Periodic properties

Periodic properties

1. Periodic table
2. Periodic properties
3. Periodicity
4. Cause of periodicity

Periodic table : . Periodic table is defined as the tabular, arrangement of elements in horizontal rows (periods) and vertical columns (groups).

1. In the periodic table, we have 118 elements, either synthetic or normal.
2. In the whole periodic table, J alphabet is not used.
3. The periodic table which is used by most of the scientist and institute in the present time is given by Henry Moseley in 1915. This table is extended form of periodic table given by Mendeleev.
4. According to modern periodic law, the physical and chemical properties of the elements, are a periodic function of their atomic numbers.

Periodic properties: the properties which are directly or indirectly related to electronic configuration of elements and show a regular variation when we move from left to right i.e. along a period or top to bottom i.e. down the group in the periodic table.

Some of the properties which are directly related to electronic configuration are effective nuclear charge, atomic radii, electron affinity, ionisation, energy, and electron negativity

Some of the properties which are indirectly related to electronic configuration are melting point, boiling point and density .

Division of elements in periodic table

1. **s Block elements**: elements in which the last electron enters the s orbital of the respective outer most shell or called s Block elements. s subshell has only one orbital which can accommodate only two electrons. Therefore there are only two groups of s Block elements.

   Electronic configuration $= ns^{1-2}$

2. **p Block elements**: elements in which the last electron enters any one of the 3p orbital of the respective outer most shell or called p block elements. p subshell has three degenerate P orbital each one of which can accommodate two electrons

   Electronic configuration $= ns^2 np^{1-6}$

3. **d Block elements**: elements in which the last electron enters any one of the five d orbital of the respective shells are called d block elements. Since the sub shell has five d orbitals each one of which can accommodate two electrons there for in all there are 10 vertical column that is 10 groups

   Electronic configuration $= ns^{1-2} np^6 (n-1)d^{1-10}$

4. **f Block elements**: elements in which the last electron enters anyone of the seven f orbital of their respective antepenultimate shell or called f block elements.

In all these element, the s orbital of last shell is completely filled. The d orbital of penultimate (n-1) shell invariably contains zero or one electron, but the f orbital of antepenultimate (n-2) gets progressively filled in this

Electronic configuration $=(n-2)f^{1-14}(n-1)d^{0-2} ns^2$

Effective nuclear charge: effective nuclear charge is also abbreviated as ENC. It is defined as the net positive charge experienced by the valance electron with nucleus.

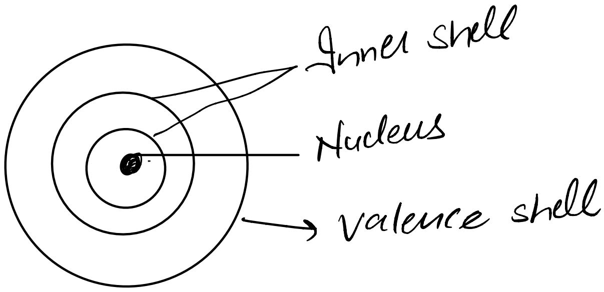
It can be represented by Zeff

Zeff = Z-S

Zeff= effective nuclear charge

Z= atomic number

S= shielding electron (inner shell electron)



Shielding effect or screening effect:

The repulsive force felt by the valance shell electron from the electrons present in inner shell is called shielding effect, or screening effect.

Penetration of electron : the ability of an electron to get close to the nucleus is known as penetration of electron. The electron in different orbital have different penetration effect and even electrons present in same shell differ in the penetration effect of their sub shell.

s>p>d>f penetration Power

[for same value of n]

' Slater's rule for effective nuclear charge

Target e-	(n)	(n-1)	(n-2)	(n-3).....
s/p orbital	0.35	0.85	1	1
d/f orbital	0.35 only for d e- others 1.	1	1	1

Ex:1 H $1s^1$

$$Z_{eff} = Z - \sigma$$
$$= 1 - 0$$
$$= 1 - 0$$
$$= 1$$

* for 1s electron $\sigma = 0.30$ (2 e^- system)

Ex:2 He $Z = 2$ $1s^2$

$$Z^* = Z - \sigma$$
$$= 2 - 0.30$$
$$Z_{eff} = 1.70$$

Ex:3 Be $\underset{(n-1)}{1s^2}\ \underset{(n)}{2s^2}$ $Z = 4$

$$Z_{eff} = Z - [(0.35 \times 1) + 0.85 \times 2)]$$
$$= 4 - 2.05$$
$$= 1.95$$

Ex:4 Ne $1s^2 2s^2 2p^6$

$$Z_{eff} = Z - [(0.35 \times 7) + (0.85 \times 2)]$$
$$= 10 - 4.15$$
$$= \underline{5.85}$$

Ex:5 $Rb = \underbrace{1s^2}_{(n-4)}\ \underbrace{2s^2\ 2p^6}_{(n-3)}\ \underbrace{3s^2\ 3p^6\ 3d^{10}}_{(n-2)}\ \underbrace{4s^2\ 4p^6}_{(n-1)}\ \underbrace{5s^1}$

$$Z_{eff} = Z - \sigma$$
$$= 37 - [0.85 \times 8 + 1 \times 28]$$
$$= 37 - [34.80]$$
$$= 2.20$$

Ex: 6

$$Ti^{\circ} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$$

$$\downarrow$$

$$\underbrace{1s^2}_{[n-3]}\ \underbrace{2s^2\ 2p^6}_{[n-2]}\ \underbrace{3s^2\ 3p^6\ 3d^2}_{[n-1]}\ \underbrace{4s^2}_{n}$$

for target e^- in $4s^2$ ↓

$$Z_{eff} = 22 - [1 \times 0.35 + 10 \times 0.85 + 1 \times 10]$$

$$= 22 - 18.85$$

$$= 3.15$$

for target e^- in $3d^2$

$$\underbrace{1s^2}_{(n-2)}\ \underbrace{2s^2\ 2p^6}_{(n-1)}\ \underbrace{3s^2\ 3p^6}_{\longrightarrow}\ \underset{\overset{\downarrow *}{n}}{3d^2}\ 4s^2$$

$$Z_{eff} = 22 - [1 \times 0.35 + 18 \times 1]$$

$$= 22 - 18.35$$

$$Z_{eff} = 3.65$$

Z_{eff} more for e^- in 3d orbital than 4s

Periodic trends of effective nuclear charge in the periodic table

Effective nuclear charge increases as we move from left to right in the periodic table i.e. in periods.

Effective nuclear charge decreases as we move down in the periodic table i.e. in groups.

Left to Right ↑

Top to Bottom ↓

Atomic radii: atomic radii is defined as the distance from the centre of the nucleus to the outer most shell containing the electrons

Or

If the atom is considered to be a sphere, the atomic radius is equal to the radius of the sphere .

It is denoted by r

Unit is picometers

Difficulties in determining atomic radii:

1. The exact size of the electron cloud cannot be determined as the probability of finding an electron even at large distances from the nucleus never become zero.
2. It is not possible to isolate a single atom for the purpose of determination of its radius
3. Atomic radii also changes when the atom is present in different orders states.

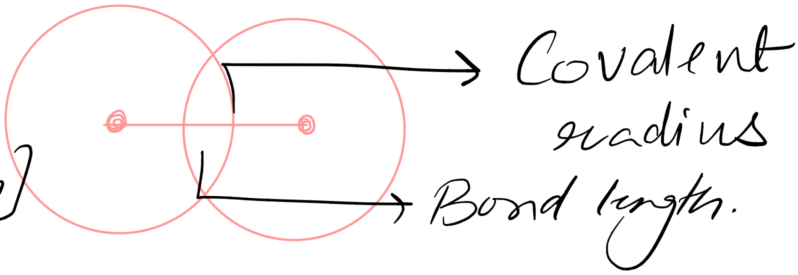
Types of atomic radii : atomic radii cannot be determined very precisely, so there are some operational definition for the radius of atom or ions. These are:

1. Covalent radii.
2. Vanderwall radii
3. Ionic radii

Covalent radii: it is defined as one half of the distance between the nucleus of ' two covalently bonded atoms of some element in a molecule.

$$r_{covalent} = \frac{1}{2}[\text{Internuclear distance})$$

$$r_{covalent} = \frac{1}{2}[\text{Bond length}]$$

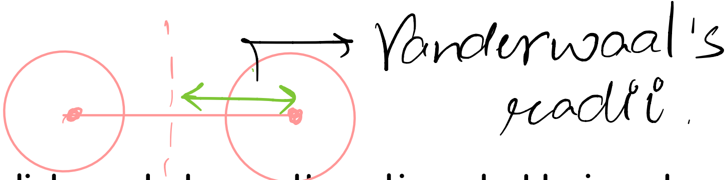


If hydrogen molecule have internuclear distance, 74 picometer, then covalent radii:

$$r_{covalent} = \frac{1}{2}[\text{Internuclear Distance}]$$
$$= \frac{1}{2}[74]$$
$$= 37\,pm$$

So covalent radius of hydrogen is 37 picometer

Vander walls radii : it is defined as one half of the distance between the nucleus of two non-bonded isolated atoms or two adjacent atoms belonging to 2 neighbouring molecules of an element in solid state.



For example, The internuclear distance between the adjacent chlorine atoms of the two neighbouring molecule in the solid state is 360 picometer. So Vander walls radius of chlorine atom is 180 picometer.

Note, Vander walls radii are always larger than the covalent radii.

Ionic radii: it is the radius of ions in an ionic crystal. It is defined as the effective distance from the nucleus of the ion up to which it has an influence in the ionic bond.

For example, atomic radius of sodium is 154 picometer and it's cation is 94 picometer

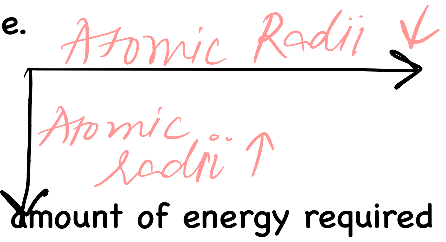
And chlorine is 99 picometer and it's anion is 150 picometer

In general, atomic radius of cation is smaller than the neutral, whereas atomic radius of anion is larger than the neutral atom.

Anion formed by gain of electron in neutral atom. This is the reason why anion is larger than the neutral atom where is cation is always smaller than their parent atom because they have lesser electron then neutral atom.

Periodic trends of atomic radii in the periodic table

Atomic radii decrease as we move from left to right in the periodic table and it increases as we move down in the periodic table.



Ionisation energy (ionisation potential)

Ionisation energy of an element is defined as the amount of energy required to remove the most loosely bounded electron from an isolated gaseous atom.

The ionisation energy gives the measure of ease with which an atom can lose electrons and change into a cation.

$$\underset{\text{Neutral gaseous atom}}{X_{(g)}} + \underset{\text{Energy}}{I.E.} \longrightarrow \underset{\text{cation}}{X^{+}_{(g)}} + \underset{\text{electron}}{e^{-}}$$

The first ionisation energy IE1 is the energy required to remove the first electron from the atom. The second ionisation energy IE2 is the energy required to remove the second electron from the positive ion of the atom and so on.

It is also known as ionisation potential as it is measured as amount of potential required to remove most loosely bound electron from gaseous atom.

It leads to formation of cation.

Its unit is kilo joule/mole

Factors affecting ionisation potential: it is affected by following factors

1. Size of atom: ionisation energy decreases with increase in size of an atom

   $Size \propto \frac{1}{I.E.}$

2. Charge on the nucleus: The attractive force between nucleus and the electron increases with increase in nuclear charge. This is because force of attraction is directly proportional to product of charge on nucleus and that on the electron therefore with increasing nucleus charge, it is more difficult to remove electron and ionisation energy increases.

   $Nuclear\ charge \propto I.E.$

3. Penetration effect: for a multi electron atom, the electron in the s orbital have maximum probability of being near the nucleus and this probability goes on decreasing in case of p, d and f orbital. Hence, the ionisation energy is greater for s as compare to p, d and f orbitals.

   $\underleftarrow{s > p > d > f}\ I.E.$

4. Electronic configuration: ionisation energy for completely filled, and half filled configuration, have unexpected value as compare to normal trend in periodic table. The noble gases have highest ionisation energy due to stable configuration. From beryllium to Boron, there is slightly decrease in energy due to stable configuration of beryllium.

As we move from nitrogen to oxygen, oxygen have lower ionisation energy than nitrogen.

$N_7 = 1s^2 2s^2 2p^3$

$O_8 = 1s^2 2s^2 2p^4$

In general along the period, ionisation energy increases, whereas down the group ionisation energy decreases.,

Vari'ation of ionisation energy in periodic table:

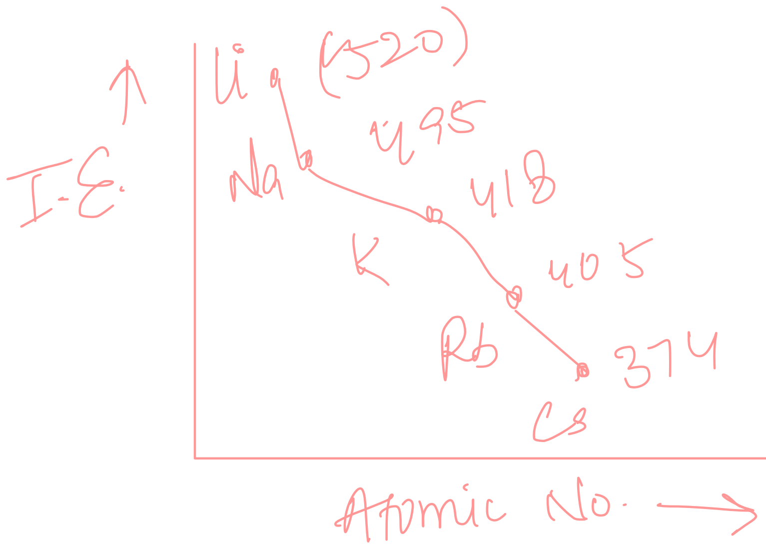
Ionisation energy of beryllium is greater than boron :

Although the nuclear charge of beryllium is greater than boron, yet ionisation, energy of beryllium, is greater than boron. This is due to fact that the electronic configuration of boron is '$1s^2 2s^2 2s^1$ is less stable than beryllium $1s^2 2s^2$ Which has completely filled orbital. In boron last electron goes to 2P orbital as a result to P. Electron of boron is not tightly bound by the nucleus as twice electrons of beryllium. Hence ionisation energy of boron is less than that of beryllium.

When we move from nitrogen to oxygen ionisation energy of nitrogen is more than that of oxygen. Why?

Although the nuclear charge of nitrogen is slightly greater than oxygen, yet, there is slight decrease in ionisation energy from nitrogen to oxygen. This is due to the fact that electronic configuration of nitrogen is half filled. In oxygen the last electron goes to 2P orbital making it unstable. Consequently 2p Orbital of oxygen is not tightly held by the nucleus as ' 2s electron of nitrogen. Hence ionisation energy of oxygen is less than that of nitrogen.

Variation of ionisation energy when we move down the group



Electron affinity (electron gain enthalpy)

Amount of energy released when one electron is added to an isolated gaseous atom is called electron affinity.
When an electron is removed from an atom, energy is required for the process of removal of a electron but energy is released when electron is added in neutral atom.

$$X(g) + e^- \longrightarrow X^{\ominus} + \text{Energy}$$

Unit of electron affinity is kilojoule/mole

Factors on which electron affinity depends :

1. With increasing the size of atom, electron affinity decreases.
2. For stable configuration, electron affinity is almost very less or almost equal to 0.
3. Electron affinity increase as the nuclear charge increases.

In general, electron affinity increases from left to right in a period and decreases from top to bottom in a group.

Electron affinity of fluorine is less than that of chlorine. Why?

The low value of electron affinity of fluorine is due to very small size of fluorine atom. As a consequence of small size there is strong inter-electronic repulsion in the relatively compact 2p sub shell of fluorine and thus the incoming electron does not feel much attraction.
As a result, its electron affinity value is small. On the other hand, the electron affinity of chlorine atom is larger where electrons is added to a relatively large 3p orbital which can easily accommodate the additional electron.

Electron affinity of noble gases as 0 why?

The electron affinity of noble gases as zero because they have stable electronic configuration and thus they have absolutely no tendency to take additional electron. This means that incoming electron does not feel any attraction for the nucleus that no energy is released and their electron affinity is 0.

Halogens have the highest electron affinity.

Electron negativity: the tendency of an atom to attract a shared electron pair in a molecule towards its self is called electron negativity.

Factors affecting electronegativity.

1. Size of an atom.: atom which have small size have a higher value of electronegativity
2. Oxidation state: electronegativity of an atom varies from one bonding state to another, depending on the oxidation state of the atom in the molecule the electronegativity increases as the positive oxidation state of atom increases. This is because with the increase in positive oxidation, state the tendency to attract the electron will increase.
3. Bond order: as the bond order increases, its electronegativity increases.
4. Type of hybridisation: with the increase in s character, the electronegativity increases

Applications

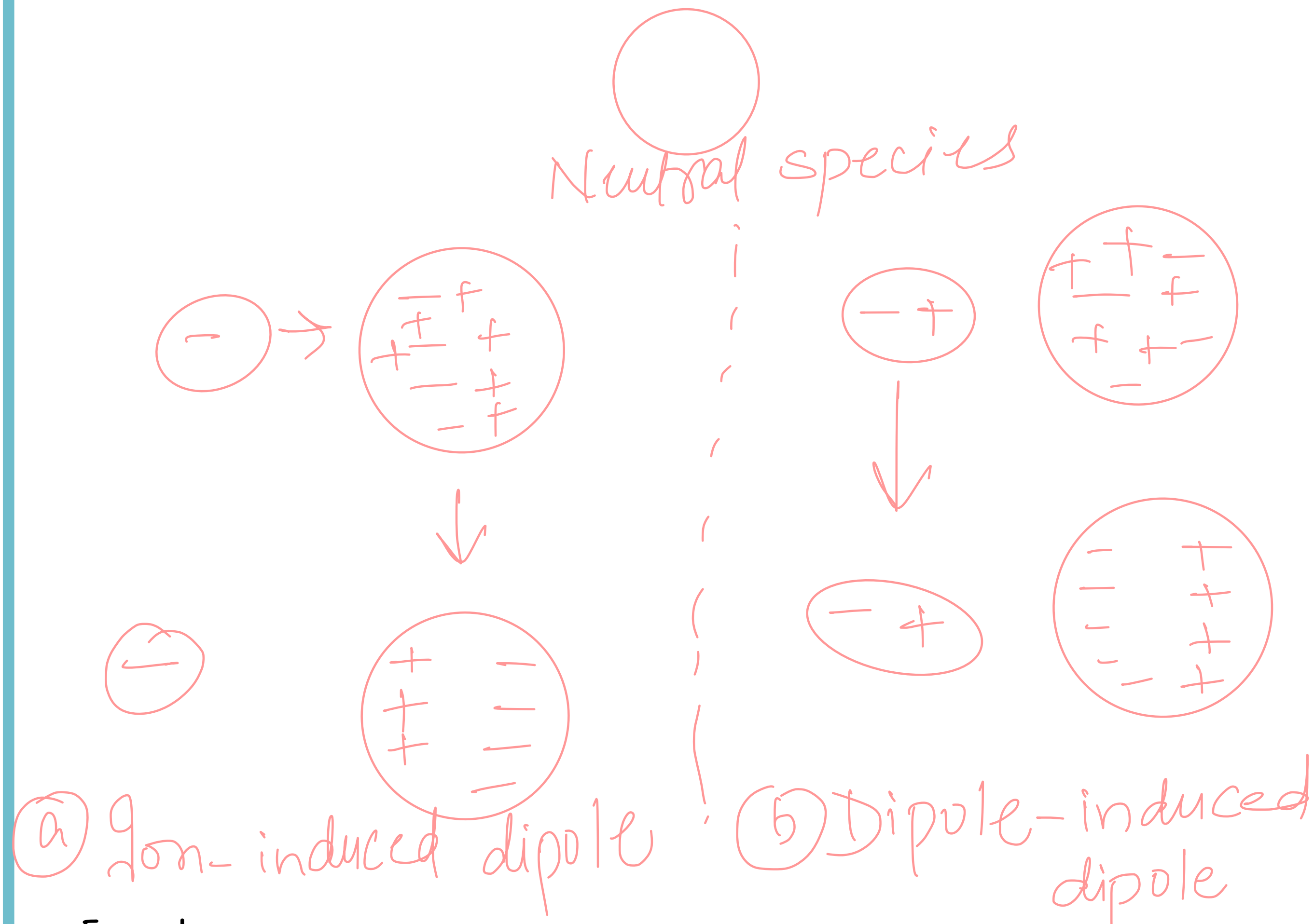
1. Bond type and bond order.
2. Tentative bond energies
3. Quantitative thermal stability

Variation in periodic table :

On moving along a period, the electronegativity increases and on moving down the group electronegativity decreases.

Polarizability:

It is defined as the ease of distortion by which an electron cloud gets distorted from its normal shape by an electric field. A species is said to be polarisable if its electron cloud can be easily distorted.



Example:

1. Larger negatively charged ion such as iodine and bromine are highly polarisable.
2. Small positively charged cation, such as magnesium and aluminium, have low polarizability

$$\text{Polarizability}(\alpha) = \frac{\text{induced dipole moment}}{\text{strength of electric field}}$$

Oxidation state or oxidation number: it is defined as the number of electron gain or loss by an atom.

Oxidation state or oxidation number maybe positive, negative or zero.

The oxidation number of a free element is always zero .

The oxidation number of a mono atomic ion equals the charge of the ion.

Coordination No.: it is defined as the number of atoms, ions molecules that a central metal atom or ions holds as it's nearest neighbours in a complex or coordination compound or in a crystal.

For example

Complex having coordination number 2

Eg: $[HgCl_2]$

$[AuCl_2]$

Complex having coordination number 4

Eg: $[Ni(CN)_4]^{4-}$

$[Cu(NH_3)_4]$. and $[Cu(CN)_4]$

Complex having coordination number 6

Eg: $[AlF_6]^{3-}$

VSEPR Theory

VSEPR: Valence shell electron pair repulsion theory

What is geometry of molecules?

Geometry or shape is defined as relative arrangement of bonded atoms present in a molecule.

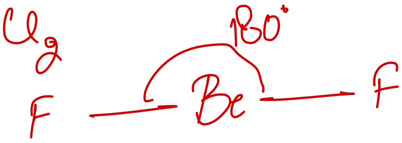
Postulates of VSEPR Theory

1. The shape of molecule is related to the number of valence shell electron pairs around the central atom in a molecule. Because there are strong repulsive force between electron pairs surrounding central atom which increase the energy of the system.
2. Valence shell electron pair around the central atom in a molecule tends to stay apart as far as possible. This is because it would minimise the repulsive electronic interactions which lead to a state of minimum energy for a molecule.
3. The orbital of non-bonding or lone pair of valence shell electrons occupies most space then the orbital having bonding pair of electrons.
4. When the central atom is surrounded by bond pair, then the geometry is regular.
5. lone pair- lone pair repulsion > lone pair - bond pair repulsion > bond pair - bond pair repulsion

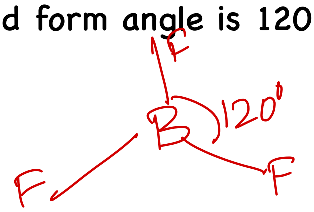
Some geometry based on VSEPR Theory:

1. Molecule in which central Atom is surrounded by two valence shell, electron pair: a molecule having only 2 valence shell electron pair around the central atom are linear in shape, and the bond angle is 180° between the atoms. For example

BeF_2, $HgCl_2$



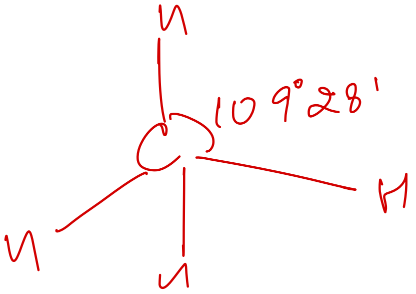
2. Molecules in which central atom is surrounded by three valence shell electron pair: In this type in which the central atom is surrounded by three pair of valance shell, electron and three atoms attached to the central atom or similar to one another and equilateral triangle in shape and form angle is 120° . For example BF_3



3. Molecules in which central atom is surrounded by four valence shell electron pair: when the central atom in a molecule is surrounded by four pair of valance shell electrons. This type of molecule have tetrahedral symmetry and each bond angle is 109’ 28°.

There are two categories

a. The molecule in which all the four electron pairs surrounding the central atom or bonding pair of electron, for example: CH_4, CCl_4, NH_4^+



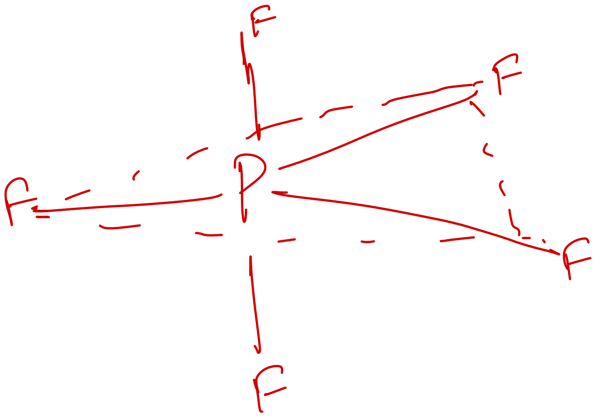
b. The molecule in which some of valence shell electron pair are bonding pair of electrons and some are non-bonding pair of electrons. for example:

H_2O, NH_3

Shape of ammonia (NH_3) : In this molecule, nitrogen is surrounded by four pair of electron three of which are bonding pair while the four is non-bonding pair. The shape of molecule is trigonal pyramidal and bond angle is 107°.

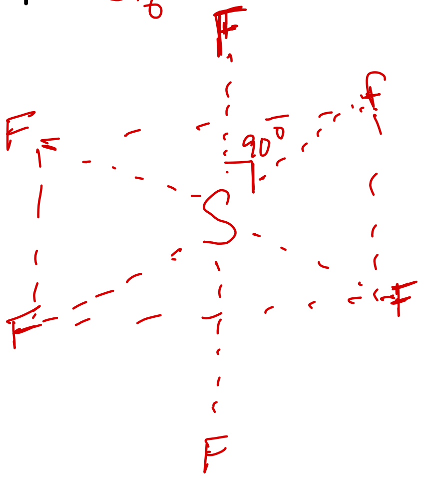
Shape of water (H_2O) : In case of water, the oxygen atom is surrounded by four pair of valence shell electrons, but two of these pairs are bonding pairs. While the other two are non-bonding pairs and the molecule shape is angular shape and bond angle is 104°.

4. Molecule in which central atom is surrounded by five valence shell electron pair: For example PF_5



In this structure, three of fluorine atom lies in the same equatorial plane as the phosphorus atom and are termed as equatorial fluorine atom. The other two fluorine atom lie above and below the equatorial plane on the axis of bipyramidal are known as axial fluorine atoms. The geometric shape is trigonal bipyramidal and the bond angle of equatorial bond is 120° and bond angle at axial bond is 90°.

5. Molecule in which central atom is surrounded by six valence shell electron pair: for example SF_6



In this structure, four of the six S-F bonds lie in the same plane at right angle to one another, the other two lie in a plane above and below the plane of the other four bonds, bond angle is 90° and 60°.

Limitations of VSEPR Theory:

1. The VSEPR model is not a theory as it does not explain any observation rather, it is an algorithm that accurately predict the structure of large number of compounds.
2. VSEPR is simple and useful, but does not work for all chemical species.

HARD AND SOFT ACID AND BASE (HSAB)

It is given by R Pearson in 1965 . It is also known as HSAB concept or Pearson concept. The principal explain the term of dynamic stability of metal complex, which depends upon the nature of ligand and the metal ion forming the complex as well as the type of bond between them.

Principle of HSAB:

It states that hard acid prefer to bind hard bases to give ionic complexes and soft acid prefer to bind soft bases to give covalent complexes.

Characteristics of hard and soft acid and base:

1. Hard acid:

\# Highly positive charge
\# Not easily polarizable
\# Small size
\# Strongly solvated
\# Empty orbital in valence shell

For example Li^+, Na^+ etc.

2. Hard base:

\# low polarizability
\# Not easily oxidised
\# High electronegativity
\# With low energy HOMOS
\# Completely filled atomic orbital

For example F^-, Cl^-, NH_3, OH^- etc

1. Soft acid:

\# Low positive charge
\# High polarizable
\# Large size
\# Completely filled atomic orbital
\# With low energy LUMOS

For example Ag^+, Au^+, Pt^{2+}, BH_3 etc.

2. Soft base:

\# High polarizability
\# easily oxidised
\# Low electronegativity
\# With high energy HOMOS
\# small size

For example SCN^-, I^-, Benzene, H^- etc.

AgI is stable while AgCl is unstable. Explain.

We know that
Ag^+ is soft acid as it is large size and is highly polar and I^- is soft base because it has high polarizability and size of I^- is intermediate. On combining Ag^+ and I^-, it forms AgI which is stable and nature by forming strong bond.
But Cl^- is a hard base and smaller in size and has low polarizability on combining with Ag^+ it forms AgCl which is unstable in nature by forming weak bond.