STUDY MATERIAL

VIVEKANANDA COLLEGE

THAKURPUKUR

NAAC Accredited Grade—A

CHEMICAL BONDING

(SEMESTER II HONS STUDENTS)

Dr. Md Selim*

*Assistant Professor, Department of Chemistry, Vivekananda College.

Introduction

The stability of the monoatomic noble gases emphasized the fact that an atomic system with eight outer most electrons (two for He) will be very stable and called as noble gas configuration. This is also known as octet rule. The above statement can be further described for the inclusion of He as, the atomic system with filled outermost shell will be stable.Atoms are connected to another homo - or hetero - atom(s) forming molecules, while, molecules of noble gases are monoatomic. This indicates that a molecule will only be formed by the combination of either homo - or hetero - atom if it tends to a low energy, filled-configuration of the outermost shell, and more stable systems than individual atomic systems.In a di or polyatomic molecules, atoms are held together by means of an attraction force. This force is called bond. A bond could be formed by equal sharing of electron density between atoms (covalent bonding), or uneven sharing of electron density together with coulomb interaction between the atoms (ionic bonding). Whatever, a stable electronic configuration should be achieved by atom either by releasing/accepting electron(s) or sharing electron(s).The inter-nuclear distance between two atoms is known as bond distance. The bond dissociation energy is the enthalpy change for complete splitting the units linked by a particular chemical bond in the gaseous state. It is also defined as the amount of energy released when the bond is formed between two neutral gaseous atoms.

Types of bonds

Elements can be subdivided mainly into two groups; electropositive and electronegative elements. Those elements which release or accept electron(s) to achieve an inert gas configuration are called electropositive and electronegative elements, respectively. Combination of electropositive and electronegative elements forms the following compounds.

(A) Ionic compounds = Ionic bond = Electropositive elements + Electronegative elements

(B) Covalent Compounds = Covalent bond = Electronegative elements + Electronegative elements

(C) Metallic Compounds = Metallic bond = Electropositive elements + Electropositive element

Examples:

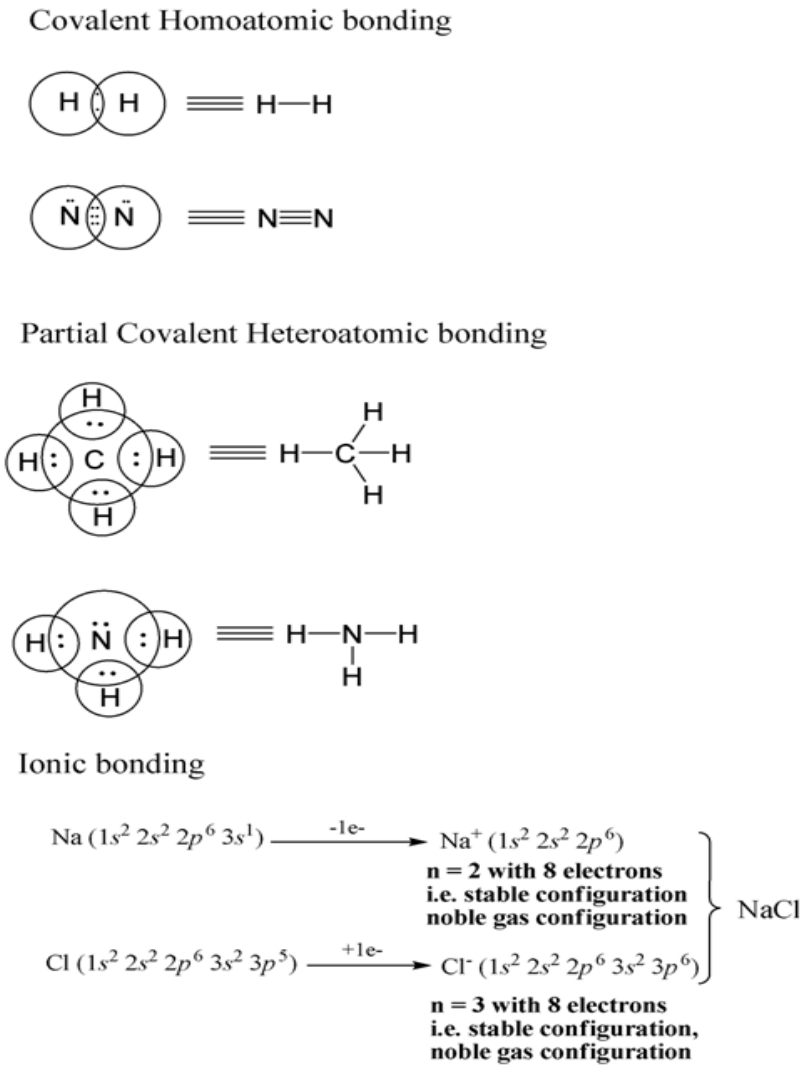


Figure: Covalent, partial covalent and ionic bonding patterns maintaining octet rule.

The ionic bond:

As stated earlier, Ionic bonds are formed when electropositive elements interact with electronegative elements. The resulting compound is known as ionic compound.

Some features of ionic compounds:

(i) Ionic compounds tend to have low ionic conductivity in solid state but highly conducting in molten state. This is because in the solid state ions are held tightly by the surrounding counter ions (lattice effect) so, they are not free to move in the presence of any external electric field, whereas, in molten state it becomes easier for the movement of ions.

(ii) Ionic compounds are high melting, hard and brittle substances.

(iii) Ionic compounds are often soluble in polar solvent with high dielectric constants. The energy of interaction of two charge particles is given by;

$$E = \frac{q^+ q^-}{4\pi r \varepsilon}$$

Where q^+ and q^- are the charges, r is the separation distance, ε is the dielectric constant of the medium.

Radius ratio rules:

In ionic compounds, ions are held together by electrostatic attraction between two oppositely charged ions. The structures of ionic compounds depend on the relative size of positive and negative ions. The accommodation of the number of ions around a particular ion, i.e. coordination number, can be found out by geometric calculation.

It is the ratio of the ionic radius of the cation to the ionic radius of the anion in a cation-anion compound.

Radius Ratio	CN	Coordination
1.0	12	Cubic closest packed (CCP) Hexagonal closest packed (HCCP)
1.0–0.732	8	Cubic
0.732–0.414	6	Octahedral
0.414–0.225	4	Tetragonal
0.225–0.155	3	Triangular
<0.155	2	Linear

Coordination number 3 (trigonal planar):

Let say, AB is an ionic compound having coordination number 3. All the three B are in contact with A but not to each other (Figure [1]). A limiting case arises when all the three are also come in contact with each other. Assume that the radius of cation is r + and anion is r -

Therefore, cos 30 ° = DC/DE

or, DE = DC / cos 30 °

or, $r_+ + r_- = r_- / 0.866$ [∴ cos 30 ° = 0.866]

or, $r_+ + r_- = 1.155 \times r_-$

or, $r_+ / r_- = 1.115\text{-}1.000 = 0.155$

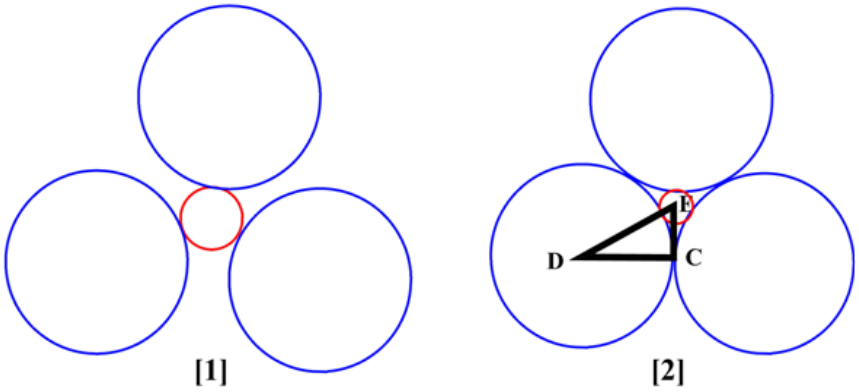


Figure : Non-limiting and limiting radius ratio for coordination number 3. Red circle represents cation and blue circles represent anion, respectively.

Simple geometry provides the limiting radius ration for coordination number 3 is 0.155.

When the radius ratio is smaller compared to 0.155, the positive ions will not be in contact with the negative ions, and therefore, a whole will be created and the resulting structure will be unstable. If the radius ration value is more than that of 0.155, it is possible to have contact between positively charged cation and a negatively charged anion. In this case the complex will be stable.

Coordination number 4 (tetrahedral):

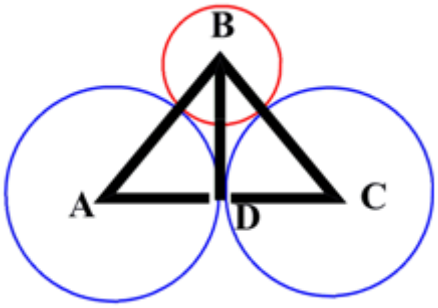


Figure: Cross section of a tetrahedral arrangement.

In case of tetrahedral arrangement, the angle ABC is 109 ° 28´ . Hence, the angle ABD is half of the angle ABC = 54 ° 44 ´

Sin ABD = AD/AB = $r_- / r_+ + r_-$ = 0.8164

or, $r_+ + r_- / r_-$ = 1.225

or, r_+ / r_- = 1.225-1.000 = 0.225

Coordination number 6 (octahedral):

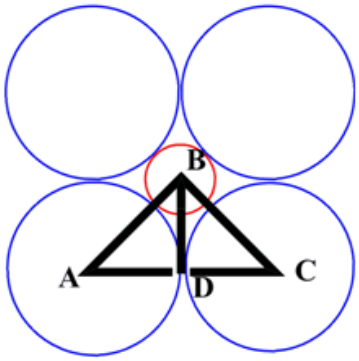


Figure: Cross section of an octahedral arrangement.

In this case, the angle BAC = 45 ° .

cos BAD = AD/AB = $r_- / r_+ + r_-$ = 0.7071

or, $r_+ + r_- / r_-$ = 1.414

or, r_+ / r_- = 1.414-1.000 = 0.414

Crystal systems:

The structures of all crystals can be classified according to the symmetry of the unit cells. There are in total 7 groups, collectively called Crystal Systems: Tricinic, Monoclinic, Orthorhombic, Tetragonal, Trigonal, Hexagonal, and Cubic. The symmetry of each group is described by the relationship between the lattice sides a, b, and c and angles α, β and γ.

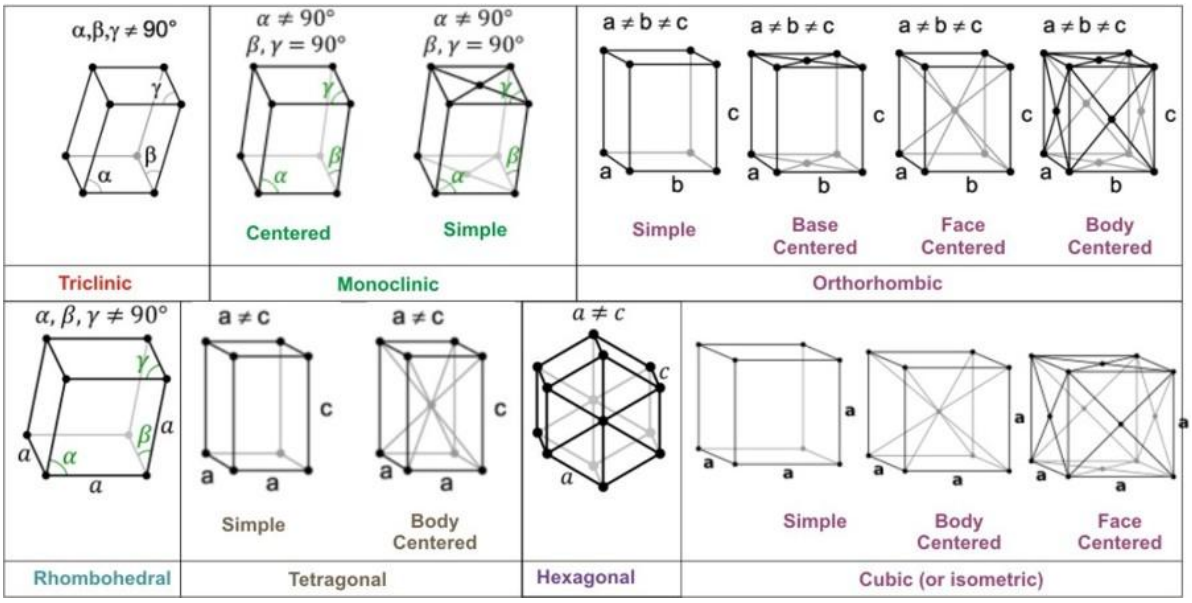


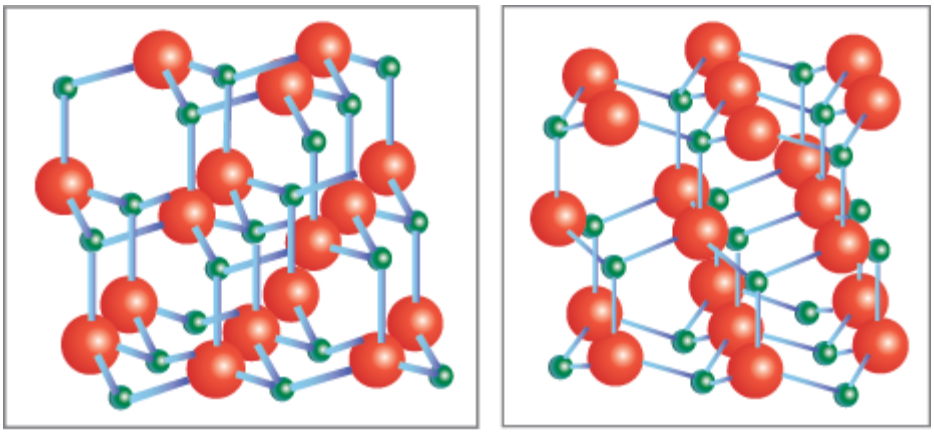
Figure: Seven crystal systems

Classification of ionic Structures

Ionic compounds to AB type:

(A) Zinc sulfide (ZnS) structure:

In ZnS, both cation (Zn) and anion (S) are in II oxidation state. The radius ratio in ZnS is 0.40 suggests a tetrahedral arrangement where each Zn^{2+} ion is surrounded by four S^{2-} anions. The coordination number of both ions is 4. Therefore, the arrangement is called 4:4 arrangement.



Zinc Blende Wurtzite

Figure: Crystal structure of zinc blend and wurtzite.

(B) Sodium chloride (NaCl) structure:

In NaCl both cation (Na) and anion (Cl) are in I state. The radius ration 0.52 suggests an octahedral arrangement around the ions. The coordination is thus 6:6.

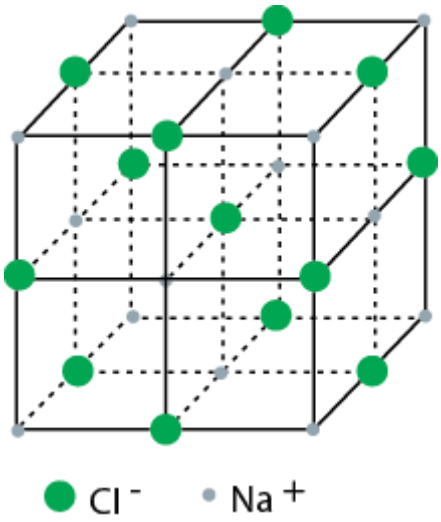


Figure: Crystal structure of NaCl.

(C) Caesium chlodire (CsCl) structure:

In CsCl both cation (Cs) and anion (Cl) are in I state. The radius ration 0.93 suggests an body centered cubic type arrangement around the ions. In this case each ion is surrounded by eight oppositely charges ions. The coordination is thus 8:8.

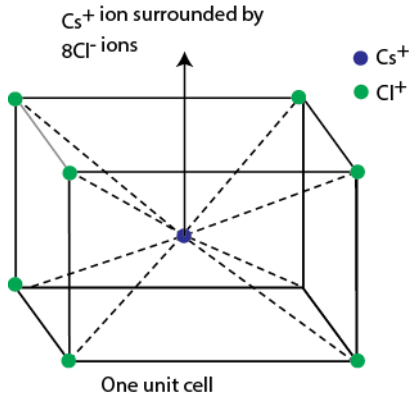


Figure: Crystal structure of CsCl.

Ionic compounds to AB $_2$ type:

(A) Calcium fluoride (CaF $_2$, fluorite) structure:

In CaF_2 the radius ratio is 0.73 or above. It has a body centered cubic arrangement of fluoride ions around calcium ion. The ratio between Ca^{2+} and F^- is 2:1. Since, there is twice as many fluoride ions as calcium ion, the coordination number of the both ions will be different. A 8:4 F^-:Ca^{2+}arrangement has been found for CaF_2 where each Ca^{2+} ions are tetrahedrally arranged around each F^- ion.

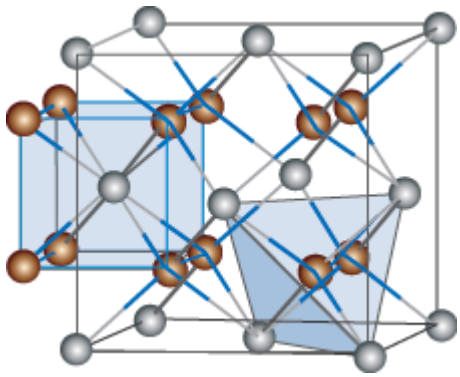


Figure: Crystal structure of CaF_2

(B) TiO $_2$ (rutile) structure:

TiO_2 exists in three different forms; (i) anatase, (ii) brookite, and (iii) rutile. In many crystals rutile structure is found and the radius ration is between 0.41 and 0.73. This indicates a

coordination number is 6. Therefore the other will be 3 (as it is AB_2 kind structure). Rutile form has a 3:6 structure where each Ti^{4+} is octahedrally surrounded by six O^{2-} ions and each O^{2-} ion has three Ti^{4+} ions around in a plane triangular fashion.

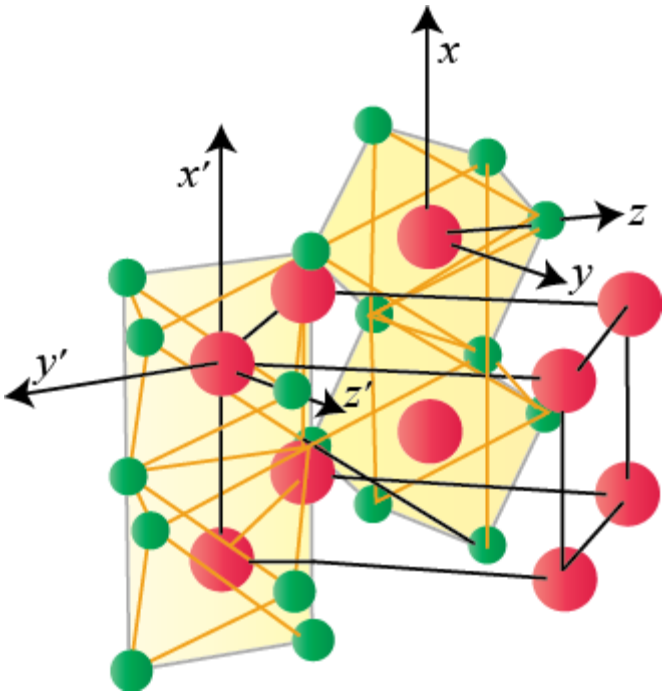


Figure : Crystal structure of TiO_2 (rutile).

The rutile structure is not close packed. The unit cell is not a cube as one of the three axes is about 30% shorter. It is convenient to describe as distorted cube.

Limitations of the radius ratio rule:

The structure adapted by the alkali metal halides may be considered to demonstrate the failure of structural prediction from the radius ratio rule. LiCl, LiBr, and LiI, the radius ratio lies around 0.3 suggesting fourfold coordination. In case of KF, KCl, RbF, RbCl, RbBr, and CsF, the radius ratio is 0.73, hence coordination number shoud be minimum 8. In fact, all the alkali metal halides adapt 6:6 (NaCl type) coordination environment except CsCl, CsBr, and CsI.

Effective radius of a cation is greatly influenced by the anions with the consequence that the radius ratio changes. For example, AgF and NaF crystallize out in NaCI type of structure with

coordination No. 6 and if we assume that the size of F- remains constant than Ag+ is bigger thanNa+. On the other hand, for a given size for a chloride ion in AgCI and NaCI, the sizes of cationsare reversed, that is, Na+ is bigger than Ag+. It is also true for their bromides. This is understandable because Ag+ is softer than N+ and introduces relatively more covalent character with Polarizable anions like CI- and Br-

It is said in the radius ratio rule that with increase of the ratio value the coordination number will increase. Let consider a AB type ionic compound, as we know that with increase of radius ration value the number of counter ions around a particular ion will increase. As the system is AB type, therefore, each cation will be surrounded by one anion. So, the gain in electrostatic attraction force will be cancelled by large repulsion force by the same charge ions as the coordination number is high. Therefore, the stability of ionic solid cannot be answered.

This rule provides a rough guide to the structure of ionic solids. Ultimately, the reason why any particular crystal structure is formed is that it gives the most favorable lattice energy.

Lattice energy:

The energy of the crystal lattice of an ionic compound is the energy released when ions in gaseous stare come together from infinite separation to form a solid crystal.

$$M(g)^+ + X(g)^- \longrightarrow MX(s)$$

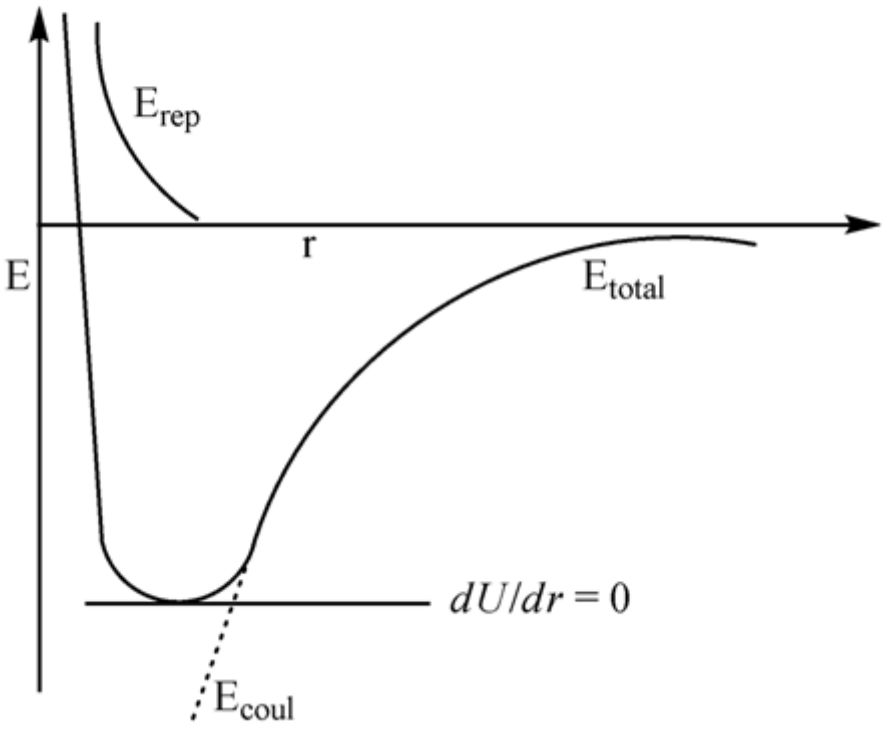


Figure . Energy curves for an ion pair.

Consider the energy of an ion pair, M^+, X^-, separated by a distance r. The electrostatic energy (E_{coul}) of attraction is obtained from coulombic law;

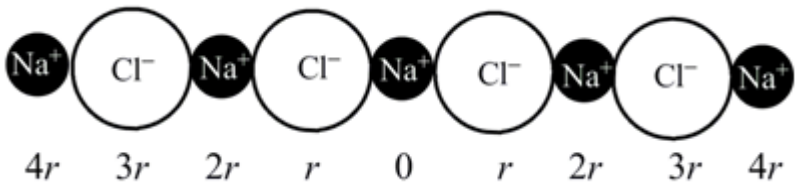
$$E_{coul} = \frac{z^+ z^- e^2}{4\pi\epsilon_0 r}$$

Since one of the charges is negative (X^-), the energy will be negative with respect to the energy at the infinite separation. The magnitude of the negative energy increases as *r* decreases.

In a crystal lattice, one ion is surrounded by several others counter ions. Therefore, both attraction and repulsion forces also exits. The summarization of all these geometrical interactions is known as the Madelung constant, A. The energy equation then becomes;

$$E_{coul} = \frac{Az^+z^-e^2}{4\pi\epsilon_0 r} \quad (1)$$

The evaluation of the Madelung constant (A):

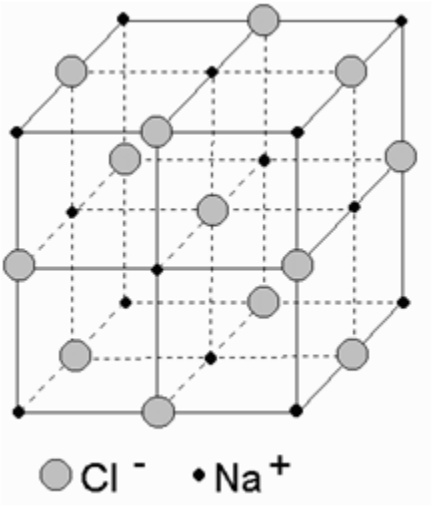


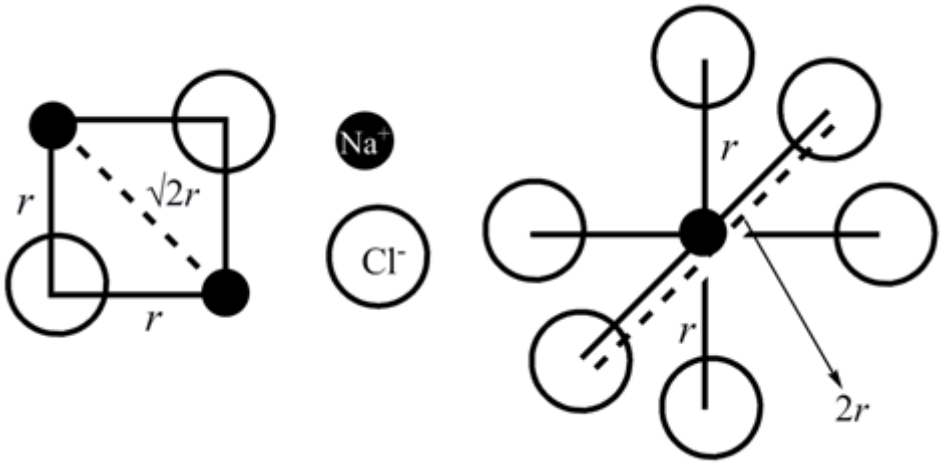
Let us consider NaCl Structure. The central Na^+ ion is attracted by two Cl^- ion at *r* and two more Cl^- ions at 3 *r* . The corresponding contribution to the potential energy would be then - $2e^2/4\pi\varepsilon_0 r$ and - $2e^2/4\pi\varepsilon_0 3r$, respectively. At the same tome there will be repulsion from sodium ions residing at 2 *r* for two and at 4 *r* for two. This will raise the potential energy with the contribution of $+2e^2/4\pi\varepsilon_0 2r$ and $+2e^2/4\pi\varepsilon_0 4r$, respectively. The procedure can be reported for the other ions present in a row. The potential energy for the centralNa^+ ion will be then;

$$E = -\frac{2e^2}{4\pi\varepsilon_0 r} + \frac{2e^2}{4\pi\varepsilon_0 2r} - \frac{2e^2}{4\pi\varepsilon_0 3r} + \frac{2e^2}{4\pi\varepsilon_0 4r} - \cdots$$

$$E = -\frac{2e^2}{4\pi\varepsilon_0 r}\left[\left(1 - \frac{1}{2}\right) + \left(\frac{1}{3} - \frac{1}{4}\right) + \cdots\right]$$

This procedure many be extended for the three dimensional lattice of a NaCl crystal.





The distance between Na^+ and Cl^- is r. Therefore, the distance between two similar ions will be $\sqrt{2}\,r$. Similarly, we can find out, 6 Cl^- ions at r, 12 Na^+ ions at $\sqrt{2}r$, 8 Cl^- ions at $\sqrt{3}\,r$, 6 Na^+ ions at $2\,r$ and so on.

In the three dimensional lattice,

$$E = -\frac{6e^2}{4\pi\varepsilon_0 r} + \frac{12e^2}{4\pi\varepsilon_0\sqrt{2}r} - \frac{8e^2}{4\pi\varepsilon_0\sqrt{3}r} + \frac{6e^2}{4\pi\varepsilon_0 2r} - \cdots$$

or,

$$E = -\frac{e^2}{4\pi\varepsilon_0 r}\left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \cdots\right]$$

or,

$$E = -\frac{Ae^2}{4\pi\varepsilon_0 r}$$

Where,

$$A = \left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \cdots\right]$$

The series within the bracket converge slowly and the limiting value is 1.74758. This value changes with the arrangement of lattice and therefore, different constant value is obtained for different crystal lattice system. This constant value for different lattice indicates a different Madelung constant (A) for different type of lattices.

Madelung constants of some crystal lattice:

Lattice type	**Madelung constant, *A***
NaCl (6:6)	1.747
CsCl (8:8)	1.763
CaF_2(8:4)	2.519

Returning to the equation (1), it is clear that unless there is repulsion energy to balance the coulomb attraction energy, a stable lattice cannot be formed. Born suggested the repulsion energy as;

$$E_{rep} = -\frac{B}{r^n}$$

Both B , and n are constants and depend on the nature of ion. B is repulsion coefficient and n is called Born exponent.

Values of the Born exponents,

Ionic configuration	n
He	5
Ne	7
Ar, Cu^+	9
Kr, Ag^+	10
Xe, Au^+	12

The net stabilization energy (lattice energy, U) gained due the formation of lattice by the combination of ions in gaseous states can be represented as the sum of E_{coul} and E_{rep}.

$$U = E_{coul} + E_{rep}$$

or,

$$U = \frac{AN.Z^+Z^-e^2}{4\pi\varepsilon_0 r} + \frac{N.B}{r^n}$$

Where, N = Avogadro number

The minimum in the curve (Figure) corresponding to the equilibrium situation (where $r = r_0$) and the energy can be given as;

$$\frac{dU}{dr} = 0 = U_0 = -\frac{AN.Z^+Z^-e^2}{4\pi\varepsilon_0 r_0^2} - \frac{n.N.B}{r_0^{n-1}}$$

$$U_0 = -\frac{AN.Z^+Z^-e^2}{4\pi\varepsilon_0 r_0} - \frac{AN.Z^+Z^-e^2}{4\pi\varepsilon_0 r_0 n}$$

$$\text{When, } B = -\frac{AZ^+Z^-e^2 r_0^{n-1}}{4\pi\varepsilon_0 n}$$

$$U_0 = \frac{AN.Z^+Z^-e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

(2)

The equation (2) is known as Born-Landé equation. It allows lattice energy calculation from the knowledge of geometry of a crystal, Madelung constant, inter atomic distance, and charge of the ions.

Important points arise from the Born-Landé equation:

(I) Lattice energy is inversely proportional to the interionic distance. Therefore, lattice energy of a system increases as the interionic distance decreases.

(II) Lattice energy id directly proportional to the product of ionic charges. Hence, lattice energy increases with the increase of ionic charge product.

Example: LiF (Both $Z^+ = Z^- = 1$), U_0 = - 1004 kJ mol^{-1}

MgO (Both $Z^+ = Z^- = 2$), U_0 = - 3933 kJ mol^{-1}

Kapustinskii equation:

The **Kapustinskii equation** calculates the lattice energy ,*U* for an ionic crystal, which is experimentally difficult to determine. It is named after Anatoli Fedorovich Kapustinskii who published the formula in 1956.

The equations that we will use to predict lattice energies for crystalline solids are the Born-Mayer equation and the Kapustinskii equation, which are very similar to one another. These equations are simple models that calculate the attraction and repulsion for a given arrangement of ions.

Born-Mayer Equation:

$$U_0 = (e^2 / 4 \pi \varepsilon_0) * (N z_A z_B / d_0) * A * (1 - (d^* / d_0))$$

$$\boldsymbol{U_0 = 1390\ (z_A z_B / d_0) * A * (1 - (d^* / d_0))\ \text{in kJ/mol}}$$

Kapustinskii equation :

$$\boldsymbol{U_0 = (1210\ \text{kJ Å / mol}) * (n z_A z_B / d_0) * (1 - (d^* / d_0))}$$

Where:
e is the charge of the electron, ε_0 is the permittivity of a vacuum
N is Avogadro's number
z_A is the charge on ion "A", z_B is the charge on ion "B"
d_0 is the distance between the cations and anions (in Å) = $r^+ + r^-$
A is a Madelung constant
d^* = exponential scaling factor for the repulsive term = 0.345 Å
n = the number of ions in the formula unit

This form of the Kapustinskii equation may be derived as an approximation of the Born–Landé equation, below. Kapustinskii replaced r_0, the measured distance between ions, with the sum of the corresponding ionic radii. In addition, the Born exponent, *n*, was assumed to have a mean value of 9. Finally, Kapustinskii noted that the Madelung constant, *M*, was approximately 0.88 times the number of ions in the empirical formula. The derivation of the later form of the Kapustinskii equation followed similar logic, starting from the quantum chemical treatment in which the final term is $1 - d/r_0$ where *d* is as defined above. Replacing r_0 as before yields the full Kapustinskii equation.

Further understanding to the stability of a lattice:

Born-Haber cycle:

Lattice energy cannot be measured experimentally. They are calculated from the other experimental data using Born-Haber cycle. The theoretical and experimental data are quite close as obtained using Born-Haber cycle.

Let us consider NaCl lattice.

NaCl is a ionic compound composed of Na^+ and Cl^- ions.

We can consider the NaCl formation stepwise;

Process		Related energy terms
Na(s)	Na(g)	+S (enthalpy of atomization)
Na(g)	$Na^+(g)$	+I (ionization energy)
½ $Cl_2(g)$	Cl(g)	+ ½ D (enthalpy of bond dissociation)
Cl(g)	$Cl^-(g)$	–E.A (electron affinity)
$Na^+(g) + Cl^-(g)$	NaCl(s)	$-U_0$ (lattice energy)
Na(s) + ½ $Cl_2(g)$	NaCl(s)	$+S + I + ½\ D - E.A - U_0 = -H_f$ (heat of formation of NaCl) H_f is negative as heat release on the formation of NaCl.

Hence, $U_0 = +S + I + ½\ D - E.A + H_f$

The lattice energy can be calculated from the other experimental data with the help of Born - Haber cycle.

Why does not $NaCl_2$ exist?

The composition of $NaCl_2$ will be Na^{2+} and $2Cl^-$.

Process		Related energy terms
Na(s)	Na(g)	+S (enthalpy of atomization)
Na(g)	$Na^{2+}(g)$	$+I = +(I_1+I_2)$ (I_1 and I_2 are respective first and second ionization energy)
$Cl_2(g)$	2Cl(g)	D (enthalpy of bond dissociation)
2Cl(g)	$2Cl^-(g)$	−2E.A (electron affinity)
$Na^{2+}(g) + 2Cl^-(g)$	$NaCl_2(s)$	$-U_0$ (lattice energy)
$Na(s) + Cl_2(g)$	$NaCl_2(s)$	$+S + I + D - 2E.A - U_0 = -H_f$ (heat of formation of NaCl) H_f is negative as heat release on the formation of NaCl.

Therefore, we can write;

$$+S + (I_1 + I_2) + D - 2E.A - U_0 = H_f$$

$NaCl_2$ would crystallize in fluorite (CaF_2) structure with $A = 2.52$. Theoretically, the U_0 for NaCl 2 obtained is 2180 $kJmol^{-1}$.

Hence,
$$\begin{aligned} H_f &= +S + (I_1 + I_2) + D - 2E.A - U_0 \\ &= +108 + (496+5462) + 242 - 2\times348 - 2180 \\ &= 2530\ kJmol^{-1} \end{aligned}$$

As the H_f is positive, hence $NaCl_2$ cannot be stabilized. Here, the very large I_2 (5462 $kJmol^{-1}$) of Na cannot be compensate by the stabilizing lattice energy.

Why does not CaCl exist?

Process		Related energy terms
$Ca(s)$	$Ca(g)$	+S (enthalpy of atomization)
$Ca(g)$	$Ca^{+}(g)$	+I (ionization energy)
½ $F(g)$	$F(g)$	½ D (enthalpy of bond dissociation)
$F(g)$	$F^{-}(g)$	E.A (electron affinity)
$Ca^{2+}(g) + Cl^{-}(g)$	$CaF(s)$	$-U_0$ (lattice energy)
$Na(s) + ½\ F_2(g)$	$NaF(s)$	$+S + I + ½\ D - E.A - U_0 = -H_f$ (heat of formation of NaCl) H_f is negative as heat release on the formation of NaCl.

Assume that CaF will be crystallized in the same geometry as KF. Therefore, the calculated lattice energy will be $U_0 = -795\ kJmol^{-1}$.

$$\text{Hence, } H_f = +S + I + ½\ D - E.A - U_0$$
$$= +178 + 590 + 79 - 328 - 795$$
$$= -276\ kJmol^{-1}$$

As the H_f value is not large ($276\ kJmol^{-1}$), the CaF is unstable and disproportionate to CaF_2 and Ca.

Lattice defects:

In reality, lattices do not acquire a perfectly ordered arrangement of the constituting ions. A defective lattice might not conform to the stoichiometric cation and anion ratio as represented by its chemical formula. Hence, lattices can be divided in (i) stoichiometric defect and (ii) non-stoichiometric defect.

Stoichiometric defect:

Frenkel defect and Schottky defect belong to this type of lattice defect.

Frenkel defect.

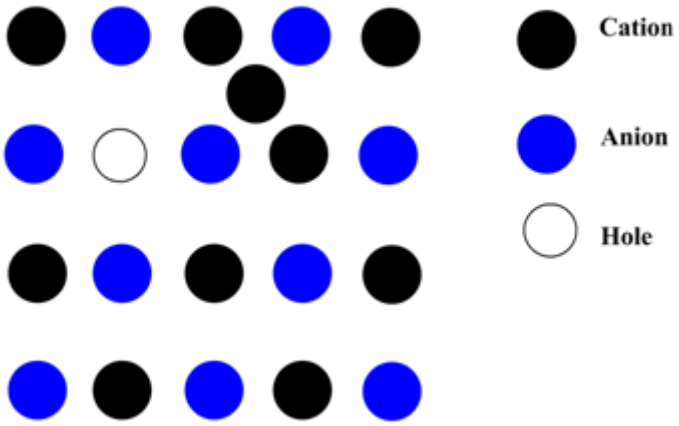


Figure: Frenkel defect

In Frenkel defect, an ion is missing from its lattice site. Therefore, a hole is generated in the lattice. The missing ion occupies some interstitial position. Crystals with small positive ions and large negative ion, like AgCl, AgBr, AgI, ZnS, etc shows this kind of defect.

Schottky defect:

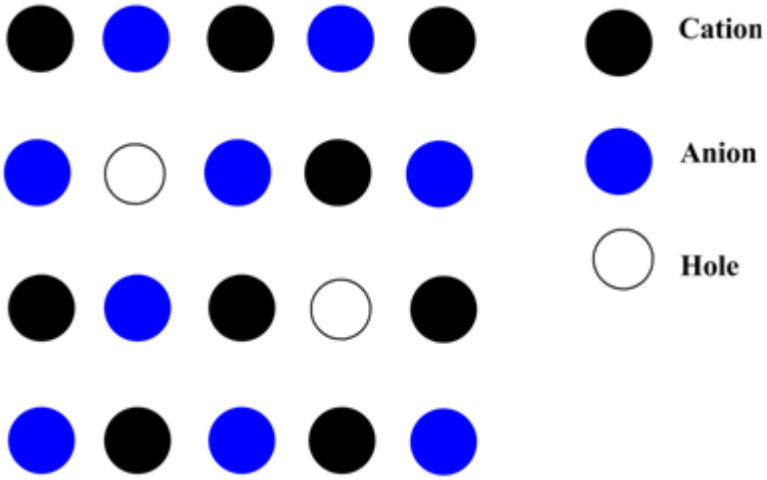


Figure: Schottky defect

In Schottky defect, both a positive ion and a negative ion are missing from its lattice site. Therefore, two holes are generated in the lattice. Some examples are NaCl, KCl, KBr etc.

Crystalline solid with these kinds of defect show some sort of electric conductivity via ion migration to the hole(s).

Non-stoichiometric Defects:

In the non-stoichiometric defect the ratio of cation and anion differ from that of the indicated chemical formula. The charge is balanced is either by extra electron or by cation according to necessary. In this type of compounds, either the matal or the non-metal atoms may be in excess.

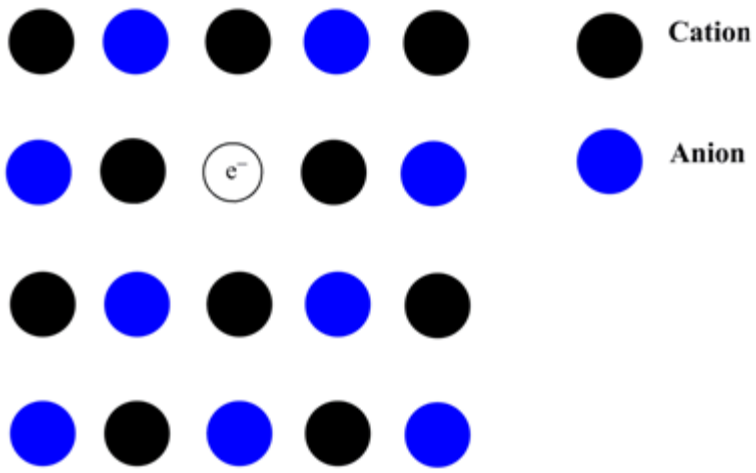


Figure: Metal-excess defect because of absent anion.

The excess of metal can be obtained by the following ways;

(A) Missing of anion from the lattice site and an extra electron in present there to balance the charge.Example: NaCl treated with Na-vapor forms such a yellow non-stoichiometric lattice. KCl with K-vapour becomes bule.

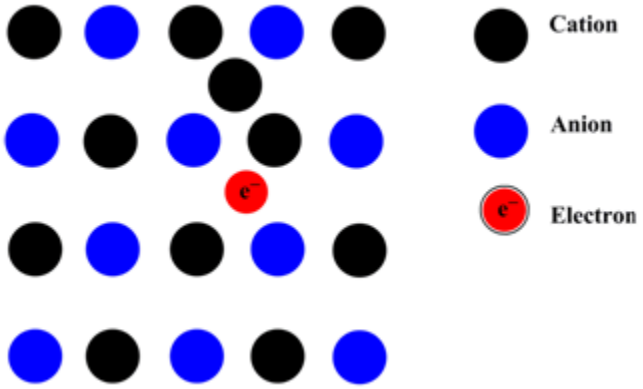


Figure: Metal excess defect because of excess of cation(s).

(B) Presence of an extra metal ion in interstitial position and extra electron in some other interstitial position to balance the charge of the lattice.

Example: ZnO, CdO, Fe_2 O_3 , etc shows such type of lattice defect. ZnO under normal room temperature is white in color but when it is heated it becomes yellow. This is because it the presence of extra electrons, at the interstitial position of ZnO lattice, undergo to higher energy excited states by absorbing heat.

The metal deficiency can be obtained by the following ways;

(C) Positive ion may absent in a lattice and a doubly charged cation maintains the charge balance.

Example: FeO, CuO, NiO, Fes, etc.

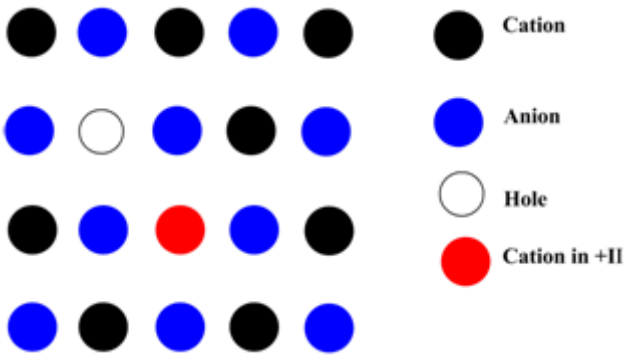


Figure: Metal deficiency because of mission cation.

(D) A non-stoichiometric defect might be possible as shown in case (C) with a additional anion in the interstitial position. No example of crystals containing this kind of anion in the interstitial position of a lattice is known.

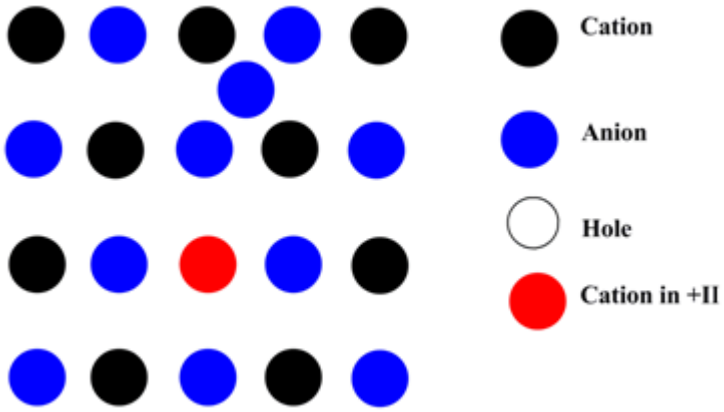


Figure: Metal deficiency because of the presence of interstitial anion.

Semiconductors:

Semiconductors are solid materials where a small energy gap, known as band gap, is present between the valence electron-containing valence band and conduction band. If the system (semiconductor) is cooled to absolute zero, the electrons will occupy the lowest possible energy according to the Boltzmann´s distribution law. Hence, the valence band will be full of electron, while, conduction band will not occupy any free electron for conduction. Therefore, this system is said to be an insulator. With increase of temperature some of electrons will occupy conduction band. Hence, an electric conduction can take place by passing electrons.

Example: Germanium (Ge) and silicon (Si) are mostly used semiconductors and will be discussed here

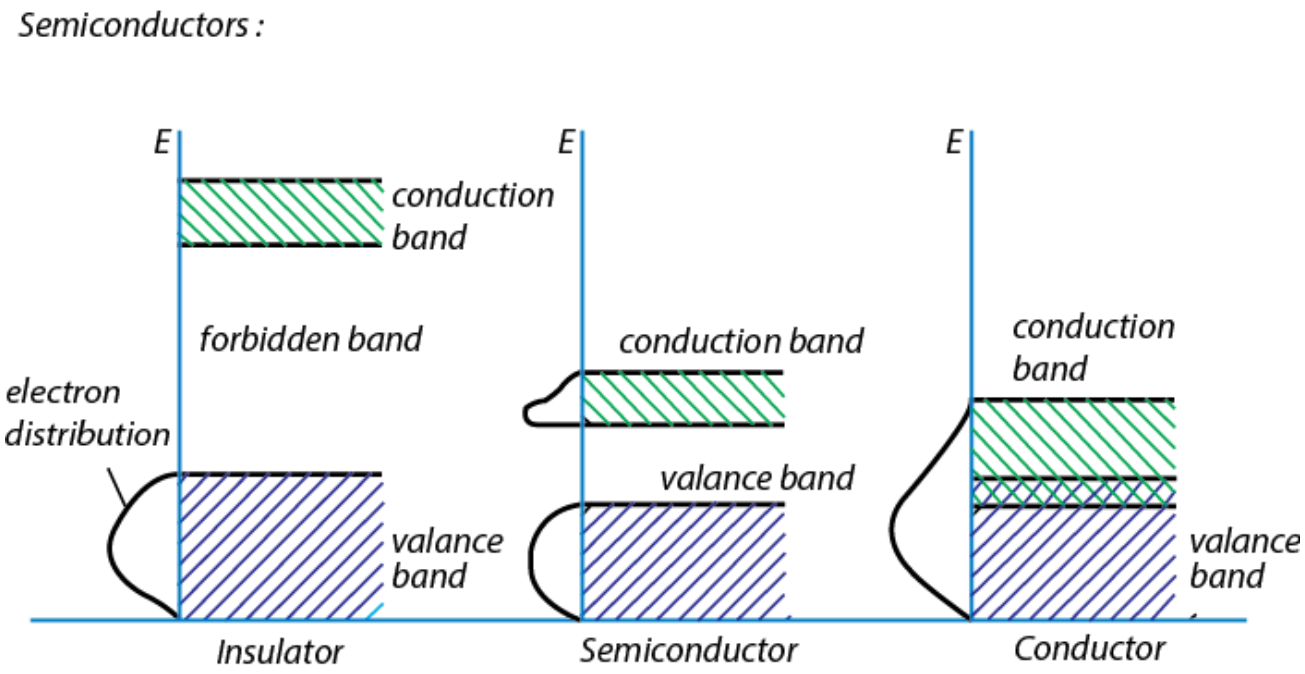


Figure: Schematic representation of band gap between valence band and conduction band in insulator, semiconductor and conductor are shown.

.

Both of them have diamond-like structure. Both of them are tetravalent, i.e. contains four electrons in the outermost shell which forms four covalent bonds with the other atoms. Both of them at very low temperature behave as an insulator. The band gap for Ge is 68 $kJmol^{-1}$ and for Si it is 106 $kJmol^{-1}$. Therefore, even at room temperature they are almost insulators. When they are connected to a electric circuit in the room temperature they are slightly conducting. This is known as intrinsic semiconduction. As the temperature increases conduction increases due to promotion of valence electrons to the conduction band.

***n* -Type and *p* -type semiconductors:**

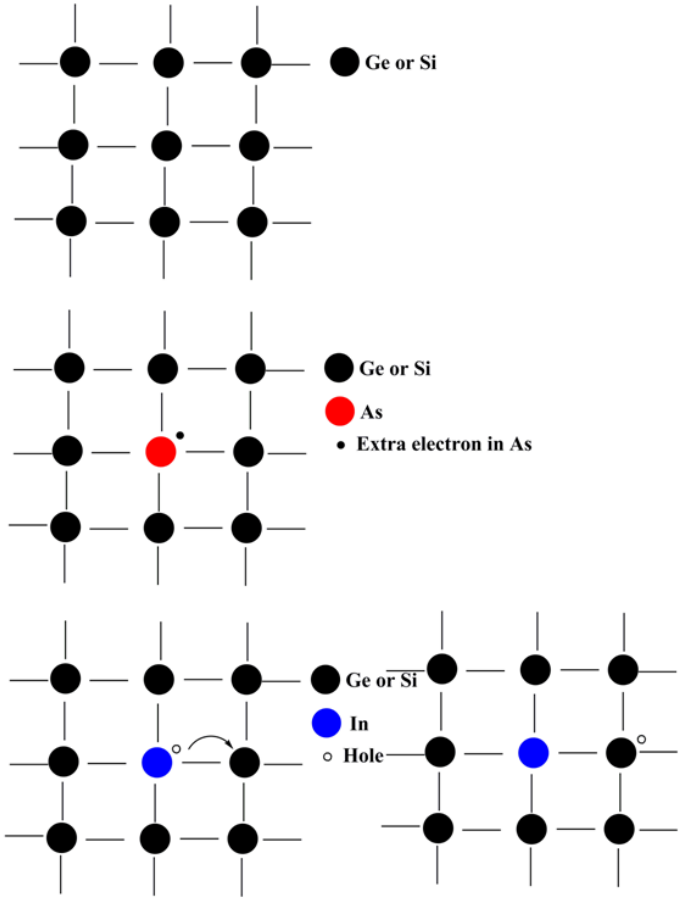


Figure: Pure lattice (top), n-type semiconductor (middle), p-type semiconductor (bottom)

***n* -Type semiconductor:**

Both Ge and Si contain four electrons in the outer most shell, *i . e .* four valence electrons. Some atoms with five outer electrons, like arsenic (As), is added to Ge or Si crystals. This process is known as doping. When one Si or Ge atom will be replaced by a As atom, four out of five valence electros of As will be used for covalent bonding with other four Ge or Si atoms and the fifth one will remained unused. At room temperature some of the fifth electrons on As are excited in to the conducting band. Therefore, current can be carried out easily even at room temperature.This is called extrinsic conduction. As current is carried out by excess electron, the semiconductor in the presence of As is known as *n* -type semiconductor.

***p* -Type semiconductor:**

When a material having outer shell electron one less than four [*e . g .* Indium (In)] is doped into Si or Ge a *p* -type semiconductor is generated.

Each In uses three of its outer electrons for covalent bonding with Si or Ge to form a three bond lattice. As Si or Ge has four outer electrons, hence, one site remains vacant and a positive hole is created. With increase of temperature electron from Si or Ge may occupy the hole position. Consequently another hole is created. Such a way a movement of positive hole occurs and electrons movement, *i . e .* current flow, is opposite to the hole movement. Since current is carried by migration of positive hole, this type of semiconductor is called *p* -type semiconductor.

Solvation energy:

In a polar solvent an inherent dipole moment exist in the solvent molecules. Therefore, when an ionic solid is placed into a polar solvent each ion get surroundings by the opposite pole of the solvent molecule. This phenomenon is called salvation and the enthalpy change takes place by this salvation is known as salvation energy. Let us consider the solvent as water (H_2O).

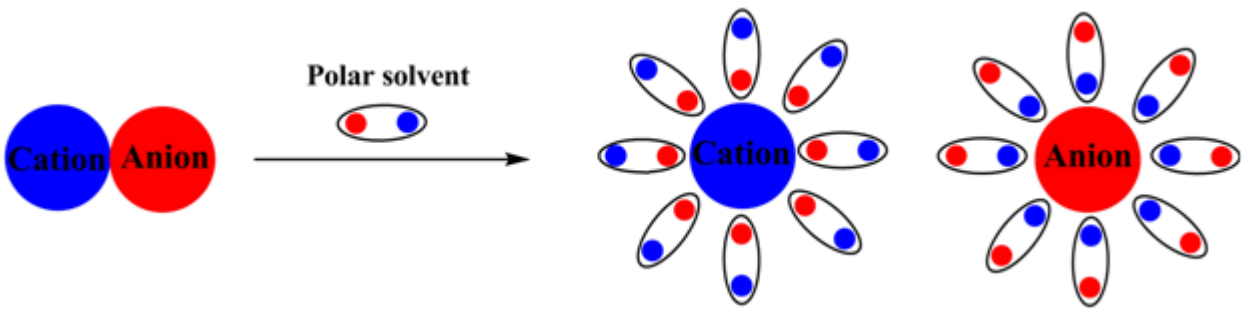


Figure: Schematic representation of salvation of an ionic solid.

When the salvation energy is more compared to the lattice energy of an ionic solid, the solid dissolves into the solvent. This indicates that the lattice will less lattice energy will be more and easily soluble in an ionic solid compared to the other which has more lattice energy.

Some Examples:

(1) Cesium iodide (CsI) has less lattice energy compared to sodium fluoride (NaF). Therefore, CsI is more soluble in water that that of NaF.

(2) CaF_2 is not soluble in water due to extremely high lattice energy, while, $CaCl_2$ is fairly soluble in water as its lattice energy is lower compared to CaF_2 .

(3) BaO having less lattice energy is about 2000 times more soluble in water than that of MgO.

(4) The solubility in water decreases in the following order for AgF, AgCl, AgBr, AgI ;

$$AgF > AgCl > AgBr > AgI$$

Here, AgI has lower lattice energy that AgF. Still, it is less soluble in water. This is because of the increasing of covalent character in the compound on moving from AgF to AgI.

(5) The radious of barium ion (Ba^{2+}) is almost double to magnesium ion (Mg^{2+}). Hence, the lattice energy of $BaSO_4$ should be lower than that of $MgSO_4$. Therefore, $BaSO_4$ should be more soluble in water than $MgSO_4$. In fact, it is reverse. The reason is the large sulphate anion (SO_4^{2-}). Small cation is less in contact with large anion. Therefore $MgSO_4$ forms less compact lattice that BaSO 4 and consequently, less lattice energy and more solubility (easily soluble).

Polarization:

In a lattice, cation(s) is(are) surrounded by anion(s) and *vice versa* . The attraction force between them is coulomb attraction. When cations and anions in a lattice come to their equilibrium

distance, the relatively loose electron cloud in the anion is attracted more by the positively charged cation. Therefore, the electron cloud around the anion undergoes deformation. This deformation is said to be polarized. The reverse polarization is extremely less as positively charged cations hold their electron cloud very tightly.

With increasing of polarization the charge cloud between cation and anion tends to mix or merge with each other. This extent of mixing determines the ionic and covalent character of a compound. Higher the mixing, higher the covalent character is.

Fajan´s Rule:

An ion will be formed most easily when ;

(i) the electronic structure of the ion is stable,

(ii) the charge on the ion is small, and

(iii) a small atom forms the anion and a large atom forms the cation.

Increased covalence is favored by ;

(i) high charge on the ions,

(ii) small size of the cation and large size of the anion,

(iii) cations with 18 electron structures, i.e. novel-gas configuration. Noble gas configuration of the cation produces better shielding and less polarizing power.

Examples: Development of covalent character with increase of cation charge (high charge on ions)

Compound	Melting point (°C)
NaBr	755
$MgBr_2$	700
$AlBr_3$	97.5

Examples: Decrease of covalent character with increase of cation radius

Compound	Radius of cation (nm)	**Melting point (°C)**
$BeCl_2$	0.031	405
$MgCl_2$	0.065	712
$CaCl_2$	0.099	772
$SrCl_2$	0.113	872
$BaCl_2$	0.135	960

Examples: Development of covalent character with increase of anionic radius

Compound	Radius of cation (nm)	**Melting point (°C)**
CaF_2	0.136	1392
$CaCl_2$	0.181	772
$CaBr_2$	0.195	730
CaI_2	0.216	575

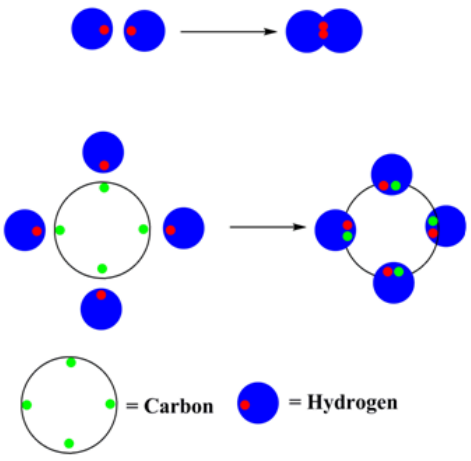
The covalent bond:

A covalent bond is a chemical bonding formed by sharing of pairs of electrons between two atoms.

Lewis Theory (Octet rule):

Rule: A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are shared. Thus, an atom continues to form bonds until an octet of electrons is made. This is known as octet rule by Lewis.

Example:



(i) Normally two electrons pairs up and forms a bond. Ex: H_2

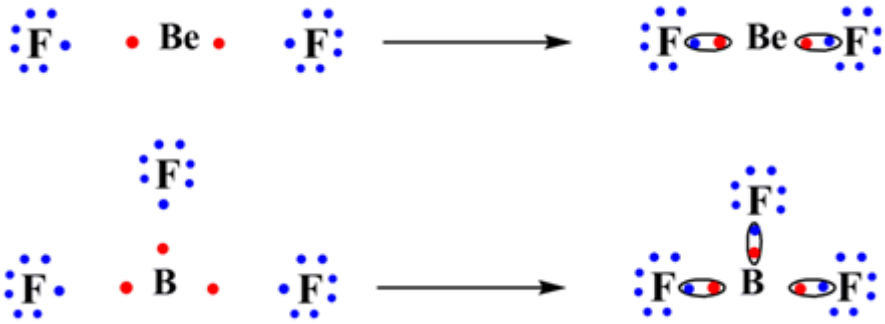
(ii) For most atoms there will be a maximum of eight electrons in the valence shell (octet structure). Ex: CH_4

Exception of the octet rule:

(A) PF 3 maintains octet rule, while PF 5 does not. PF 5 has ten outer electrons.

(B) Molecules comprised of odd number of electrons do not follow octet rule. Ex: NO, ClO_2 , etc. This rule even does not explain the origin of paramagnetic character in O_2 molecule.

(C) For atoms like Be and B which have less than four outer electrons. Even if all the outer electrons used to form bonds an octet will not be resulted for Be and B.



The octet rule has been further extended to include the exceptional part. Hence, the following rules are added to the octet rules.

(iii) For elements with available *d* orbitals, the valence shell can be expanded beyond an octet.

This rule explained the formation of PF 5 . Here P has low-energy *d* orbitals.

(iv) The molecule will seek the lowest overall energy. This means the maximum number of bonds will form, that the strongest possible bonds will form, and that the arrangement of the atoms in molecule will be in such as to minimize adverse repulsion energy.

Valence Bond Theory:

Atoms containing unpaired electron(s) tend to combine with other atom(s) which also possess(es) unpaired electron(s). In this process unpaired electron(s) paired up and attained a stable noble gas configuration. Two electrons shared by two atoms constitute a bond. The number of bonds formed by an atom is same as the number of unpaired electrons in the ground

state (lowest energy state). However, in some cases the atom may form more bonds than that of its acquired unpaired electron. This takes place by the excitation of an atom that promotes paired-electrons in the ground state to the excited state in a suitable empty orbital as unpaired electron.

The shape of a molecule is preliminary determined by the direction in which the participating orbitals point. Electrons in the valence shell of the original orbital are known as lone pairs.

A covalent bond is resulted by pairing of electrons from each atom. In this case the spin of the electrons must be opposite to each other.

Limitations:

(i) Relative stability of different molecules cannot be explained.

(ii) Paramagnetic nature of complexes or molecules cannot be explained.

(iii) Different shape of molecules cannot be explained.

Hybridization:

Hybridization is the mixing of atomic orbitals prior to overlap that change the partial distribution of orbitals.

Due to this hybridization mainly two different kind of bonds forms, (i) sigma (σ) and (ii) pi (π) bond.

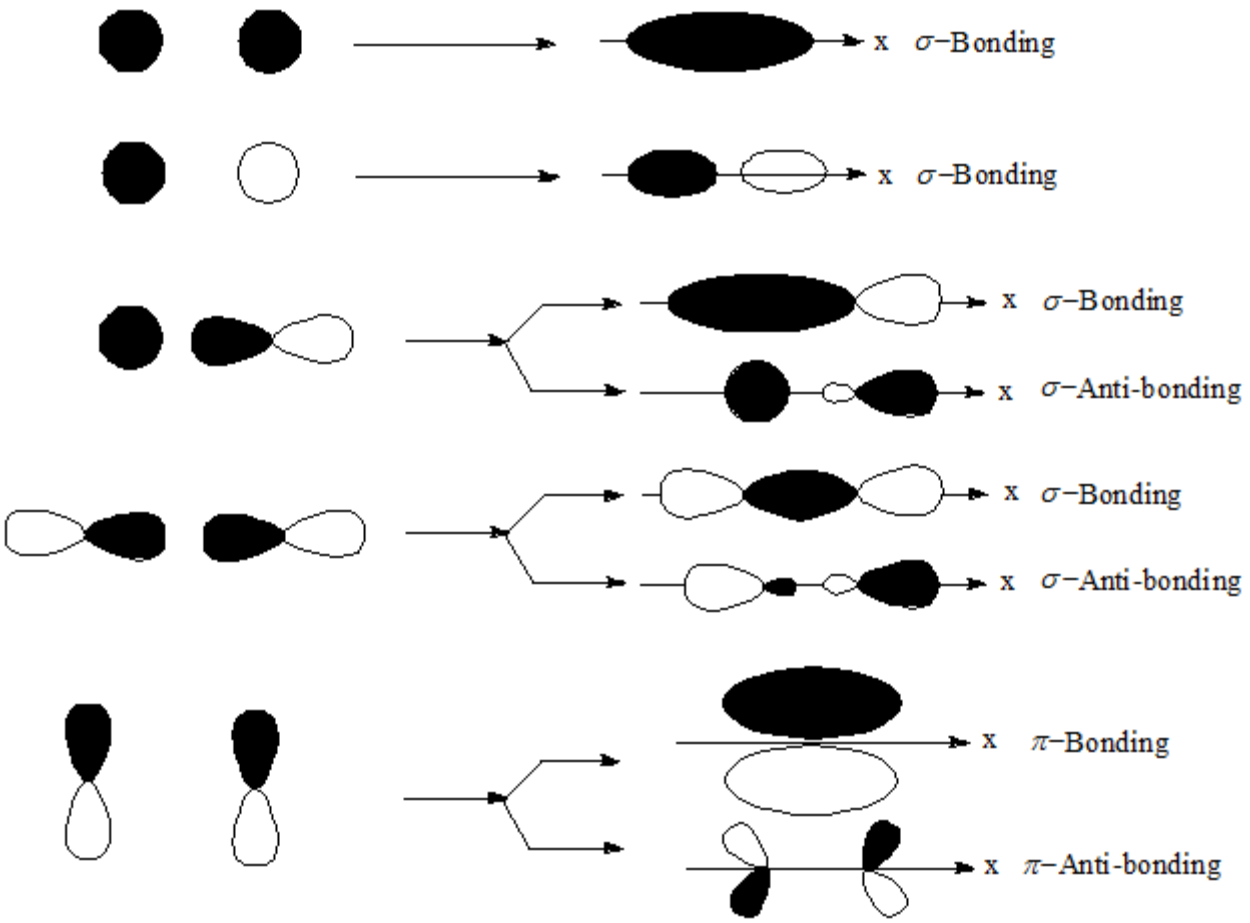


Figure: Sigma (σ) and pi (π) bonding and anti - bonding by the combination of s and p orbitals.

Sigma (σ) bond: A covalent bond established between two atoms having the maximum density of the electron cloud along the axis connecting the centers of the two participating atoms is called sigma (σ) bond.

Pi (π) bond: A bond is formed by the lateral overlap between two atomic orbitals possessing maximum electron density on both sides of the overlapping axis is known as pi (π) bond.

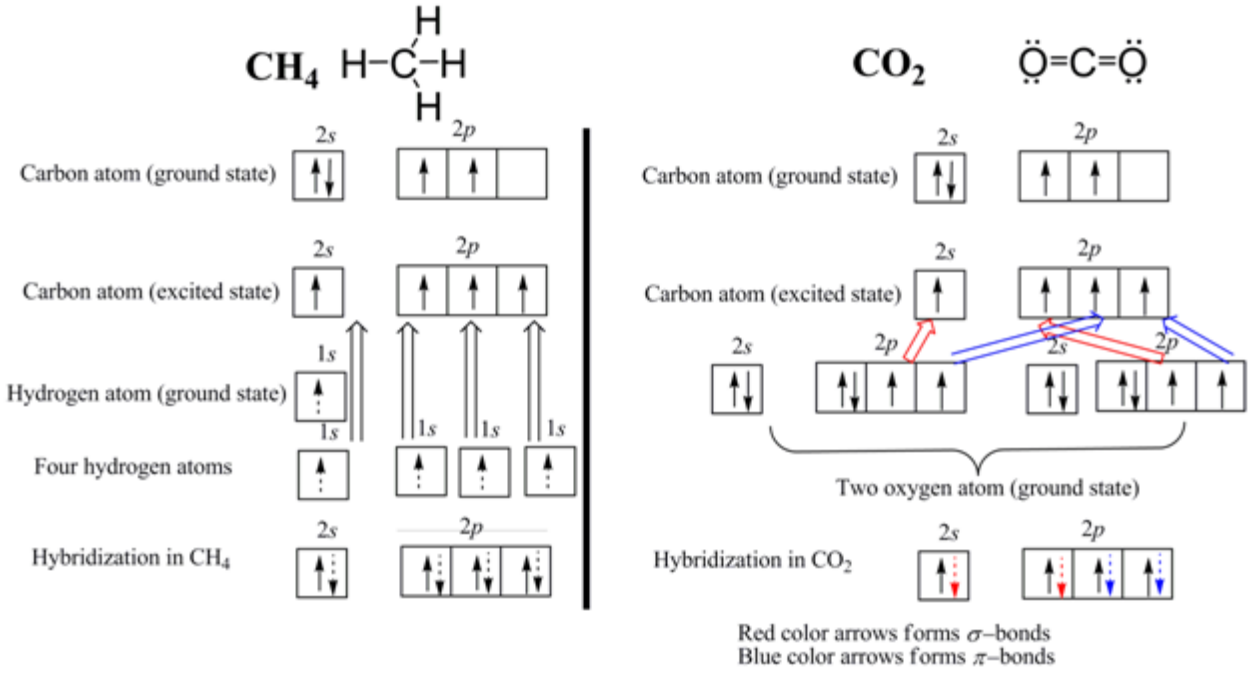
Therefore, from the definition it is clear that sigma (σ) bonds are more strong than pi (π) bonds.

Sigma (σ) bonds may arises from the overlap between s, p, and d orbitals, like (i) *s* - *s* orbitals, (ii) *s* - *p* prbitals, (iii) *p* - *p* orbitals, (iv) *s* - *d* orbitals, so on.

s orbitals are spherical, while p , d orbitals are dumbbell shaped. Hence, *s* - *s* over lap is weaker compared to *s* - *p* , *p* - *p* overlaps.

**Herein, it is important to note that due to hybridization of two atomic orbitals two molecular orbitals formed. One is called bonding orbital and the other is called anti - bonding orbital. Hence, *n*number of atomic orbitals forms *n* /2 bonding and *n* /2 anti - bonding orbitals.

Examples:



In the formation of CH_4 one s orbital and three p orbital of the central carbon atom participate.

Similarly, in the CO_2 molecule one *s* orbital and three *p* orbital of the central carbon atom participate but here two *p* orbitals of carbon atom forms two π - bonds. Therefore, CH_4 is sp^3hybridized and CO_2 is sp^2 hybridized.

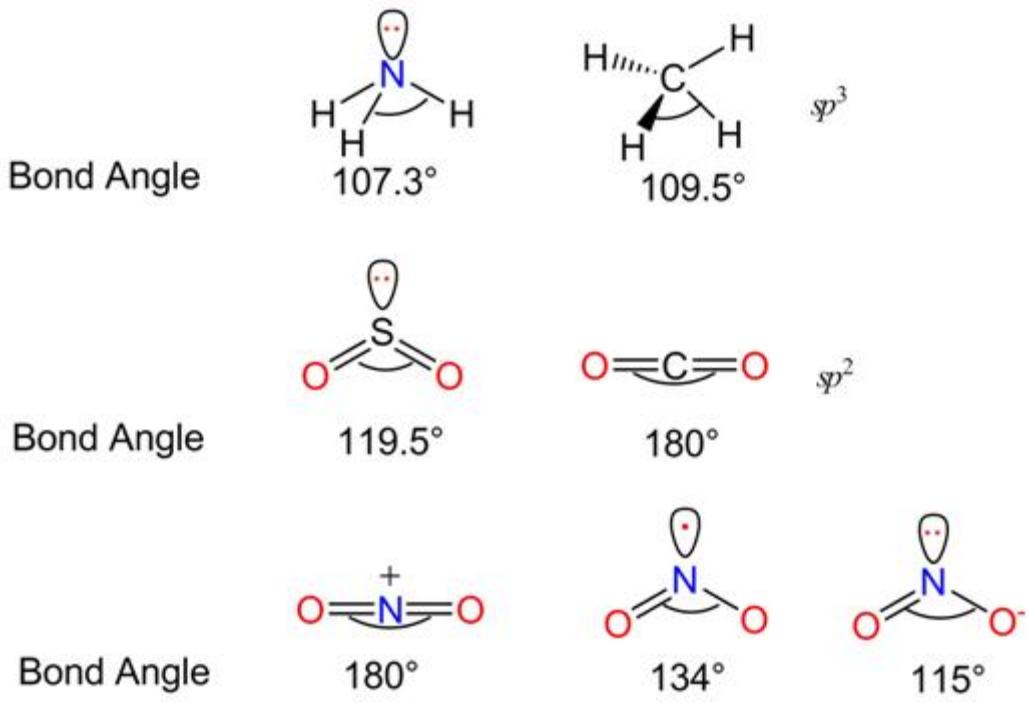
Hybridization	Geometry	Angles(deg)	%*s*, %*p*, and %*d* character
sp	Linear	180	50, 50, and 0
sp^2	trigonal planar	120	33, 67, and 0
sp^3	tetrahedral	109.5	25, 75, and 0
sp^3d	trigonal bipyramidal	90, 120, and 180	20, 60, and 20
sp^3d^2 *or* d^2sp^3	octahedral	90, and 180	16.67, 50, and 33.33

Different molecules having same hybridization but acquire different shape. To explain these phenomena in 1957 Gillespie and Nyholm provided a theory that is known as Valence Shell Electron Pair Repulsion Theory (VSEPR theory).

Valence Shell Electron Pair Repulsion (VSEPR) Theory:

(i) Lone pairs of electrons (lp) repel each other more strongly than that of bond pair (bp) of electrons. The decreasing order of repulsion is lp - lp > lp - bp > bp - bp.

Examples:



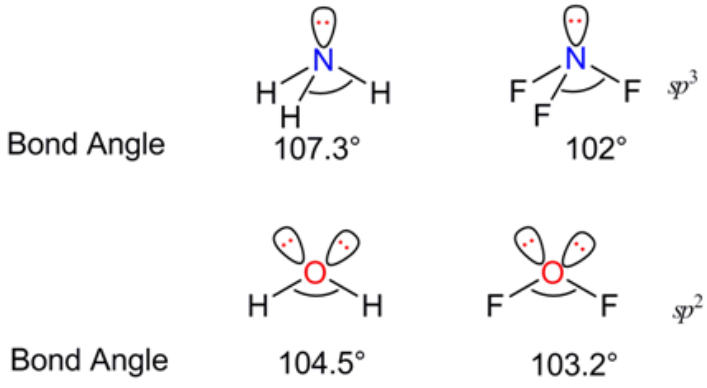
In CH_4 only bp-bp repulsion exist while, in NH_3 two types of repulsive force present, lp - bp repulsion and bp - bp repulsion. lp - bp repulsion dominates over bp - bp repulsion. Because of this the bonds in NH_3 is more compressed than that in CH_4 which provides lower band angle in NH 3 .

In CO_2 the central C atom does not occupy any lone pair of electron, hence in CO_2 only bp - bp repulsion exists. The central S atom in SO_2 contains one lone pair of electron. Therefore, in SO_2 lp - bp repulsion and bp - bp repulsion present. As we know that lp - bp repulsion dominates over bp - bp repulsion, the O-S-O bonds is compressed by dominating lp - bp.

NO_2^+ does not contain any paired or unpaired electron on the central N atom. Here, only bp - bp repulsion exists. In NO_2 the central N atom contains one unpaired electron, while in NO_2^- the N atom contains one lone pair of electrons. As in NO_2 only one unpaired electron present, the lp - bp repulsion is lower compared to lp - bp repulsion in NO_2^- . Hence, the dominating lp - bp is more pronounced in NO_2^- compared to NO_2 .

(ii) Repulsion between bond pairs decreases as the electronegativity of the atom bound to the central atom increases.

A bond is formed by the sharing of electrons. When the difference in electronegativity between the two connecting atoms increases the electron pair is shifted towards the more electronegative atom. With increases of electronegativity this shift is more to the electronegative atom. This decreases the repulsion effect between two bond pairs.



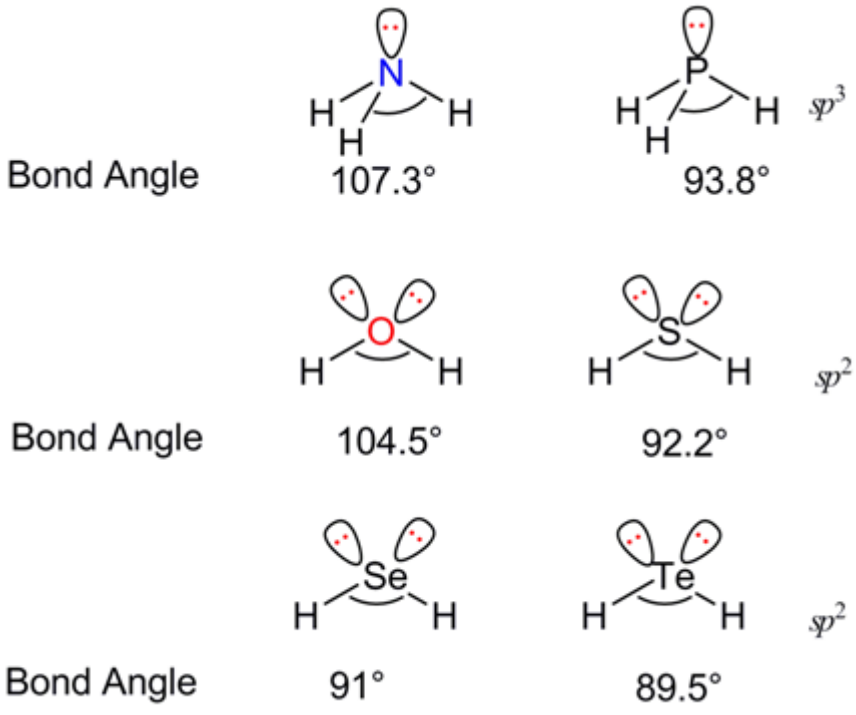
F is more electronegative that that of H. Therefore, compared to NH_3 , in NF_3 the bond forming lone pair of electron is more shifted to the F atom. This decreases bp - bp repulsion. Therefore, in NF_3 the lp - bp repulsion is more predominating that that of NH_3 and makes F-N-F bond angle 102° compared to H-N-H bond angle 107.3° .

Same (above) argument is valid for having higher H-O-H bond angle in H_2O compared to F-O-F bond angle in OF_2 .

(iii) Electronpairs in filled shell repel stronger that electronpairs in incomplete shell.

When the electron pair containing atom contains low-energy lying suitable vacant orbitals the electron pair of electrons can undergoes diffusion to the vacant orbitals. Hence, the lp - bp repulsion diminishes dramatically and bp - bp repulsion dominates. In this case, the bond angles around the central metal increase.

Example:

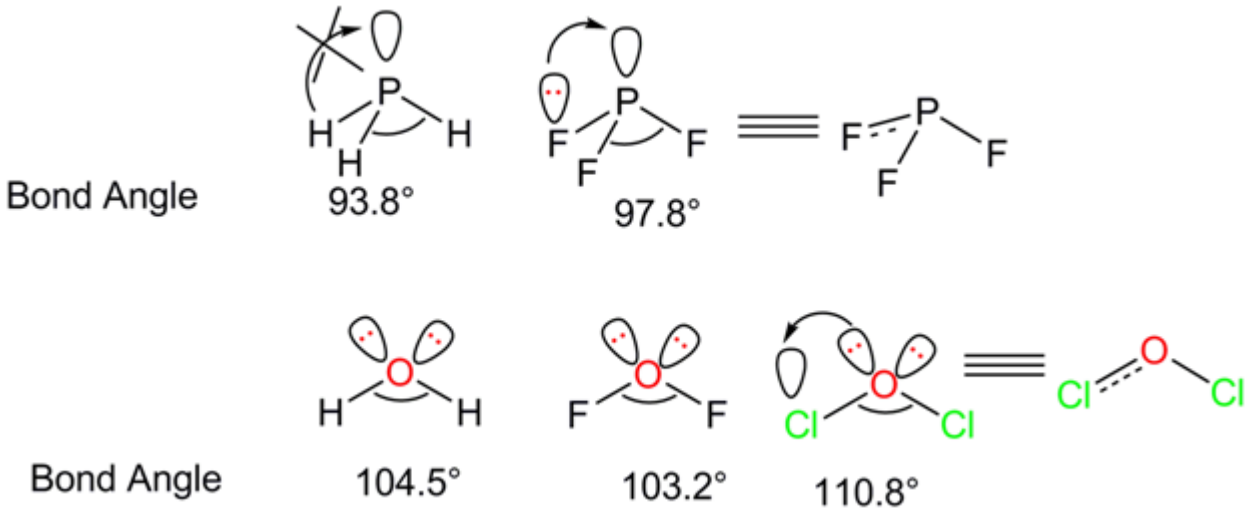


On going from O to Te the size of the central atom increases. Therefore, diffusion is more predominating which further decreases lp - bp repulsion.

(IV) Lone pair of electron can be transferred from a filled shell to a energetically suitable empty shell of the other bonded atom.

Due to transfer of lone pair of electron the bond accumulate some sort of double bond character. This enhances the bp - bp repulsion and consequently, causing a bigger bond angle.

Example:



P and Cl contain low-lying vacant *d* orbitals. Lone pair of electron from the filled orbitals of F or O can be transferred to the vacant orbital. This causes a partial - multiple bond that enhances the bp - bp repulsion. Hence, the bond angle increases.

(V) Multiple bond orbitals repel each other more strongly than single bond orbitals.

Examples:

O = PF_3 (F-P-F bond angle = 103°), while in O = PBr_3 (Br-P-Br bond angle = 108°)

Molecular Orbital Theory (MO-theory):

In the Valence bond theory, the individuality of atomic properties of the constituting atoms forming a molecule is retained too some extent. Whereas, in the molecular orbital theory it is

considered that molecular orbitals are formed by the linear combination of the two constituting atomic orbitals´ wave functions.

Let us consider, ψ(A) and ψ(B) are two atomic orbitals which are combining to form molecular orbitals for A - B bond. Molecular orbitals will also be wave functions anf they can be represented as;

$$\psi(MO_b) = \psi(A) + \psi(B);\ y\ (MO_b) = \text{bonding MO wave function}$$

and

$$\psi(MO_{ab}) = \psi(A) - \psi(B);\ \psi(MO_{ab}) = \text{anti-bonding MO wave function}$$

Conditions for the favorable combination of atomic orbitals:

(A) Atomic orbitals must have comparable energies.

(B) They must have comparable energies.

(C) They must have same symmetry with respect to the bonding molecular axis, *i . e .* if the atomic orbitals are perpendicular to each other there will be no overlap or linear combination between them.

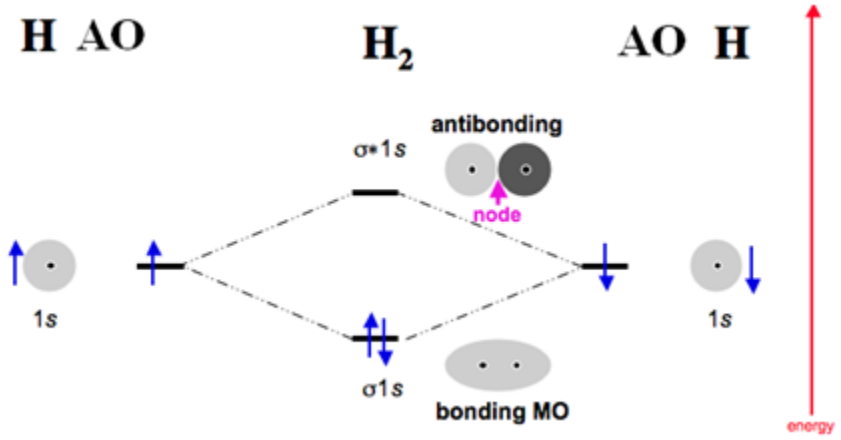
Bond order:

Bond order (BO) of a bond is defined as;

BO = [No of electron in bonding MO - no of electron in anti - bonding MO]/2

Starting from hydrogen to fluorine atom the energy difference between the 2 *s* and 2 *p* orbitals increases due to increase in electronegativity. It is important to note that up to nitrogen, the energy difference between the 2s and 2p orbital is sufficient for *sp* type hybridization. Therefore, up to nitrogen nitrogen molecule the energy level follow the order 1σ , 1σ *, 2π , 2σ , 2σ *, 2π * (i.e. energy of 2σ *> 2π*) and for oxygen and nitrogen molecules the order is 1σ , 1σ *, 2σ , 2π , , 2π *, 2σ *are (i.e. energy of 2σ *<2π *).

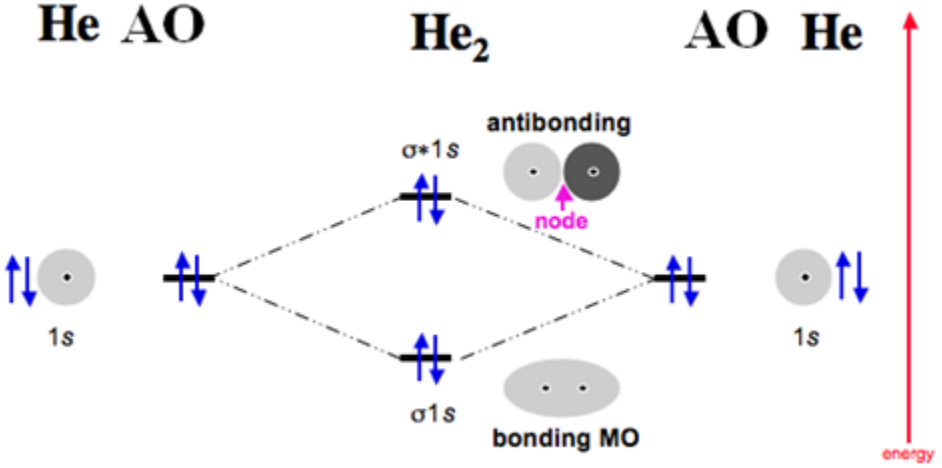
MOs of H_2 Molecule:



Bond Order = [2-0]/2 = 2/2 = 1

Here * represents anti-bonding orbital.

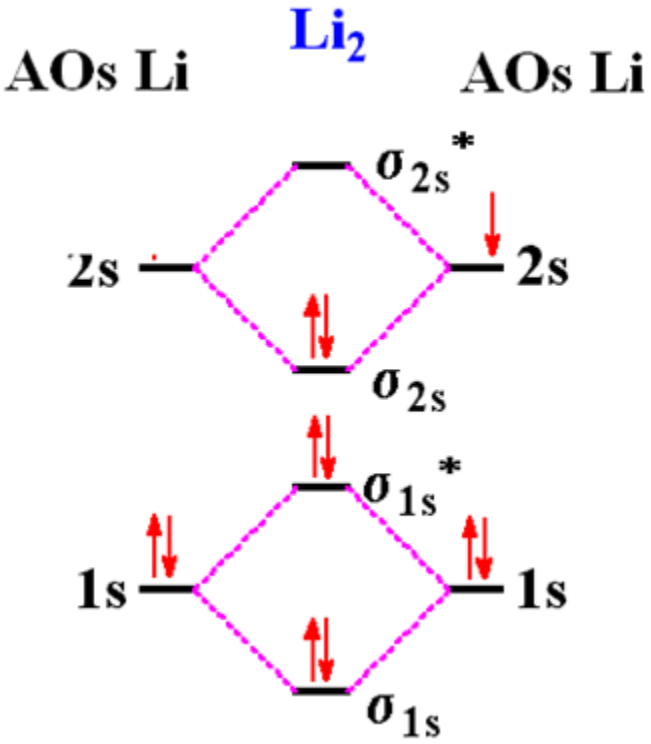
MOs of He_2 Molecule:



Bond Order = [2-2]/2 = 0/2 = 0.

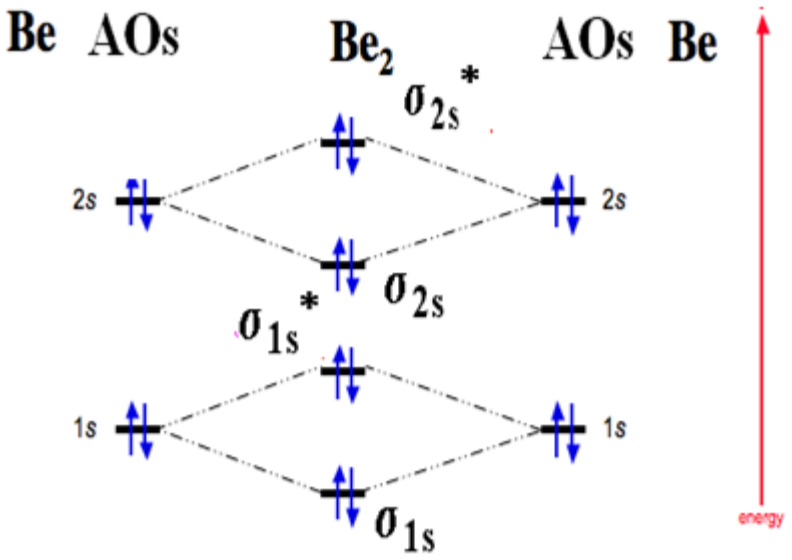
As the BO is zero, there is no bond between He 2 molecule. This means He is monoatomic molecule.

MOs of Li_2 Molecule:



Bond Order = [4-2]/2 = 2/2 = 1

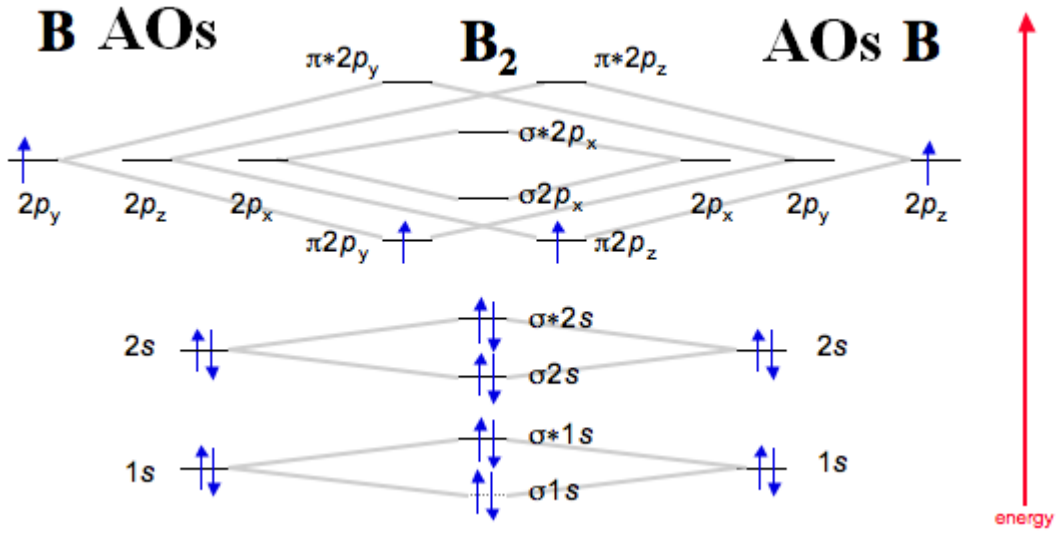
Os of Be_2 Molecule:



Bond Order = [4-4]/2 = 0/2 = 0

That is no bond between Be atom. Be molecule is monoatomic.

MOs of B_2 Molecule:



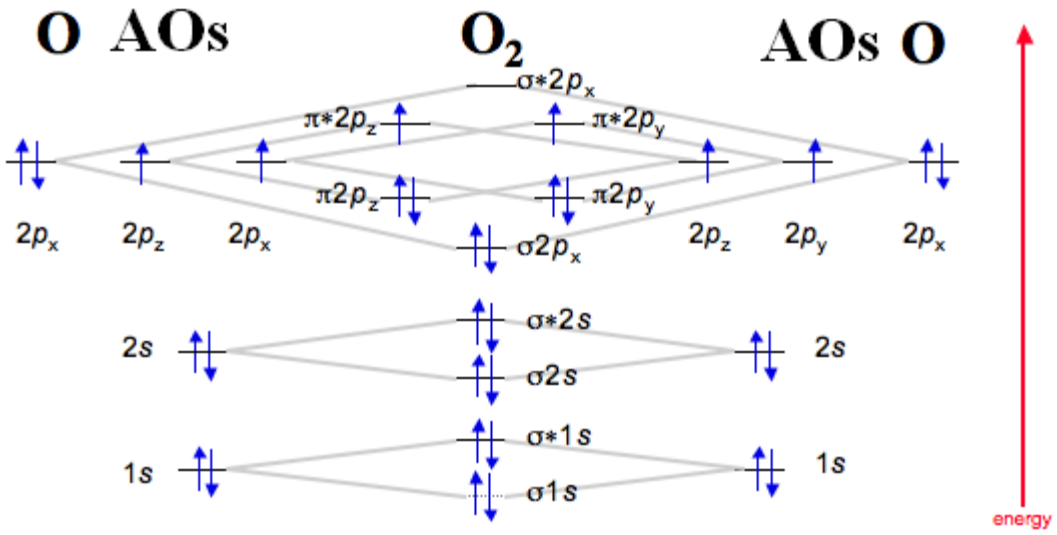
Bond Order = [6-4]/2 = 2/2 = 1

Carbon and nitrogen have same MO energy distribution as in B_2 .

In Carbon and nitrogen the electron distributions in MO are;

	Carbon	**Nitrogen**
σ1S	2	2
σ*1S	2	2
σ2S	2	2
σ*2S	2	2
$\pi 2p_y$	2	2
π2pz	2	2
$\sigma 2P_x$	0	2
Bond order	[8-4]/2 = 4/2 = 2	[10-4]/2 = 6/2 = 3

MOs of O_2 Molecule:



Oxygen, fluorine and neon have same MO energy distribution.

	Oxygen (O_2)	**Fluorine (F_2)**	**Neon (Ne)**
$\sigma 1S$	2	2	2
$\sigma^* 1S$	2	2	2
$\sigma 2S$	2	2	2
$\sigma^* 2S$	2	2	2
$\sigma 2P_x$	2	2	2
$\pi 2p_y$	2	2	2
$\pi 2p_z$	2	2	2
$\pi^* 2p_y$	1	2	2
$\pi^* 2p_z$	1	2	2
$\sigma^* 2P_x$	0	0	2
Bond order	[10-6]/2 = 4/2 = 2	[10-8]/2 = 2/2 = 1	[10-10]/2 = 0/2 = 0

Note.

1. In O_2 molecule each $\pi^* 2p_y$ and $\pi^* 2p_z$ contains one unpaired electron. Therefore O_2 is paramagnetic.

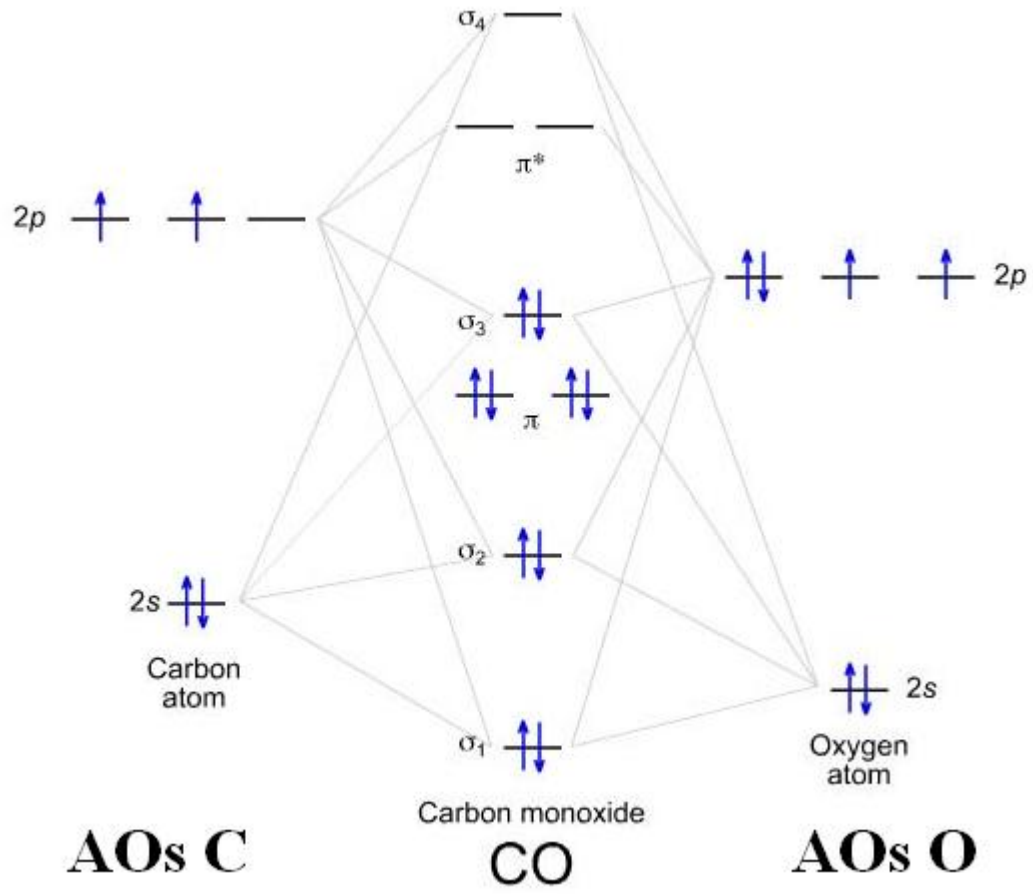
2. If O_2 is oxidized to O_2^+ , the one electron is removed from a π^* orbital which is anti - bonding orbital. Therefore, the bond order increases, [10-5]/2 = 5/2 = 2.5.

3. If O_2 is reduced to O_2^- , the one electron is added to a π^* orbital which is anti - bonding orbital. Therefore, the bond order decreases, [10-7]/2 = 3/2 = 1.5.

4. If N_2 is oxidized to N_2^+ , the one electron is removed from a π orbital which is bonding orbital. Therefore, the bond order decreases, [9-4]/2 = 5/2 = 2.5.

5. If N_2 is reduced to N_2^- , the one electron is added to a π^* orbital which is anti - bonding orbital. Therefore, the bond order decreases, [10-5]/2 = 5/2 = 2.5. This fact indicates that the bond distance between two N atoms in N_2^+ or N_2^- is same.

MOs of CO:



Here the energy of *p* and *s* atomic orbitals of C is higher than that of O. When the electronegativity of an atom increases, effective nuclear charge also increases and hence, energy decreases. Oxygen is more electronegative that carbon. Therefore, the energy of *p* and *s* atomic orbitals of O is lower than that of C. It is also important to note that the energy gap between the *s* and *p* orbitals increases with increase of effective nuclear charge.

MOs of HF Molecule:

The electronic of hydrogen and fluorine are $1s^1$ and $1s^2 2s^2 2p^5$ respectively. In the formation of HF molecule ,only 2p electrons of fluorine atom would combine effectively with the solitary electron of hydrogen atom. As has been already explained ,only a pz orbital is able to combine with s orbital. The combination of px or py orbital with s orbital is ruled out on symmetry

consideration. The 2pz orbital of fluorine gives a highly effective overlap with the s orbital of hydrogen to form σ(sp) bonding molecular orbital and σ*(sp) antibonding molecular orbital .The bonding molecular orbital is fully filled with two electrons .The rest of the electrons remain in their atomic orbitals. The molecular orbitals formed in the case of HF molecule will not be symmetrical. The symmetry occurs because the energies of H(1s) and F(2pz) atomic orbitals are not the same.Molecular orbital diagram for HF molecule is given as.

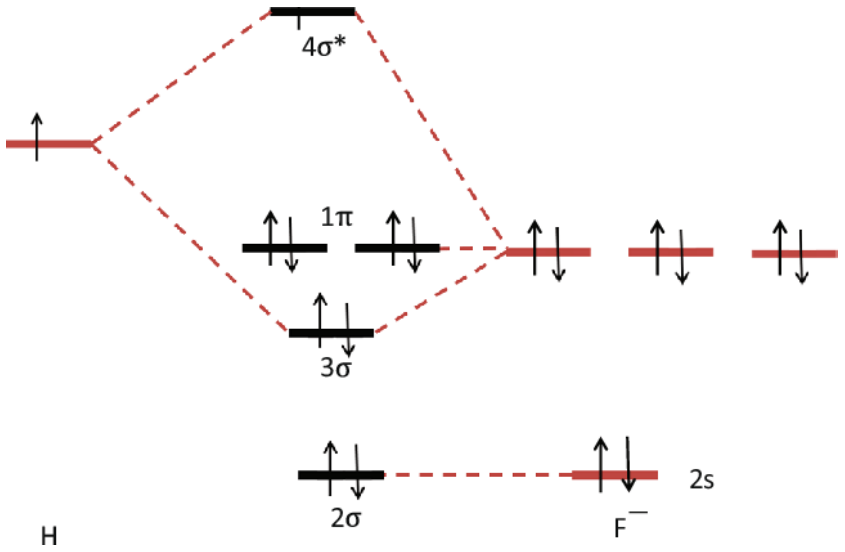


Figure: MO diagram of HF molecule

The carbon dioxide MO diagram is based on a C atom and an O--O ligand fragment. Carbon has 2S and $2P_{x,y,z}$ orbitals and the O--O fragment has 2S and $2P_{x,y,z}$ orbitals that are involved in the formation of molecular orbitals. Since CO_2 has $D_{\infty h}$ symmetry the central atom's orbital symmetry lables can be obtained from the corresponding point group table: $2S=\sigma_g$, $2P_z=\sigma_u$ and $2P_{x,y}=\Pi_u$. The LGO symmetry lables can be calculated using the point group table as well: $\Gamma_\sigma=2\sigma_g + 2\sigma_u$ and $\Gamma_\pi=2\Pi_g + 2\Pi_u$. The MO diagram for CO_2 is more complicated than the diagram for B_2. The follwing diagram fails to label orbital symmetries but the LGO $2P_{x,y}$ particpate in the formation of π double bonds. The $2\Pi_g$ orbiatls are nonbonding because the C $2P_{x,y}$ atomic orbitals are Π_u. The LGO $2P_z$ orbitals are involved in σ bonds.

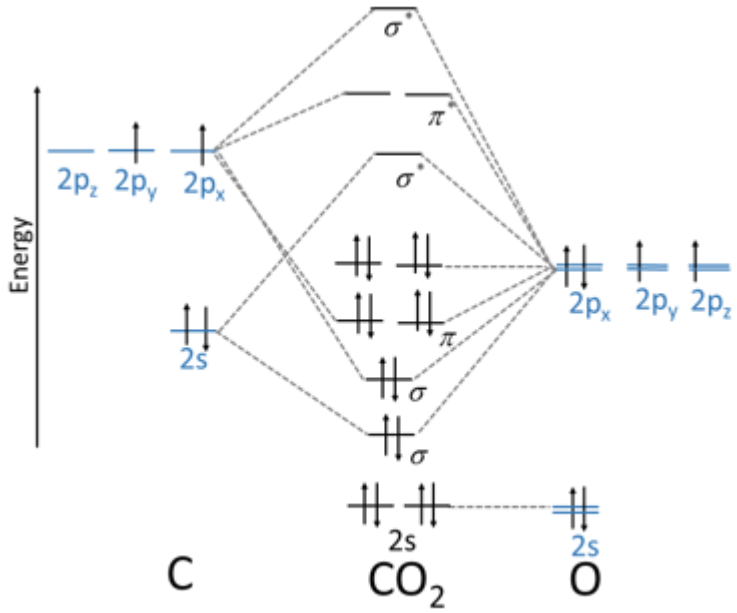


Figure: MO diagram of CO_2 molecule