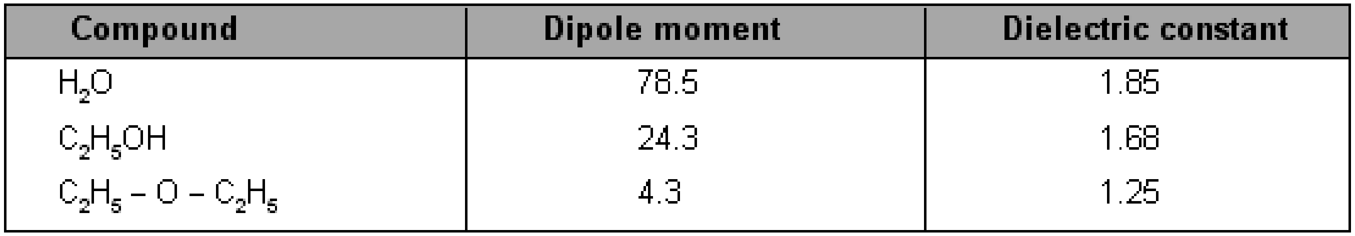


higher than the formula weights. The apparent molecular weight decreases with increasing temperature due to dissociation of dimer into monomer.

A monomer-dimer hydrogen-bonded equilibrium is the simplest explanation of these results. Increase in temperature increases the average kinetic energy of the molecules, breaking more hydrogen bonds and shifting the equilibrium to left.

(6) Dielectric constants and Dipole moments

The formation of hydrogen-bond, A -- H...B leads to an increased polarity of the bond A -- H, and hence, to a larger dielectric constant and greater dipole moment.



Compound	Dipole moment	Dielectric constant
H_2O	78.5	1.85
C_2H_5OH	24.3	1.68
$C_2H_5 - O - C_2H_5$	4.3	1.25

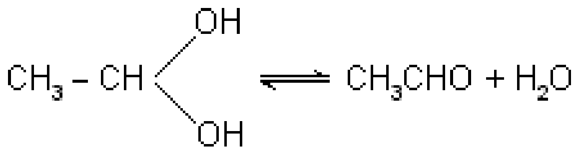
(7) Low density of ice than water

In the crystal structure of ice the oxygen atom of water is surrounded by four hydrogen atoms, two attached with covalent bonds and two with hydrogen bonds. Thus in ice every water molecule is associated with four other water molecules in tetrahedral pattern. Ice has an open structure with large empty space due to existence of hydrogen-bonds. When ice melts a number of hydrogen bonds are broken and the space between water molecules decreases and the density of water increases, therefore from 0° to 4°C, it is maximum. Above 4°C the increase in kinetic energy of the molecules disperse them and the result is that the density now decreases with increasing temperature.

(8) Stability of unusual structures

Generally, the organic compounds with two -- OH groups on the same carbon atom are unstable and soon liberate water molecule.

For example :



$$CH_3-CH(OH)_2 \rightleftharpoons CH_3CHO + H_2O$$

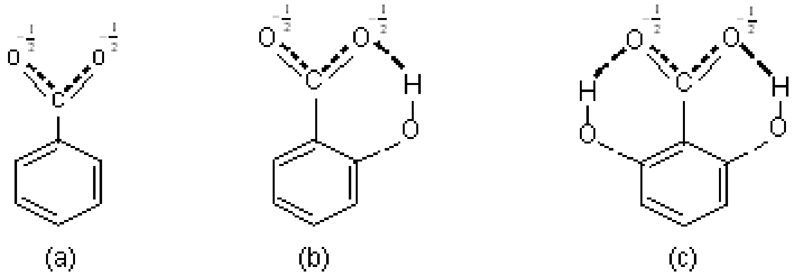
The stability of compounds like chloral hydrate, CCl_3 -- $CH(OH)_2$ can be explained on the basis of intramolecular hydrogen-bonding.

(9) Chain, Sheet and Three dimensional structures

Hydrogen bonding leads to the formation of chains (HCN, HF, HCOOH), sheet (orthoboric acid, oxyde acid) and three dimensional network (water, KH_2PO_4) structures.

(10) Dissociation constants of carboxylic acids

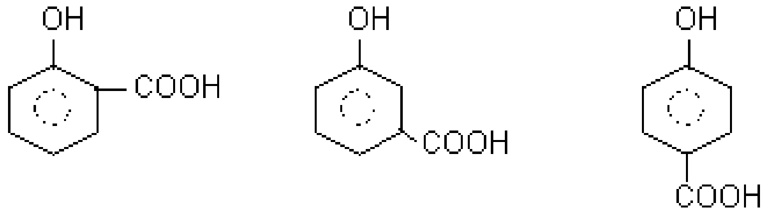
The dissociation constant of an acid depends on the stability of its ion. If the stability of anion of an acid is increased due to intramolecular hydrogen-bonding, the acid strength is greatly enhanced i.e., pKa value decreases. The carboxylate ion of o-hydroxy benzoic acid is stabilized by intermolecular hydrogen-bonding, thus o-salicylic acid is more stronger (pKa = 2.89) than benzoic acid (pKa = 4.17).



Carboxylate ions of (a) benzoic acid, (b) o-hydroxybenzoic acid, (c) 2,6-dihydroxybenzoic acid.

It can be seen that two hydrogen-bonds would be expected to bring more stabilization than one hydrogen bond, and 2,6-dihydroxy benzoic acid is much more stronger (pKa = 2.30) than o-salicylic acid.

Similarly, o-salicylic acid (pKa = 2.98) is much stronger due to intramolecular hydrogen bonding than its meta (pKa = 4.08) and para (pKa = 4.58) isomers.

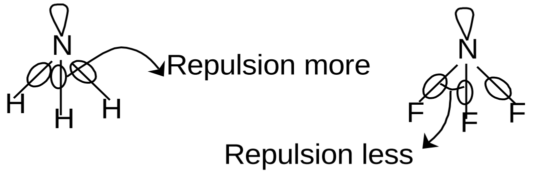


ortho meta para

Salicylic acid

Problem 1:The bond angle of NF_3 is less than that of NH_3. Explain.

Solution: Both NH_3 and NF_3 have a lone pair of electrons. But fluorine being highly electronegative, the bond pair electrons are drawn more towards F in NF_3, whereas in NH_3 it is drawn towards N. So in NF_3 the bond pairs being displaced away from the central atom has very little tendency to open up the angle. But in NH_3 this opening up is more as the bond pair electrons are closer to each other. So bond angle of NF_3 is less than NH_3.



Problem 2:Why is that Lithium salts have a greater degree of covalent character than other halides of the group?

Solution: The small size of Li^+ gives it a large polarising power, hence covalent nature of its compound increases. It can be viewed in terms of Fajan's rule

☞ Smaller the cation

☞ Larger the anion

☞ Greater the charge density as the surface causes greater polarising power of Li^+

Hence, greater the covalent nature.

Problem3:The solubility of the hydroxides of the alkaline earth metals increases i.e. Ba(OH)$_2$ has got a higher solubility in water compared to Mg(OH)$_2$-. Why?

Solution: Here both the cations Ba^{2+} and Mg^{2+} have the same charge, but as the radius of Ba^{2+} is more therefore ϕ of Ba^{2+} is less which implies that $Ba(OH)_2$ having higher degree of ionic character is more soluble in polar solvents like water.

But now if I ask to predict the solubility of $MgSO_4$& $BaSO_4$. The answer seems to be quite similar to the earlier one and $BaSO_4$ turns out to be the one having higher solubility. But contrary to our expectation the trend is reversed here. $BaSO_4$ is sparingly soluble in water. The question comes why? In case of hydroxide it is something. In case of sulfate it’s the other way around. Is there any way by which we can a predict the solubility trend? The answer is yes.

When a lattice is dissolved in water, the ions became solvated and the solvated ions are more stable than a free ion and due to this stability energy is released. This energy released is called solvation energy and if this overcomes the lattice energy then it is soluble. The lattice energy of NaCl is 778 kJ mol^{-1} and the heats of hydration of Na^+ and Cl^- is –787 kJ mol^{-1}. As it is more than the lattice energy of NaCl therefore it is soluble.

Now we should focus our attention to the solubility trend in a given series. For a comparison of the solubility both the lattice energy and hydration energy factors have to be taken into account. If in a series the decrease of lattice energy is more compared to the decrease in hydration energy then the substance becomes soluble.

Now the hydration enthalpy of a salt is given by

$$\Delta H_{hydration} = \frac{k_1}{r_+} + \frac{k_2}{r_-}$$

where k_1 and k_2 are constants

& lattice energy $U = \frac{k_3}{r_+ + r_-}$ k_3 = constant

Case (i): When $r_+ << r_-$ the contribution of the anion to the hydration enthalpy is small so the total $\Delta H_{hydration}$ would be dominated by the cation alone. In a series of salts of a large anion, the hydrational enthalpy will decrease in magnitude with increasing cation size. Now how does the lattice energy respond to this changing cation radius? The lattice energy is inversely proportional to $(r_+ + r_-)$. Since $r_- >> r_+$, the sum will not change significantly as r_+ increases. Consequently the lattice energy will not decrease as fast as the hydration energy with increasing cationic size. The more quickly diminishing hydration energy results in a decrease in solubility.

E.g. Solubility of LiI>NaI> KI…

$MgSO_4 > CaSO_4 > SrSo_4 > BaSO_4$

Case (ii): $r_+ \approx r_-$

Here the lattice energy decreases with increasing cationic size more rapidly than the hydration energy which therefore results in an enhanced solubility in a series.

E.g. Solubility of $LiF < NaF < KF$

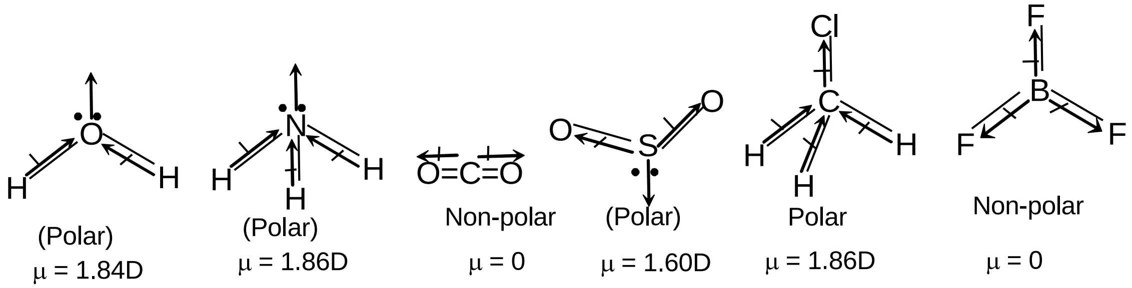
$Mg(OH)_2 < Ca(OH)_2 < Ba(OH)_2$

Problem 4:The melting point of NaCl is higher than that of AgCl. Explain

Solution: Now whenever any comparison is asked about the melting point of the compounds which are fully ionic from the electron transfer concept it means that the compound having lower melting point has got lesser amount of ionic character than the other one. To analyse such a question first find out the difference between the 2 given compounds. Here in both the compounds the anion is the same. So the deciding factor would be the cation. Now if the anion is different, then the answer should be from the variation of the anion. Now in the above example, the difference of the cation is their electronic configuration. Na^+ = [Ne]; Ag^+ = [Kr] $4d^{10}$. This is now a comparison between a noble gas core and pseudo noble gas core, the analysis of which we have already done. So try to finish off this answer.

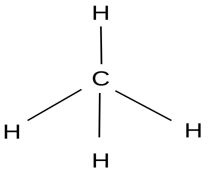
Problem 5:Which of the following molecules are polar: H_2O, NH_3,CO_2,SO_2,$CHCl_3$,BF_3?

Solution:

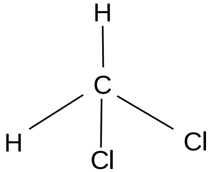


Problem 6: ***CH_4 has zero dipole moment but CH_2Cl_2 has an appreciable dipole moment. Why?***

Solution: Both CH_4 & CH_2Cl_2 have tetrahedral structure but CH_4 is symmetrical while CH_2Cl_2 is unsymmetrical.



Symmetrical

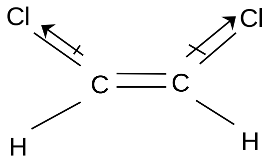


Unsymmetrical

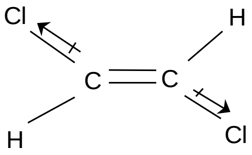
Due to the symmetrical structure of CCl_4 the resultant of bond dipoles comes out to be zero. But in case of CH_2Cl_2 it is not possible as the presence of hydrogen introduces some dissymmetry.

Problem 7:Compare the dipole moment of Cis 1,2dichloroethylene and trans 1,2 dichloroethylene.

Solution :



Cis



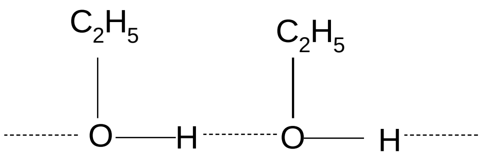
Trans

In the trans compound the C-Cl bond dipoles are equal and at the same time acting in opposition cancel each other while Cis compound the dipoles do not cancel each other resulting in a higher value.

Generally all trans compounds have a lower dipole moment compared to the corresponding cis isomers, when both the substituents attached to carbon atom are either electron releasing or electron withdrawing.

Problem 8: Explain why ethyl alcohol (C_2H_5OH) has got a higher boiling point than dimethyl ether (CH_3-O-CH_3) although the molecular weight of both are same?

Solution: Though ethyl alcohol and dimethyl ether have the same molecular weight but in ethyl alcohol the hydrogen of the O-H groups forms intermolecular hydrogen bonding with the OH group in another molecule. But in case of ether the hydrogen is linked to C is not so electronegative to encourage the hydrogen to from hydrogen bonding.

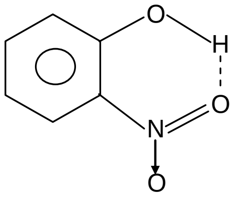


$$\cdots\cdots\overset{C_2H_5}{\overset{|}{O}}-H\cdots\cdots\overset{C_2H_5}{\overset{|}{O}}-H\cdots\cdots$$

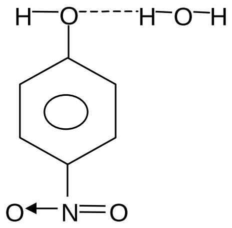
Due to intermolecular H-bonding, ethyl alcohol remains in the associated form and therefore boils at a higher temperature compared to dimethyl ether.

Problem 9: Explain why O-nitrophenol is more volatile than p-nitrophenol?

Solution: More volatility means it has got lower boiling point. Now p-nitrophenol remains associated through intermolecular hydrogen bonding. But in o-nitrophenol only intramolecular H- bonding formation takes places, as a result of which there is no association. So p-nitrophenol which remains as an associated species has got higher boiling point and so less volatile.



o-Isomer



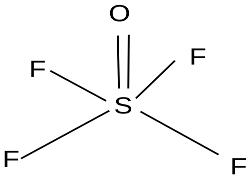
p-isomer

Problem 10: ***Draw the structure of the following***

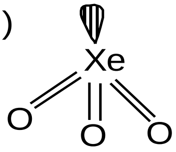
(i) SOF_4 ***(ii) XeO_3*** ***(iii) $POCl_3$***

Solution:

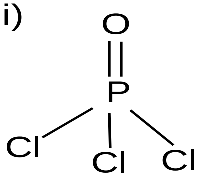
i)



ii)

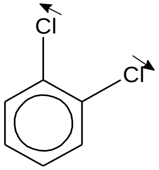


iii)



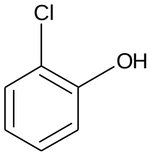
Problem 11: ***In o-dichlorobenzene the observed value of dipole moment is 6.00 D while it theoretical value is 6.30 D why?***

Solution: o-dichlorobenzene due to dipole-dipole repulsion bond angle increase. Therefore dipole moment decreases.

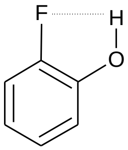


Problem 12: ***Dipole moment of o-chlorphenol is less than o-fluoro-phenol. Explain***

Solution:



no H-bonding



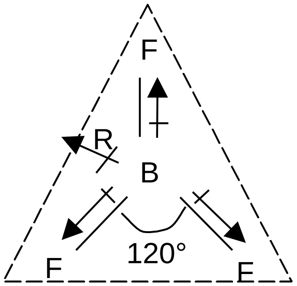
Due to H-bonding on o-fluorophenol bond angle decrease (< 60°) hence dipole moment is increased.

Problem 13: ***$BiCl_5$ does not exist. Explain***

Solution: Due to inert pair effect, stability of $Bi^{3+} > Sb^{3+} > As^{3+}$ and $Bi^{5+} < Sb^{5+} < As^{5+}$

Hence Bi^{5+} salts are least stable; so $BiCl_5$ does not exist.

Problem 14: Dipole moment of BF_3 is zero. Explain



Solution: BF_3 is a planar molecule with the bond angles being 120°. In each B-F bond the bond dipole is projected towards Fluorine. Now the direction of the resultant bond dipoles of these two bonds is shown in the diagram as R. If R is equal to the dipole of the 3rd B-F bond then R and B-F dipole will neutralize each other as equal dipoles acting in opposite direction cancel each other. Now let’s see the magnitude of R. As dipole moment is a vector quantity, so the resultant of two dipoles can be obtained from the law of vector addition. Suppose the bond dipole is μ_1.

$R = \sqrt{a^2 + b^2 + 2ab\cos\theta}$ a & b are the individual vectors

$= \sqrt{\mu_1^2 + \mu_1^2 + 2\mu_1\mu_1 \cos 120^\circ}$ θ = angle between vectors

$= \sqrt{2\mu_1^2 + 2\mu_1^2\left(-\frac{1}{2}\right)}$ $\cos 120^\circ = \left(-\frac{1}{2}\right)$

$= \sqrt{2\mu_1^2 - \mu_1^2} = \mu_1 = \mu_{B\text{–}F}$

$\therefore$ R is equal in magnitude to B-F bond dipole. Similar is the case with the other two resultants. So the net dipole of BF_3 is zero.

Problem 15: ***Carbon has a co-ordination number of four while other elements of this group have co-ordination number of six. Why?***

Solution: The normal valency of the elements is four, but apart from carbon, the elements can make more than four bonds. This because they make use of a set of d-orbitals in bonding. The availability of d-orbitals empty but electrons of ns^2 and np^2 can be excited into this is responsible for the ability of the elements, except carbon, to make complex ions such as SiF_6^{2-}

Example16: KHF_2 exists but $KHCl_2$ does not explain

Solution: Due to inability of H – Cl to from H – bond with Cl^- , the formation of HCl_2^- is not possible. On the other hand , H – F can easily form H – bond with F^- resulting in the formation of HF_2^- .

Example17: ClF_3 exists but FCl_3 does not. Explain

Solution: Chlorine can expand its octet due to the presence of vacant d – orbitals which are not available in fluorine.

Example18: $N(CH_3)_3$ is pyramidal whereas $N(SiH)_3$ is planar. Explain

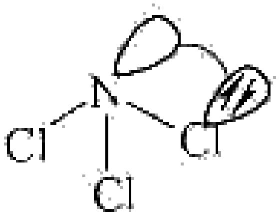
Solution: Lone pair of electron is localized on nitrogen in $N(CH_3)_3$ lone pair delocalised in vacant d – orbitals of silicon.

Example19: Water has maximum density at 4°C. Explain:

Solution: At 0° there is sufficient H – bonding in water molecules and thus open cage – like structure exists which has larger volume and makes the density low. On heating, to increases in density. This is the case up to 4°C . After this, the increase in volume due to expansion of the liquid water dominates over the decrease in volume due to cleavage of H – bonds.

Example20: Among NCl_3 and NF_3 which will have higher bond angle and why?

Solution: NCl_3 will have higher bond angle than NF_3. this due to the $p_\pi - d_\pi$ back bonding between filled p orbital of N and vacant d orbital of Cl atoms in NCl_3 which is not possible in NF_3 due to in availability of d – orbitals in N atoms.



BOOST YOUR LEARNING

Problem 1 Which of the following will provide the most efficient overlap?

(A)s – s   (B)s – p   (C)$sp^2 – sp^2$ (D)sp – sp

Solution: Overlapping between hybrid orbitals will be more efficient than that between the pure orbitals.

∴ **(C)**

Problem 2: In which of the following molecules the Vander Waal's forces is likely to be most important in determining the melting and boiling point?

(A)CO   (B)H_2S (C)Br_2 (D)HCl

Solution: Br_2 is non-polar molecules and hence its melting and boiling points depend only on Vander Waal's forces while all other molecules are having dipole moments hence their melting and boiling points depends upon dipole-dipole interactions.

∴ **(C)**

Problem 3: Which of the following has highest viscosity?

(A)Glycerol (B)Glycol (C)Ethanol (D)Water

Solution: Due to 3 O–H groups, glycerol shows extensive intramolecular H-bonding and hence it has highviscosity.

$\therefore$ **(A)**

Problem 4: Hybridisation of C atom is same in $C_{12}H_{22}$ as that of C in

(A)C_2H_6 (B)CO_2 ` (C)Benzene (D)C (diamond)

Solution: **(B)**

Problem 5: Indicate the type of bond angles present in IF_5

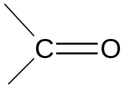
(A) 90° (B) 90°,120° (C) 90°, 180° (D) 90°, 120°, 180°

Solution: Iodine undergoes sp^3d^2hybridisation with 5 bond pairs and one lone pair having square pyramidal structure. $\therefore$**(C)**

Problem 6:The compound in which all carbon atoms make use of sp^3 hybrid orbitals for bond formation is

(A)HCOOH (B)$(H_2N)_2CO$ (C)$(CH_3)_3COH$

(D)CH_3CHO

Solution: (A), (B), (D) contains  group where carbon is sp^2hybridised

$\therefore$ **(C)**

Problem 7: The correct increasing bond angle among BF_3, PF_3 and ClF_3 follow the order

(A)$BF_3 < PF_3 < ClF_3$ ***(B)$PF_3 < BF_3 < ClF_3$***

(C)$ClF_3 < PF_3 < BF_3$ ***(D)All have equal bond angle***

Solution: In BF_3, B is sp^2hybridised with bond angle 120°C. In PF_3, P is sp^3hybridised but bond angle is less than 109°28 due to lone pair bond pair repulsion. In ClF_3, Cl is sp^3d hybridised having T-shape with bond angle 90°C.

$\therefore$ **(C)**

Problem 8: The molecular size of ICl and Br_2 is approximately same, but boiling point of ICl is about 40° higher than that of Br_2. It is because

(A) ICl bond is stronger than Br – Br bond

(B) I.E. of I $<$ I.E. of Br

(C) ICl is polar while Br_2 is non-polar

(D) I has larger size than Br

Solution: Polar molecule also have dipole-dipole interactions which increase the boiling point

$\therefore$ **(C)**

Problem 9: Which of the following has highest percentage of ionic character?

(A)HF (B)HCl (C)HBr (D)HI

Solution: The electronegativity difference in HF is highest and hence HF has high percentage of ionic character.

$\therefore$ **(A)**

Problem 10:** **The interatomic distances in H_2 and Cl_2 are 74 pm and 198 pm respectively. The bond length of HCl is

(A) 272 pm (B) 136 pm (C) 124 pm (D) 248 pm

Solution: $r_H = \frac{74}{2} = 37$ pm

$r_{Cl} = \frac{198}{2} = 99$ pm Bond length of HCl = $r_H + r_{Cl} = 136$ pm ∴ **(B)**

Problem 11: The bond energies in NO, NO^+ and NO^- follow the order

(A)$NO^+ > NO > NO^-$ (B)$NO > NO^+ > NO^-$

(C)$NO^- > NO > NO^+$ (D)$NO^+ > NO^- > NO$

Solution: Bond order NO = $\frac{1}{2}$ (10 – 5) = 2.5

Bond order in NO^+ = $\frac{1}{2}$ (10 – 4) = 3.0 Bond order in NO^- = $\frac{1}{2}$ (10 – 6) = 2.0

Since bond energies are directly related to bond order.

Therefore correct order of increasing bond energies is $NO^+ > NO > NO^-$

$\therefore$ **(A)**

Problem 12: The molecule which has zero dipole moment is

(A)CH_2Cl_2 (B)BF_3 (C)NF_3 (D)ClO_2

Solution: BF_3 is trigonal planar and hence has zero dipole moment.

$\therefore$**(B)**

Problem 13: ***H_2O has higher boiling point than H_2S because***

(A) H_2S is a smaller molecule and hence more closely packed

(B) the bond angle of H_2O is more than H_2S and hence H_2O molecule are more tightly packed

(C) the intermolecular hydrogen bonding in liquid H_2O

(D) the latent heat of vapourisation is higher for H_2O than for H_2S.

Solution: **(C)**

Problem 14: ***Among the following species, identify the isostructural pairs***

NF_3, NO_3^-, BF_3, H_3O^+, HN_3

(A) [NF_3, NO_3^-] and [BF_3, H_3^+O] (B) [NF_3, HN_3], [NO_3^-, BF_3]

(C) [NF_3, H_3^+O] and [NO_3^-, BF_3] (D) [NF_3, H_3^+O] and [HN_3, BF_3]

Solution: [NF_3 and H_3^+O] are pyramidal while [NO_3^- and BF_3] are trigonal planar

$\therefore$ **(C)**

Problem 15: ***Among the following compounds, the one that is polar and has central atom with sp^2 hybridisation is***

(A) H_2CO_3 ***(B) SiF_4*** ***(C) BF_3*** ***(D) $HClO_2$***

Solution: H_2CO_3 and BF_3 have sp^2 hybridisation while SiF_4 and $HClO_2$ have sp^3 hybridisation. But in BF_3 it is symmetrical so dipole moment is zero while in H_2CO_3 resultant dipole is not zero so it is also polar.

$\therefore$ **(A)**

Problem 16: ***N_2 and O_2 are converted into monocations, N_2^+ and O_2^+ respectively. Which of the following is wrong***

(A) In N_2^+, N – N bond weakens ***(B) In O_2^+, the O – O bond order increases***

(C) In O_2^+, paramagnetism decreases ***(D) N_2^+ becomes diamagnetic***

Solution: B.O. in $N_2 = (10 - 4)/2 = 3$ B.O. in $N_2^+ = (9 - 4)/2 = 2.5$

B.O. in $O_2 = (10 - 6)/2 = 2$ B.O. in $O_2^+ = (10 - 5)/2 = 2.5$

N_2^+ contains one unpaired electron and hence it is paramagnetic. Thus option (D) is wrong.

$\therefore$ **(D)**

Problem 17: ***The correct order of increasing C–O bond length of CO, CO_3^{2-} and CO_2***

(A) $CO_3^{2-} < CO_2 < CO$ ***(B)*** $CO_2 < CO_3^{2-} < CO$

(C) $CO < CO_3^{2-} < CO_2$ ***(D)*** $CO < CO_2 < CO_3^{2-}$

Solution: B.O. of C - O in CO is 3, that of O = C = O is 2 while that of CO_3^{2-} ion is 1.33. Since the bond length increases as the bond order decreases i.e.

$CO < CO_2 < CO_3^{2-}$ order is correct $\therefore$ **(D)**

Problem 18: ***A diatomic molecule has dipole moment of 1.2 D. If the bond distance is 1Å what percentage of electronic charge exists on each atom?***

(A) 12% of e ***(B) 19% of e***

(C) 25% of e ***(D) 29% of e***

Solution: Fraction charge of electron = $\frac{\text{Dipole moment}}{\text{Distance}} = \frac{1.2\text{D}}{1\text{A}}$

$$= \frac{1.2 \times 10^{-18}\,\text{esu cm}}{1 \times 10^{-8}\,\text{cm}} = 1.2 \times 10^{-10}\text{esu}$$

$$\% \text{ of electronic charge} = \frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} \times 100 = 25\% \qquad \therefore \textbf{(C)}$$

Problem 19: ***The true statements from the following are***

1. PH_5 and $BiCl_5$donot exist ***2.$p\pi - p\pi$ bond is present in SO_2***

3. Electrons travel at the speed of light ***4.SeF_4 and CH_4 have same shape***

5. I_3^+ has bent geometry

(A) 1, 3 ***(B) 1, 2, 5***
(C) 1, 3, 5 ***(D) 1, 2, 4***

Solution: The statement 3 i.e. electron travel at the speed of light and statement 4, i.e. SeF_4 and CH_4 have same shape are incorrect. SeF_4 has distorted tetrahedral shape (sp^3d hybridisation) while methane tetrahedral shape (sp^3hybridisation) $\therefore$ **(B)**

Problem 20: ***The atomic orbitals used by As atom in the formation of AsF_5 are***

(A) $d_{x^2-y^2}$, d_{z^2}, p_x, p_y, p_z **(B)** d_{xy}, s, p_x, p_y, p_z

(C) s, p_x, p_y, p_z, d_{z^2} **(D)** $d_{x^2-y^2}$, d_{z^2}, p_x, p_y, s

Solution: Hybridisation and shape of AsF_5 are sp^3d and trigonalbipyramidal respectively. Three hybrid orbitals should be in equatorial plane and two hybrid orbitals will orient themselves along axial positions. $\therefore$ **(C)**

Problem 21: ***NCl_3 molecules is pyramidal and BCl_3 molecules is planar because***

(A) B – Cl bond is more polar than N – Cl bond

(B) BCl_3 does not contain unused electron pair while NCl_3 does.

(C) Boron atom is smaller than nitrogen atom

(D) N – Cl bond is more covalent than B – Cl bond.

Solution: BCl_3 does not contain any lone – pair, so it is trigonal planar. NCl_3 has one lone pair of electrons. Due to lp – bp repulsion, it acuries pyramidal shape. $\therefore$ **(B)**

Problem 22: ***Among LiCl, $BeCl_2$, BCl_3 and CCl_4, the covalent character follows the order***

(A) LiCl> $BeCl_2$> BCl_3> CCl_4 ***(B) LiCl> $BeCl_2$> BCl_3> CCl_4***

(C) LiCl< $BeCl_2$< BCl_3< CCl_4 ***(D) LiCl> CCl_4 > $BeCl_2$> BCl_3***

Solution: Electropositive character decreases in the order Li > Be > B > C. hence covalent character increases from LiCl to CCl_4 $\therefore$ **(C)**

Problem 23: ***The correct order of decreasing bond angles is***

(A) $NH_3 > NH_2^- > \overset{+}{N}H_4$ ***(B) $\overset{+}{N}H_4 > NH_3 > NH_2^-$***

(C) $NH_2^- > NH_3 > \overset{+}{N}H_4$ ***(D) $\overset{+}{N}H_4 > NH_2^- > NH_3$***

Solution: As the number of lone pair of electrons of N increases, bond angle decreases. $\overset{+}{N}H_4$, NH_3 and NH_2^- contain 0, 1 and 2 lone pairs respectively. $\therefore$ **(B)**

Problem 24: ***An atom of an element 'X' has three electrons in its outermost shell and that of 'Y' has six electrons in the outermost shell. The formula of compound between these two elements would be***

(A) X_2Y_4 ***(B)*** X_2Y_3 ***(C)*** X_3Y_2 ***(D)*** X_2Y

Solution: Since 'X' has 3 valence electrons, it will lose three electrons to acquire noble gas configuration. Similarly 'Y' will gain 2 electrons to acquire octet in its outermost shell.

$\therefore$ **(B)**

Problem 25: ***In which of the following compounds, all the bond angles are same.***

(A) CCl_4 ***(B)*** $CHCl_3$ ***(C)*** CH_3Cl ***(D)*** CH_2Cl_2

Solution: Since all 4 C – Cl bonds are at equivalent position $\therefore$ **(A)**

Problem 26: ***The correct order of bond angle is***

(a) $PF_3 < PCl_3 < PBr_3 < PI_3$ ***(b)*** $PF_3 < PBr_3 < PCl_3 < PI_3$

(c) $PI_3 < PBr_3 < PCl_3 < PF_3$ ***(d)*** $PF_3 > PCl_3 < PBr_3 < PI_3$

Solution: $PCl_3 < PBr_3 < PI_3$, the bond angle order is explained in terms of increasing electronegativity ofhalogens, whereas $PF_3 > PCl_3$, bond angle order is explained in terms of $p_\pi - d_\pi$ bonding PF_3. $\therefore$ **(D)**

Problem 27: ***The following compounds have been arranged in order of their increasing thermal stability. Identify the correct order :***

K_2CO_3(I) $MgCO_3$(II) $CaCO_3$(III) $BeCO_3$(IV)

(A) I < II < III <IV ***(B) IV < II < III < I***

(C) IV < II < I < III ***(D) II < IV < III < I***

Solution: The stability of carbonates increases with increasing electropositive character of the metal. ∴ **(B)**

Problem 28: ***The molecules with zero dipole moment is:***

(A) SO_2 ***(B) ClO_2*** ***(C) NO_2*** ***(D) $HgCl_2$***

Solution: $HgCl_2$ is sp hybridized and linear $\therefore$ **(D)**

Problem 29: ***The bond order of*** C_2^+ ***is***

(A) 1 ***(B) 2*** ***(C) 3/2*** ***(D) ½***

Solution: Molecular orbital configuration of

$$C_2^+ = \sigma_{1a}^2\ \sigma_{2s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \pi_{2py}^1\ \pi_{2px}^2 \quad \Rightarrow \quad B.O = \frac{7-4}{2} = 3/2 \quad \therefore \textbf{(C)}$$

***Problem 30:* Which does not use sp^3 hybride orbitals in its bonding**

(A) BeF_3^- **(B)** OH_3^+ **(C)** NH_4^+ **(D)** NF_3

Solution: **(A)** BeF_3^- involves sp^2 hybridization