UNIT 1
SOME BASIC CONCEPTS OF CHEMISTRY

Chemistry: Chemistry is the branch of science that deals with the composition, structure and properties of matter. Chemistry is called the science of atoms and molecule

Branches of Chemistry

- Organic Chemistry -This branch deals with study of carbon compounds especially hydrocarbons and their derivatives.
- Inorganic Chemistry-This branch deals with the study of compounds of all other elements except carbon. It largely concerns itself with the study of minerals found in the Earth's crust.
- Physical Chemistry-The explanation of fundamental principles governing various chemical phenomena is the main concern of this branch. It is basically concerned with laws and theories of the different branches of chemistry.
- Industrial Chemistry-The chemistry involved in industrial processes is studied under this branch.
- Analytical Chemistry-This branch deals with the qualitative and quantitative analysis of various substances.
- Biochemistry-This branch deals with the chemical changes going on in the bodies of living organisms; plants and animals.
- Nuclear Chemistry-Nuclear reactions, such as nuclear fission, nuclear fusion, transmutation processes etc. are studied under this branch.

PROPERTIES OF MATTER AND THEIR MEASUREMENT--Every substance has unique or characteristic properties. These properties can be classified into two categories – **physical properties** and **chemical properties**.

Physical properties are those properties which can be measured or observed without changing the identity or the composition of the substance. E.g. colour, odour, melting point, boiling point, density etc.

The measurement or observation of **chemical properties** requires a chemical change to occur. e.g. Burning of Mg-ribbon in air

Chemical properties are characteristic reactions of different substances; these include acidity or basicity, combustibility etc.Many properties of matter such as length, area, volume, etc., are quantitative in nature.

Metric System was based on the decimal system.

The International System of Units (SI)

The International System of Units (in French Le Systeme International d'Unites– abbreviated as SI) was established by the 11th General Conference on Weights and Measures (CGPM from *ConferenceGenerale des Poids at Measures*). The SI system has seven *base units*

Quantity	Unit	Symbol
Length	metre	m
Mass	kilogram	kg
Time	second	S
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A
Luminous intensity	candela	Cd

Prefixes in SI system

Multiple	Prefix	Symbol
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	μ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
10	deca	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T

Mass and Weight-- **Mass** of a substance is the amount of matter present in it while **weight** is the force exerted by gravity on an object. The mass of a substance is constant whereas its weight may vary from one place to another due to change in gravity. The mass of a substance can be determined very accurately by using an analytical balance

Volume-- Volume has the units of (length)^3. So volume has units of m^3 or cm^3 or dm^3.A common unit, litre (L) is not an SI unit, is used for measurement of volume of liquids. 1 L = 1000 mL, 1000 cm^3 = 1 dm^3

Density: Density of a substance is its amount of mass per unit volume.SI unit of density = SI unit of mass/SI unit of volume = kg/m^3 or kg m^{-3}This unit is quite large and a chemist often expresses density in g cm^{-3}.

Temperature--There are three common scales to measure temperature — °C (degree celsius), °F (degree Fahrenheit) and K (kelvin). Here, K is the SI unit.

$$°F = \frac{9}{5}(°C) + 32$$

K = °C + 273.15

Note—Temperature below 0 °C (i.e. negative values) are possible in Celsius scale but in Kelvin scale, negative temperature is not possible.

Scientific Notation

In which any number can be represented in the form $N \times 10^n$ (Where n is an exponent having positive or negative values and N can vary between 1 to 10).

e.g. We can write 232.508 as 2.32508 $x10^2$ in scientific notation. Similarly, 0.00016 can be written as 1.6×10^{-4}.

Precision refers to the closeness of various measurements for the same quantity. **Accuracy** is the agreement of a particular value to the true value of the result

Significant Figures

The reliability of a measurement is indicated by the number of digits used to represent it. To express it more accuratelywe express it with digits that are known with certainty. These are called as Significant figures. They contain all thecertain digits plus one doubtful digit in a number.

Rules for Determining the Number of Significant Figures

- All non-zero digits are significant. For example, 6.9 has two significant figures, while 2.16 has three significantfigures. The decimal place does not determine the number of significant figures.
- A zero becomes significant in case it comes in between non zero numbers. For example, 2.003 has four significantfigures, 4.02 has three significant figures.
- Zeros at the beginning of a number are not significant. For example, 0.002 has one significant figure while 0.0045has two significant figures.
- All zeros placed to the right of a number are significant. For example, 16.0 has three significant figures, while 16.00has four significant figures. Zeros at the end of a number without decimal point are ambiguous.
- In exponential notations, the numerical portion represents the number of significant figures. For example, 0.00045 isexpressed as 4.5×10^{-4} in terms of scientific notations. The number of significant figures in this number is 2, while inAvogadro's number (6.023×10^{23}) it is four.
- The decimal point does not count towards the number of significant figures. For example, the number 345601 has sixsignificant figures but can be written in different ways, as 345.601 or 0.345601 or 3.45601 all having same number ofsignificant figures.

Retention of Significant Figures - Rounding off Figures

The rounding off procedure is applied to retain the required number of significant figures.

1. If the digit coming after the desired number of significant figures happens to be more than 5, the precedingsignificant figure is increased by one, 4.317 is rounded off to 4.32.
2. If the digit involved is less than 5, it is neglected and the preceding significant figure remains unchanged, 4.312 isrounded off to 4.31.
3. If the digit happens to be 5, the last mentioned or preceding significant figure is increased by one only in case ithappens to be odd. In case of even figure, the

preceding digit remains unchanged. 8.375 is rounded off to 8.38 while8.365 is rounded off to 8.36.

Dimensional Analysis During calculations generally there is a need to convert units from one system to other. This is called **factor label method** or **unit factor method** or **dimensional analysis**.

For example- 5 feet and 2 inches (height of an Indian female) is to converted in SI unit

1 inch = 2.54×10^{-2} m

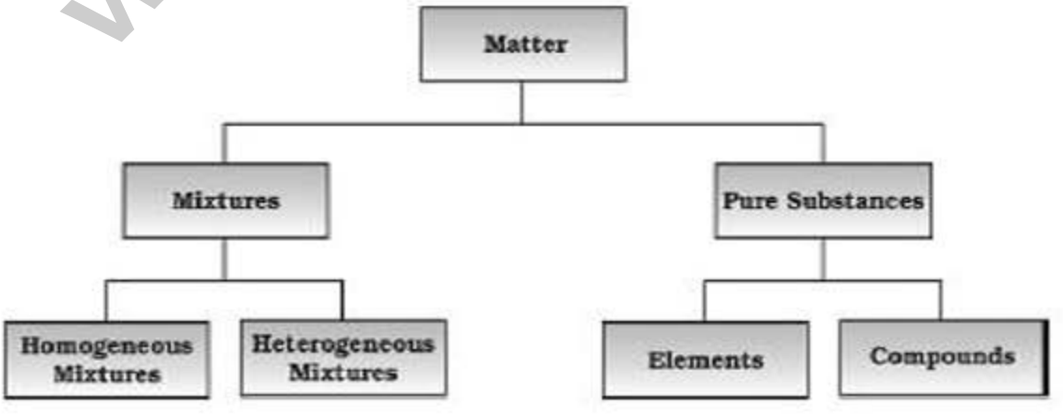
$1 = \frac{2.54 \times 10^{-2}\ m}{1\ inch}$ then, 5 feet and 2 inch = 62 inch

$= 62\ inch \times \frac{2.54 \times 10^{-2}\ m}{1\ inch} = 1.58\ m$

Physical Classification of Matter

Properties	**Solid**	**Liquid**	**Gas**
1. volume	Definite	Definite	Indefinite
2. Shape	Definite	Indefinite	Indefinite
3. Inter molecular force of attraction	Very high	Moderate	Negligible / Very low
4. arrangement of molecules	Orderly arranged	Free to move within the volume	Free to move every where
5. Inter molecular space	Very small	Slightly greater	Very great
7. Compressibility	Not compressible	Not compressible	Highly compressible
8. Expansion on heating	Very little	Very little	Highly expand
9. Rigidity	Very rigid	Not rigid knownas fluid	Not rigid and known as fluid
9. Fluidity	Can't flow	Can flow	Can flow
10. Diffusion	They can diffuse due to kinetic energy of liquid/gases	Can diffuse And rate of diffusion is very fast	Can diffuse And rate of diffusion is very fast

Chemical Classification of matter---



Elements

An element is the simplest form of matter that cannot be split into simpler substances or built from simpler substances by any ordinary chemical or physical method. There are 114 elements known to us, out of which 92 are naturally occurring while the rest have been prepared artificially.

Elements are further classified into metals, non-metals and metalloids.

Compounds

A compound is a pure substance made up of two or more elements combined in a definite proportion by mass, which could be split by suitable chemical methods.

Characteristics of compound

- Compounds always contain a definite proportion of the same elements by mass.
- The properties of compounds are totally different from the elements from which they are formed.
- Compounds are homogeneous.
- Compounds are broadly classified into inorganic and organic compounds. Inorganic compounds are those, which areobtained from non-living sources such as minerals. For example, common salt, marble and limestone. Organiccompounds are those, which occur in living sources such as plants and animals. They all contain carbon. Commonorganic compounds are oils, wax, fats etc.

Mixtures

A mixture is a combination of two or more elements or compounds in any proportion so that the components do not lose their identity. Air is an example of a mixture

Mixtures are of two types, homogeneous and heterogeneous.

Homogeneous mixtures have the same composition throughout the sample. The components of such mixtures cannot be seen under a powerful microscope. They are also called solutions. Examples of homogeneous mixtures are air, seawater, gasoline, brass etc.

Heterogeneous mixtures consist of two or more parts (phases), which have different compositions. These mixtures have visible boundaries of separation between the different constituents and can be seen with the naked eye e.g., sand and salt, chalk powder in water etc.

LAWS OF CHEMICAL COMBINATIONS

Law of Conservation of Mass (Given by Antoine Lavoisier in 1789).

It states that matter (mass) can neither be created nor destroyed.

Law of Definite Proportions or Law of Constant Composition:

This law was proposed by Louis Proust in 1799, which states that:

'A chemical compound always consists of the same elements combined together in the same ratio, irrespective of the method of preparation or the source from where it is taken'.

Law of Multiple Proportions Proposed by Dalton in 1803, this law states that:

'When two elements combine to form two or more compounds, then the different masses of one element, which combine with a fixed mass of the other, bear a simple ratio to one another'.

Gay Lussac's Law of Gaseous Volumes (Given by Gay Lussac in 1808.)

According to this law when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume provided all gases are at same temperature and pressure.

e.g. $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

1V 1V 2V

All reactants and products have simple ratio 1:1:2.

Avogadro Law (In 1811, Given by Avogadro)

According to this law equal volumes of gases at the same temperature and pressure should contain equal number of molecules.

Dalton's Atomic Theory

- All substances are made up of tiny, indivisible particles called atoms.
- Atoms of the same element are identical in shape, size, mass and other properties.
- Atoms of different elements are different in all respects.
- Atom is the smallest unit that takes part in chemical combinations.
- Atoms combine with each other in simple whole number ratios to form compound atoms called molecules.
- Atoms cannot be created, divided or destroyed during any chemical or physical change.

Atoms and Molecules

The smallest particle of an element, which may or may not have independent existence is called an atom, while the smallest particle of a substance which is capable of independent existence is called a molecule.

Molecules are classified as homoatomic and heteroatomic. Homoatomic molecules are made up of the atoms of the same element and heteroatomic molecules are made up of the atoms of the different element have different atomicity (number of atoms in a molecule of an element) like monoatomic, diatomic, triatomic and polyatomic.

Atomic Mass Unit

One atomic mass unit is defined as a mass exactly equal to one twelfth the mass of one carbon -12 atom. And 1 amu = 1.66056×10^{-24} g.

Today, 'amu' has been replaced by 'u' which is known as unified mass.

Atomic Mass

Atomic mass of an element is defined as the average relative mass of an atom of an element as compared to the mass of an atom of carbon -12 taken as 12.

$$\text{Atomic mass} = \frac{\text{mass of an atom}}{1/12 \text{ mass of a carbon atom}(^{12}C)}$$

Gram Atomic Mass

The quantity of an element whose mass in grams is numerically equal to its atomic mass. In simple terms, atomic mass of an element expressed in grams is the gram atomic mass or gram atom.

For example, the atomic mass of oxygen = 16 amu
Therefore gram atomic mass of oxygen = 16 g

Molecular Mass

Molecular mass of a substance is defined as the average relative mass of its molecule as compared to the mass of an atom of C-12 taken as 12. It expresses as to how many times the molecule of a substance is heavier than 1/12th of the mass of an atom of carbon.

For example, a molecule of carbon dioxide is 44 times heavier than 1/12th of the mass of an atom of carbon. Therefore the molecular mass of CO_2 is 44 amu.

It is obtained by adding the atomic masses of all the atoms present in one molecule.

Gram Molecular Mass

A quantity of substance whose mass in grams is numerically equal to its molecular mass is called gram molecular mass. In simple terms, molecular mass of a substance expressed in grams is called gram molecular mass.

e.g., the molecular mass of oxygen = 32 amu
Therefore, gram molecular mass of oxygen = 32 g

Formula Mass-

Sum of atomic masses of the elements present in one formula unit of a compound. It is used for the ionic compounds.

Mole Concept.

Mole is defined as the amount of a substance, which contains the same number of chemical units (atoms, molecules, ions or electrons) as there are atoms in exactly 12 grams of pure carbon-12.

A mole represents a collection of 6.022×10^{23} (Avogadro's number) chemical units..

The mass of one mole of a substance in grams is called its molar mass.

Molar Volume

The volume occupied by one mole of any substance is called its molar volume. It is denoted by Vm. One mole of all gaseous substances at 273 K and 1 atm pressure occupies a volume equal to 22.4 litre or 22,400 mL. The unit of molar volume is litre per mol or millilitre per mol

PERCENTAGE COMPOSITION—

The mass percentage of each constituent element present in any compound is called its percentage composition

$$\text{Mass \% of the element} = \frac{\text{Mass of element in 1 molecule of the compound}}{\text{Molecular mass of the compound}} \times 100$$

Empirical Formula and Molecular Formula—

An **empirical formula** represents the simplest whole number ratio of various atoms present in a compound. E.g. CH is the empirical formula of benzene.

The **molecular formula** shows the exact number of different types of atoms present in a molecule of a compound. E.g. C_6H_6 is the molecular formula of benzene.

Relationship between empirical and molecular formulae

The two formulas are related as Molecular formula = n x empirical formula

$$n = \frac{\text{Molecular mass}}{\text{empirical formula mass}}$$

Chemical Equation-
Shorthand representation of a chemical change in terms ofsymbols and formulae of the substances involved in the reaction is called chemical equation..
The substances that react among themselves to bring about the chemical changes are known as reactants, whereas the substances that are produced as a result of the chemical change, are known as products.
Limiting Reagent- The reactant which gets consumed first or limits the amount of product formed is known as **limiting reagent**
Reactions in Solutions-- The concentration of a solution can be expressed in any of the following ways.

1. **Mass Percent** is the mass of the solute in grams per 100 grams of the solution.
   $$\text{Mass \% of the solute} = \frac{\text{Mass of the solute}}{\text{Mass of the solution}} \times 100$$
   A 5 % solution of sodium chloride means that 5 g of NaCl is present in 100g of the solution.
2. **Volume percent** is the number of units of volume of the solute per 100 units of the volume of solution.
   $$\text{Volume \% of the solute} = \frac{\text{Volume of the solute}}{\text{Volume of the solution}} \times 100$$
   A 5 % (v/v) solution of ethyl alcohol contains 5 cm^3 of alcohol in 100 cm^3 of the solution
3. **Molarity** of the solution is defined as the number of moles of solute dissolved per litre (dm^3) of the solution. It isdenoted by the symbol M. Measurements in Molarity can change with the change in temperature because solutionsexpand or contract accordingly.
   $$\text{Molarity of the solution} = \frac{\text{No. of moles of the solute}}{\text{Volume of the solution in litre}} = \frac{n}{V}$$

The Molarity of the solution can also be expressed in terms of mass and molar mass

$$\text{Molarity of the solution} = \frac{\text{Mass of the solute}}{\text{Molar mass of the solute X volume of the solution in liter}}$$

In terms of weight, molarity of the substance can be expressed as:

$$\text{Molarity} = \frac{W_g}{M\ g\ mol^{-1} \times V\ litre} = \frac{W}{M \times V}\ mol/L$$

Molarity equation
To calculate the volume of a definite solution required to prepare solution of other molarity, the following equation is used:
M1V1 = M2V2, where M1= initial molarity, M2= molarity of the new solution, V1= initial volume and V2= volume of the new solution.

4. Molality- Molality is defined as the number of moles of solute dissolved per 1000 g (1 kg) of solvent. Molality is expressed as 'm'.
   $$\text{Molality} = \frac{\text{Moles of the solute}}{\text{Wt. of Solvent (in gm)}} \times 1000$$

5. Mole Fraction is the ratio of number of moles of one component to the total number of moles (solute and solvents) present in the solution. It is expressed as 'x'.

Mole fraction of the solute = $\frac{\text{Moles of the solute}}{\text{Moles of solute + Moles of solvent}}$

Mole fraction of the solvent = $\frac{\text{Moles of the solvent}}{\text{Moles of solute + Moles of solvent}}$

Mole fraction of the solute + Mole fraction of solvent = 1

One Mark questions with answers

1. What is the significant figures in 1.050×10^4?

Ans. Four

2. What is the S.I. unit of Density?

Ans. Kg m^{-3}

3. What do mean by Mole fraction?

Ans. Mole Fraction is the ratio of number of moles of one component to the total number of moles (solute and solvents) present in the solution. It is expressed as 'x'.

4. Round off up to 3 significant figure (a) 1.235 (b) 1.225

Ans. (a) 1.24 (b) 1.22

5. What is AZT?

Ans. Azidothymidine.

6. What is limiting reagent?

Ans.The reactant which gets consumed first or limits the amount of product formed is known as **limiting reagent**

7. What is the relation between temperature in degree Celsius and degree fahrenheit?

Ans.

$$°F = \frac{9}{5}(°C) + 32$$

8. Define one mole?

Ans. One mole is the amount of a substance that contains as many particles as there are atoms in exactly 12 g of the carbon-12.

9. Calculate the formula mass calcium chloride.

Ans. Formula mass of $CaCl_2$= 40+2 x35.5=40+71 = 111 u

10. What is the law called which deals with the ratios of the volumes of the gaseous reactants and products?

Ans. Gay Lussac's law of gaseous volumes.

Two Marks questions with answers

1. Give the two points of differences between homogeneous and heterogeneous mixtures.

Ans.

Homogeneous mixture	Heterogeneous mixture
1. Homogeneous mixtures have the same composition throughout the sample. 2. The components of such mixtures cannot be seen under a powerful microscope.	1. Heterogeneous mixtures consist of two or more parts (phases), which have different compositions. 2. These mixtures have visible boundaries of separation between the different constituents and can be seen with the naked eye

2. Copper oxide obtained by heating copper carbonate or copper nitrate contains copper and oxygen in the same ration by mass. Which law is illustrated by this observation? State the law.

Ans.**Law of Definite Proportions** This law states that: A chemical compound always consists of the same elements combined together in the same ratio, irrespective of the method of preparation or the source from where it is taken.

3. Write the empirical formula of the following:
   (a) N_2O_4 (b) $C_6H_{12}O_6$ (c) H_2O (d) H_2O_2

Ans. (a)NO_2 (b) CH_2O (c) H_2O (d) HO

4. Briefly explain the difference between precision and accuracy.

Ans. Precision refers to the closeness of various measurements for the same quantity. However, accuracy is the agreement of a particular value to the true value of the result.

5. Define the law of multiple proportions. Explain it with one example.

Ans.When two elements combine to form two or more compounds, then the different masses of one element, which combine with a fixed mass of the other, bear a simple ratio to one another. For example- carbon combines with oxygen to form two compounds CO and CO_2.

Compound	CO	CO_2
Mass of C	12	12
Mass of O	16	32

Masses of oxygen which combine with a fixed mass of carbon (12g) bear a simple ratio of 16:32 or 1:2.

6. Chlorine has two isotopes of atomic mass units 34.97 and 36.97. The relative abundance of the isotopes is 0.755 and 0.245 respectively. Find the average atomic mass of chlorine.

Ans. Average atomic mass = 34.97 x 0.755 +36.97 x 0.245 = 35.46 u

7. Calculate the percentage composition of water.

Ans. Mass % of an element = $\frac{\text{mass of that element in the compound} \times 100}{\text{molar mass of the compound}}$

Molar mass of water = 18.02 g

Mass % of hydrogen = $\frac{2 \times 1.008 \times 100}{18.02}$

$= 11.18$

Mass % of oxygen = $\frac{16.00 \times 100}{18.02} = 88.79$

8. State the number of significant figures in each of the following:

(i) 208.91 (ii) 0.00456 (iii) 453 (iv) 0.346

Ans.

(i) 208.91 has five significant figures.

(ii) 0.00456 has three significant figures.

(iii) 453 has three significant figures.

(iv) 0.346 has three significant figures.

8. Express the results of the following calculations to the appropriate number of significant figures.

(i) $\frac{3.24 \times 0.08666}{5.006}$ (ii) $\frac{(1.36 \times 10^{-4})(0.5)}{2.6}$

Ans.

(i) $\frac{3.24 \times 0.08666}{5.006}$

$= 0.05608 = 0.0561$

(ii) $\frac{(1.36 \times 10^{-4})(0.5)}{2.6}$

$= 0.2615 \text{ x } 10\text{-}4 = 0.3 \text{ x } 10^{-4}$

9. How are 0.50 mol Na2CO3 and 0.50 M Na2CO3 different?

Ans. Molar mass of Na2CO3= 2 x 23 +12 + 3 x 16 = 106 g / mol

0.50 molNa2CO3means 0.50 x 106 = 53 g

0.50 M Na2CO3 means 0.50 mol i.e. 53 g of Na2CO3 are present in I L of the solution.

Three Marks questions with answers-

1. What is unit factor method? Express the following in SI units - 93 million miles (distance between earth and sun)

Ans. Method to convert units from one system to other is called unit factor method.

93 million miles = $93 \text{ x } 10^6$ miles

1 mile = 1.60934 km = $1.60934 \text{ x } 10^3$ m

$$1 = \frac{1.60934 \times 10^3 \text{ m}}{1 \text{ mile}}$$

$$93 \text{ million mile} = 93 \times 10^6 \text{ mile} \times \frac{1.60934 \times 10^3 \text{ m}}{1 \text{ mile}}$$

$$= 1.5 \text{ x } 10^{11} \text{ m}$$

2. Write the three points of difference between compound and mixture.

Ans.

Compound	Mixture
Constituents are always present in a fixed ratio by mass	Constituents may be present in any ratio
May or may not be homogeneous in nature	Always homogeneous in nature
Constituents can be easily separated	Constituents cannot be easily

by simple mechanical means	separated by simple mechanical means
Properties are midway between those of its constituents.	Properties are entirely different from those of its constituents.

3. What do mean bygram atomic mass.One million silver atoms weigh 1.79 x 10^{16} g. Calculate the gram atomic mass of silver.

Ans.atomic mass of an element expressed in grams is the gram atomic mass
Number of silver atoms = 1 million = 1 x 10^6
Mass of one million Ag atoms = 1.79 x 10^{16} g

$$\text{Mass of } 6.023 \times 10^{23} \text{ atoms of silver} = \frac{1.79 \times 10^{16} \text{ g} \times 6.023 \times 10^{23}}{1 \times 10^6}$$
$$= 107.8 \text{ g}$$

4. What is the percentage of carbon, hydrogen and oxygen in ethanol?

Ans. Molecular formula of ethanol is : C_2H_5OH
Molar mass of ethanol is : (212.01 + 61.008 + 16.00) g = 46.068 g
Mass per cent of carbon = (24.02g / 46.068g) ×100 = 52.14%
Mass per cent of hydrogen = (6.048g / 46.068g)×100 = 13.13% Mass per cent of oxygen = (16.00 g / 46.068g)×100 = 34.73%

5. What do mean by molarity .Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.
Ans.The number of moles of solute dissolved per litre (dm^3) of the solution is called molarity
Since molarity (M) = No. of moles of solute /Volume of solution in litres
=(Mass of NaOH/Molar mass of NaOH)/0.250 L
=(4 g / 40 g 0.1 mol)/0.250L =0.1 mol/0.250 L
= 0.4 mol L^{-1}
= 0.4 M

6. Classify the following as pure substances or mixture-
(a) ethyl alcohol (b) oxygen (c) blood (d) carbon (e) steel (f) distilled water
Ans. Pure substance- ethyl alcohol ,oxygen , carbon, distilled water
Mixture- blood, steel

7. What are the rules for rounding off?

Ans.1. If the digit coming after the desired number of significant figures happens to be more than 5, the precedingsignificant figure is increased by one,
2. If the digit involved is less than 5, it is neglected and the preceding significant figure remains unchanged,

3.If the digit happens to be 5, the last mentioned or preceding significant figure is increased by one only in case it happens to be odd. In case of even figure, the preceding digit remains unchanged.

8. Define –(a) Average atomic mass (b) Molecular mass (c) Formula mass
   Ans. (a) Average atomic mass- Atomic mass of an element is defined as the average relative mass of an atom of an element as compared to the mass of an atom of carbon -12 taken as 12.
   (b) Molecular mass- it is sum of atomic masses of the elements present in a molecule.
   (c) Formula mass- it is sum of atomic masses of the elements present in a formula unit of a compound.
9. Express the following in the scientific notation with 2 significant figures-
   (a) 0.0048 (b) 234,000 (c) 200.0
   Ans. (a) 4.8×10^{-3} (b) 2.3×10^{5} (c) 2.0×10^{2}
10. Calculate the number of atoms in each of the following (i) 52 moles of Ar
    (ii) 52 u of He (iii) 52 g of He
    Ans. **(i)** 1 mole of Ar = 6.022×10^{23} atoms of Ar
    $\therefore$ 52 mol of Ar = $52 \times 6.022 \times 10^{23}$ atoms of Ar
    = 3.131×10^{25} atoms of Ar
    (ii) 1 atom of He = 4 u of He
    Or,
    4 u of He = 1 atom of He

    1 u of He = 1/4 atom of He
    52u of He = 52/4 atom of He
    = 13 atoms of He
    (iii) Molar mass of He = 4 g/mol
    4 g of He contains = 6.022×10^{23} atoms of He
    52 g of He contains = $\frac{6.022 \times 10^{23} \times 52}{4}$ = 78.286×10^{23} atoms of He

Five Marks questions with answers-

1. What is the difference between empirical and molecular formula? A compound contains 4.07 % hydrogen, 24.27 % carbon and 71.65 % chlorine. Its molar mass is
   98.96 g. What are its empirical and molecular formulas?

Ans. An empirical formula represents the simplest whole number ration of various atoms present in a compound whereas the molecular formula shows the exact number of different types of atoms present in a molecule of a compound.

Name of element	Percentage of elements	Step-1Conversion of mass per cent to grams.	Step 2. number moles of each element	Step 3. Divide the mole value by the smallest number
C	24.27%	24.27g	24.27/12 = **2.0225**	**2.0225/2.018 = 1**
H	4.07%	4.07g	4.07/1= **4.07**	**4.07/2.018 =2**
Cl	71.65%	71.65g	71.65/35.5 = **2.018**	**2.018/2.018 = 1**

The empirical formula of the above compound is CH2Cl.
empirical formula mass is 12 + (1x2) + 35.5 = 49.5
n= molecular mass/ empirical formula mass =98.96/49.5 = 2
Hence molecular formula is $C_2H_4Cl_2$

2. Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation:

$$N_{2(g)} + H_{2(g)} \rightarrow 2NH_{3(g)}$$

(i) Calculate the mass of ammonia produced if 2.00×10^3 g dinitrogen reacts with 1.00×10^3 g of dihydrogen.
(ii) Will any of the two reactants remain unreacted?
(iii) If yes, which one and what would be its mass?

Ans. (i) Balancing the given chemical equation, $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

From the equation, 1 mole (28 g) of dinitrogen reacts with 3 mole (6 g) of dihydrogen to give 2 mole (34 g) of ammonia.

$\Rightarrow 2.00 \times 10^3$ g of dinitrogen will react with $\frac{6\text{ g}}{28\text{ g}} \times 2.00 \times 10^3\text{ g}$ dihydrogen i.e.,

2.00×10^3 g of dinitrogen will react with 428.6 g of dihydrogen.

Given,

Amount of dihydrogen = 1.00×10^3 g

Hence, N_2 is the limiting reagent.

$\therefore$ 28 g of N_2 produces 34 g of NH_3.

Hence, mass of ammonia produced by 2000 g of N_2 $= \frac{34\text{ g}}{28\text{ g}} \times 2000\text{ g}$

= 2428.57 g

(ii) N_2 is the limiting reagent and H_2 is the excess reagent. Hence, H_2 will remain unreacted.

(iii) Mass of dihydrogen left unreacted = 1.00×10^3 g – 428.6 g

= 571.4 g

3. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula.

Ans. **(i)** 1 mole (44 g) of CO_2 contains 12 g of carbon.

3.38 g of CO_2 will contain carbon $= \frac{12\text{ g}}{44\text{ g}} \times 3.38\text{ g}$

= 0.9217 g

18 g of water contains 2 g of hydrogen.

0.690 g of water will contain hydrogen $= \frac{2\text{ g}}{18\text{ g}} \times 0.690$

= 0.0767 g

Since carbon and hydrogen are the only constituents of the compound, the total mass of the compound is:= 0.9217 g + 0.0767 g= 0.9984 g

Percent of C in the compound $= \frac{0.9217\text{ g}}{0.9984\text{ g}} \times 100$

= 92.32%

Percent of H in the compound $= \frac{0.0767\text{ g}}{0.9984\text{ g}} \times 100$

= 7.68%

Moles of carbon in the compound $= \frac{92.32}{12.00}$

= 7.69

Moles of hydrogen in the compound = $\frac{7.68}{1}$

= 7.68

Ratio of carbon to hydrogen in the compound = 7.69: 7.68= 1: 1

Hence, the empirical formula of the gas is CH.

(ii) Given,

Weight of 10.0L of the gas (at S.T.P) = 11.6 g

Weight of 22.4 L of gas at STP $= \frac{11.6\text{ g}}{10.0\text{ L}} \times 22.4\text{ L}$

= 25.984 g≈ 26 g

Hence, the molar mass of the gas is 26 g.

CONCEPT OF HYBRIDIZATION

Hyperidisation

* It is redistribution of energy and it cannot be seen by any instruement.

* Bond formation is always exothermic because it increases stability.

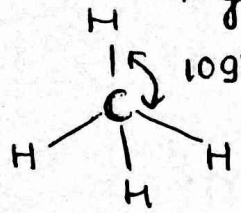
Covalent bond is parents bond.

External feacture = shape / structure

Geometry = Ideal structure

CH_4

Geometry = Tetrahedral



$C = 1s^2\ 2s^2\ 2p^2$

$= 1\downarrow\ \uparrow\ \uparrow\ —$

$\overset{*}{C} = \uparrow\downarrow\ \uparrow\ \uparrow\ \uparrow$

$\uparrow\ \uparrow\ \uparrow\ \uparrow$

$\times\ \times\ \times\ \times$

$H\ H\ H\ H$

$2s-1s$ $2p-1s$

HYBRIDISATION —

* It is the process to mix & redistribution different orbital to make them identical.

* CH_4 is tetrahedral because it is stable in tetrahedral form. It is stable because angle is bigger.

Certaria :-

* New orbital - hybrid orbitals (Non-real)

* Hybrid orbital ⟶ directional in Nature ⟶ Show more effective overlapping (which make strong bond)

* S-orbital is Non-directional / omni directional
* p-orbital is directional

Sp^n-types :-

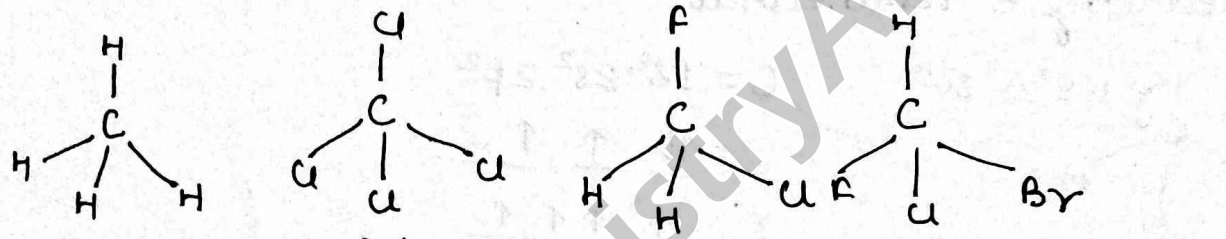
shape same but different in size

- Sp Hybrid orbital — S–p 50% 50%
- Sp^2 Hybrid orbital — $S–p^2$ 33% 66%
- Sp^3 Hybrid orbital — Sp3 25% 75%

length ∝ p-orbital/character

width ∝ S-character

* Order of general size, we take length.



CH_4 Perfect Tetrahedral

CCl_4 Perfect tetrahedral

CH_2FCl Distorted tetrahedral

$CHBrFCl$ Distorted tetrahedral

$$\cos\theta = \frac{S}{S-100}$$

$S = s\%$

$s\% \propto \theta$

① $\theta = 180$

$$\cos 180 = \frac{S}{S-100}$$

$$-1 = \frac{S}{S-100}$$

$S\% = 50$

$p\% = 100 - 50 = 50\%$.

② $\theta = 120$

$$\cos\theta = \cos 120$$

$$-1/2 = \frac{S}{S-100}$$

$S\% = 33.3\%$

$p\% = 66.6\%$

③ $\theta = 109°28'$

$\cos 109°28' = \frac{S}{S-100}$

$S\% = 25\%$

$p\% = 75\%$

④ $\theta = 105°$

$\cos 105° = \frac{S}{S-100}$

$S\% = 20$

$p\% = 80$

⑤ $\theta = 90$

$\cos 90 = \frac{S}{S-100}$

$0 = \frac{S}{S-100}$

$S\% = 0$

$p\% = 100\%$

let

If $p\% = 99.9$

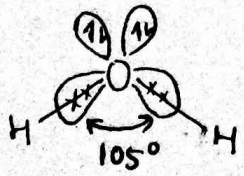
$S\% = 0000\ldots$

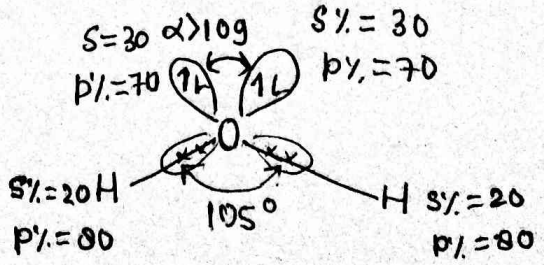
θ	S%	p%	$s^i p^i$	Hybrid Index
180°	50	50	$s^{50}p^{50}$	sp
120°	33.3	66.6	$s^{33.3}p^{66.6}$	sp^2
109°	25	75	$s^{25}p^{75}$	sp^3
105°	20	80	$s^{20}p^{80}$	sp^4
90°	0	100	s^0p^{100}	p

* HCl (zero angle / No angle)

* In methane 25% S-character for one orbital

In H_2O





$\cos 105° = \frac{S}{S-100}$

$S\% = 20$

$p\% = 80\%$

Ques What is hybridisation Index of O–H bond ?

Ans - sp^4

Ques What is hybridisation index of lone pair containing orbital.

Ans. $sp^{2.3}$

Ques - Total orbital in sp^4 hybridisation ?

$1+3=4$
no. of orbitals

Note In sp^4 1 + 4 shows ratio of 's' & 'p' character.

* Over all hybridation is cannot be fractional but a particular hybridisation index may be fractional.

* In actually angle b/w two lone pair is not exist

* α = angle b/w lone pair of H_2O.

Experimently – not possible / cannot be determined
But mathematically can be calculated as

$$\cos\theta = \frac{S}{S-100}$$

$$\boxed{\alpha = 115^\circ}$$

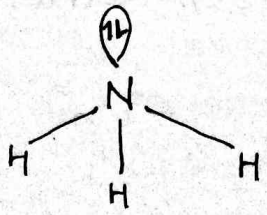
Mathematically angle b/w lone pair in H_2O in 115°.

Ques - N–H hybrid Index in NH_3 ?

Ans

Ques – Hybrid Index of lone pair ?

Ans



Ques - What is hybridisation index of lone pair containing orbital.

Ans - $sp^{2.3}$

Ques - Total orbital in sp^4 hybridisation?

$1+3=4$
no. of orbitals

Note In sp^4 1 + 4 shows ratio of 's' & 'p' character.

* Over all hybridation is cannot be fractional but a particular hybridisation index may be fractional.
* In actually angle b/w two lone pair is not exist
* α = angle b/w lone pair of H_2O.

Experimently - not possible / cannot be determined
But mathematically can be calculated as

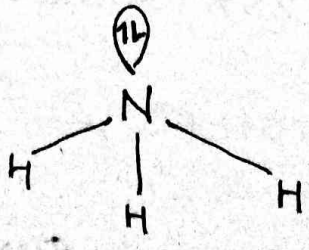
$$\cos\theta = \frac{S}{S-100}$$

$$\boxed{\alpha = 115^\circ}$$

Mathematically angle b/w lone pair in H_2O in 115°.

Ques - N-H hybrid Index in NH_3?
Ans

Ques - Hybrid Index of lone pair?
Ans



$NH_2^{\ominus}$ Hybridisation in $NH_2^{\ominus}$ is sp^3

Schemes of Hybridisation :-

Steric No. $\rightarrow$ S = H (Hybrid Number)

S = no. of lone pair + no. of bond pair

= no. of l.p + no. of σ-bond

$$S = H = \frac{1}{2}[V + m - C + A]$$

V = no. of valence of central atom

m = no. of monovalent species directly attached to C.A. (C, H, Br, I, Cl, F, (-OH, -OR, $-NH_2$, -NHR, $-NR_2$))

C = cationic charge

A = Anionic charge

Example

CH_4

$S = H = \frac{1}{2}[4+4] = 4$, sp^3

CH_2Cl_2

$S = H = \frac{1}{2}[4+2+2] = 4$, sp^3

$CHCl_2Br_2$

$S = \frac{1}{2}[4+4] = 4$, sp^3

BrF_3

$S = \frac{7+3}{2} = 5$, sp^3d

BrF_5

$S = \frac{7+5}{2} = 6$, sp^3d^2

IF_7

$S = \frac{7+7}{2} = 7$, sp^3d^2

$NO_2^{\ominus}$

$S = \frac{5+1}{2} = 3$, sp^2

NO_2^{+}

$S = \frac{5-1}{2} = 2$, sp

NO_3^{-} - sp^2

$S = \frac{5+1}{2} = 3$, sp^2

CO

$S = \frac{4}{2} = 2$, sp

CO_2

$S = 2$, sp.

CO_3^{--}

$S = \frac{4+2}{2} = 3$, sp^3

H_2CO_3

$S = \frac{4+2}{2} = 3$, sp^2

$Li^{+}(AlH_4)^{-}$ covalent

$S = \frac{3+4+1}{2} = 4$, sp^3

$AlCl_3$

$S = \frac{1}{2}[3+3] = 3\ sp^2$

$AlCl_4^{\ominus}$

$S = \frac{1}{2}[3+4+1] = 3,\ sp^2$

$BeCl_2$

$S = \frac{2+2}{2} = sp$

$BeF_4^{2\ominus}$

$S = \frac{2+4+2}{2} = 3,\ sp^3$

$BeF_3^{\ominus}$

$S = \frac{2+3+1}{2} = 3, sp^2$

$Be(OH)_4^{2\ominus}$

$S = \frac{2+4+2}{2} = 4,\ sp^3$

PCl_5

$S = \frac{5+5}{2} = 5, sp^3d$

H_3PO_4 ($H_xP_yO_z$)

oxo acid

H_3PO_4

$PO_4^{3\ominus}$ (P-O charged)

Phosphate

H_3PO_3

$HPO_2^{\ominus}$

$H_2PO_3^{\ominus}$

~~H_2PO_3~~ $HPO_4^{2\ominus}$

All are sp^3 hybrid^n

$I_3^{\ominus}$ $\frac{7+2+1}{2} = 5, sp^3d$ $(I^+ I_2)^-$

$I_3^{\oplus}$ $\frac{7+2-1}{2} = 4, sp^3$ $(I-I_2)^+$

$ICl_2^{\ominus}$ $\frac{7+2+1}{2} = 5, sp^3d$

$ICl_3^{\oplus}$ $S = \frac{7+2-1}{2} = sp^3$

$PCl_4^{\oplus}$

$S = \frac{5+4-1}{2} = 4\ sp^3$

PCl_6^{-}

$S = \frac{5+6+1}{2} = 6, sp^3d^2$

SiO_2 sp^3

Si_3O_9 sp^3

$Si_4O_{11}^{-6}$ sp^3

$Si_2O_5^{2-}$ sp^3

Si–O silicates all silicates are sp^3 hybridisation

SCl_2 $S = \frac{1}{2}[6+2] = 4, sp^3$

$SCl_3^{\oplus}$ $S = \frac{1}{2}[6+3-1] = 4, sp^3$

SF_4

$S = \frac{1}{2}[6+4] = 5, sp^3d$

SO_2Cl_2

$S = \frac{6+2}{2} = 4$

PCl_5

$S = \frac{5+3}{2} = 4, sp^3$

PCl_5^{-}

$S = \frac{5+6+1}{2} = 6, sp^3d$

$HClO_4$
$HClO_3$
$HClO$
ClO_4^{-}
ClO_3^{-}
ClO_2^{-}
} sp^3

* Cl–O → Neutral oxide
* ClO_x^{n-} chlorate
* $H_xCl_yO_z$ → oxo acid

P_4O_9
P_2O_5
P_2O_3
P_4O_{10}
P_4O_6
P_4O_7
P_4O_8
} sp^3

$BF_3 = sp^2$

$BCl_3 = sp^2$

$BF_4^{\ominus} - sp^3$

$BH_4^{\ominus} - sp^3$

SO_2 sp^2 $H_2SO_4^-$ SO_4^{--} SO_3^{--} S_2O_3

SO_3 - sp^2

sp^3

$S_2O_7^{2-}$, $S_4O_7^{2-}$, H_2SO_4, H_2SO_3 } sp^3

$H_xS_yO_z$ – Neutral oxoacids

$(H_xS_yO_z)^{n-}$ – (Charged) sulphates / ite / ate } sp^3

XeO_2 sp^3 | XeO_3 sp^3 | XeO_4 sp^3 | XeO_2F_2 sp^3d | $XeOF_4$ sp^3d^2

XeO_3F_2 sp^3d | $XeO_2F_2^{\ominus}$ sp^3d | $XeO_2F_3^{\oplus}$ sp^3d | XeF_2 sp^3d | XeF_4 sp^3d^2 | XeF_6 sp^3d^3

XeF_5^+ $\frac{8+5-1}{2}=\frac{12}{2}=6$ sp^3d^3

XeF_5^- $\frac{8+5-1}{2}=\frac{10}{2}=5$ sp^3d

XeF_7^+ sp^3d^3

$XeF_7^{\ominus}$ sp^3d^4

* $Xe_2F_3^{\ominus}$ Abnormal example

$IF_4^{\oplus}$ sp^3d | $IF_4^{\ominus}$ sp^3d^2 | $IF_6^{\ominus}$ $\simeq p^3d^3$ $\simeq p^3d^3$ | $IF_8^{\ominus}$ sp^3d^4 | $IF_6^{\oplus}$ sp^3d^2

PPh_5 $\frac{5+5}{2}=10$ sp^3d | $SbPh_5$ sp^3d | $SbPh_5$ sp^3d | $CH_3-\ddot{O}-CH_3$ $\frac{6+2}{2}=4$ sp^3 | O_3 $\frac{6}{2}=3$ sp^2

Special Example :-

N_2 – sp hybridisation

P_4, O_2 Cl_2 → No hybridisation

PH_3 H_2Se H_3O^+

NH_4^+ $H_5O_2^+$ } sp^3

AsH_3 $H_9O_4^+$

HgO_4^+

BiH_3 $\quad \overset{\ominus}{S}H_3$ $\quad H_2S$

$HgOH^+$ $\quad \overset{\ominus}{O}H$ $\quad \overset{\oplus}{D}_2H_3$

N_2H_4 $\quad P_2H_4$ $\quad B_2F_4$

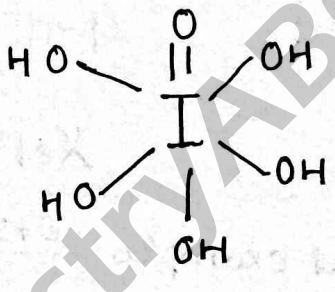
B_2Cl_4

Special example

$HIO_4 \cdot 2H_2O = H_5IO_6$

oxidising

$\frac{7+5}{2} = 6 = sp^3d^2$



* In true sense no hybridisation in N_2 but due to
* In some complex formation ability Sp hybridisation suppose to be present.

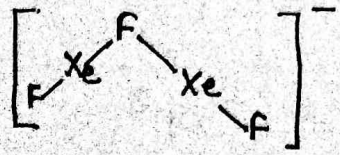
$N_2P_4O_3$ → No hybrisation possible

* $\underbrace{F_2, Cl_2, Br_2, I_2, H_2, O_2}$

No Hybridisation

* Special example

$Xe_2F_3^{\ominus}$



$\frac{8+2}{2} = 5$ sp^3d

T-shape

* XeF_7^+ $\frac{8+7-1}{2} = 7 \approx sp^3d^3$

* XeF_7^- $\frac{8+7+1}{2} = 8 \approx p^3d^4$

* XeF_8^{--} $\frac{8+8+2}{2} = 9 \approx p^3d^5$

ICl_2Br^+

$\frac{7+2-1}{2} = \frac{8}{2} = 4\ sp^3$

* N_2H_4 (Hydrazine)

NH_2 — NH_2 $\frac{5+3}{2} = 4\ sp^3$ { 2-Hydrogen monovalent, 1 – NH_2 Cmonovalent }

NH_2 → sp^3

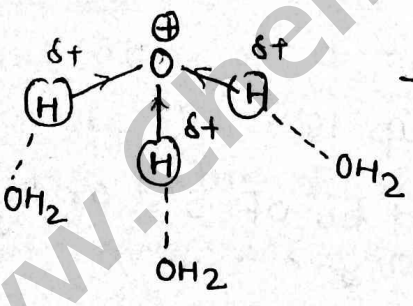
* B_2F_4 ($BF_2 - BF_2$) → sp^3

$\frac{3+2+1}{2} = 3\ sp^3$

$H_2O \rightleftharpoons H^+ + \bar{O}H$

↓

H_3O^+



→ $H_5O_2^+$ (sp^3) $\xrightarrow{H_2O}$ $H_7O_3^+$ (sp^3) $\xrightarrow{H_2O}$ $H_9O_4^-$ (sp^3)

* Any acidic solution only these type of H_3O^+, $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$

$\bar{O}-H \xrightarrow{OH_2} \bar{O}H\text{---}OH_2$

or

$H_3O_2^-$

sp^3

H_2O_2 $(SCN)_2$

S_2Cl_2 O_2F_2

S_2H_2 OF_2

$(CN)_2$

Dargo Rule :-

	Group - 15	Angle	
Shape of all trigonal pyramidal	NH_3	~ 107°	} Hybridisation is valid for NH_3 not for BiH_3
	PH_3 Phosphine	~ 94°	} Angle around 90±
	AsH_3 Arsine	~ 92°	
	SbH_3 Stibine	~ 91°	
	BiH_3 Bismuthine	~ 90°	

Dargo Rule Conditions

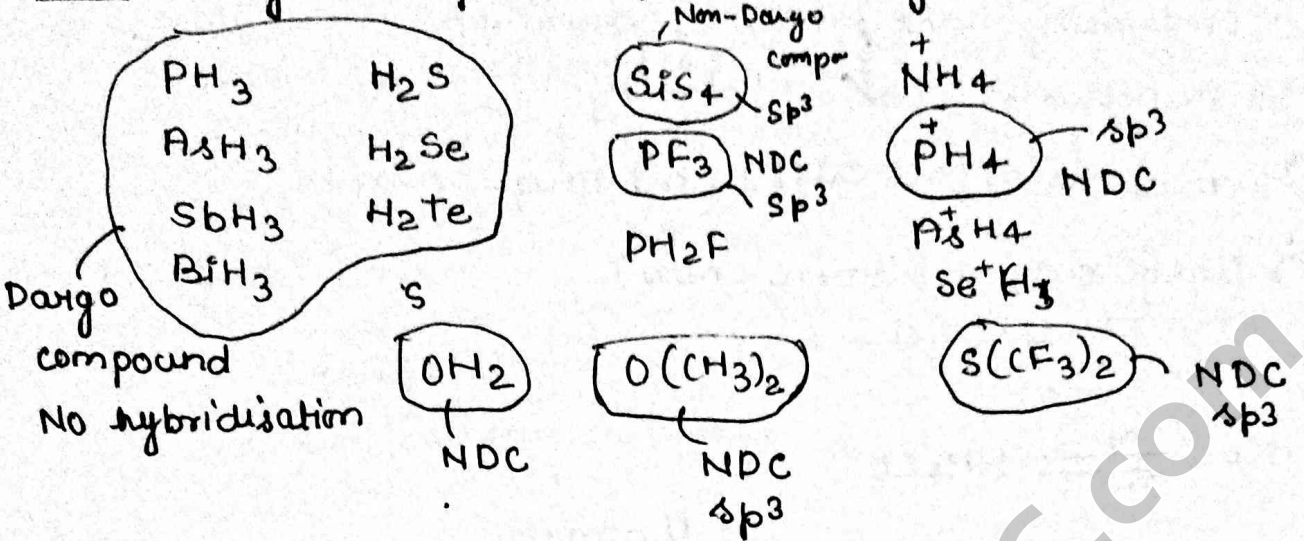
1. Valid for Group 15 and Group 16.

Central atom (C.A.) = should be of 3rd or higher period.

Surrounding atom (S.A.) = it's $\chi < 2.5$; χ = electronegativity

Elements	χ (electronegativity)
F	4.0
O	3.5
Cl ≃ N	3.0
Br	2.8
C ≃ S ≃ I	2.5

Ques Dargo compound & Non-Dargo compound are.



④ Compound should be neutral compound.

⑤ When any one are e ~~negative~~ electronegative atom greater than 2.5, then compounds are Non-Drago compound.

⑥ Bent angle 90 ± 5 formed by almost pure orbitals.

Drago Rules :—

" If central atom of a neutral molecules belongs to 15–16 group and of 3rd or higher periods and all surrounding atoms electronegativity less than 2.5 then such molecules are called Dargo compound. and donot undergo hybridisation and in them angles is around 90° ± 5° and Bonds are formed usually by almost pure orbitals.

sp^3 $H_3\ddot{N}$ + H^+ $\rightleftharpoons$ $[H_3N-H]^+$ (sp^3-1s) or $NH_4^{\oplus}$ (Hybrid compound or stable)

No hybridisation $H_3P + H^+ \rightleftharpoons [H_3P-H]^+$ ($3s-1s$) or $\overset{+}{P}H_4$

NH_4Cl (thermally stable) ↓ decrease thermal stability

PH_4Cl – do not exist

NH_4I – small cation (not exist) and large anion

PH_4I – (large cation & large anion) that exist

$NH_3 + HCl \underset{}{\overset{K_1}{\rightleftharpoons}} NH_4Cl$

$NH_3 + HBr \overset{K_2}{\rightleftharpoons} NH_4Br$

$NH_3 + HI \overset{K_3}{\rightleftharpoons} NH_4I$

↓ Thermal stability decreases

$\therefore K_1 > K_2 > K_3$

$H_3P + HCl \overset{K_1}{\rightleftharpoons} PH_4Cl$

$H_3P + HBr \overset{K_2}{\rightleftharpoons} PH_4Br$

$H_3P + HI \overset{K_3}{\rightleftharpoons} PH_4I$

↓ increase thermal stability

$K_1 < K_2 < K_3$

$\ddot{N}H_3$

$\ddot{P}H_3$

AsH_3

SbH_3

BiH_3

↓ Lewis Base

Lewis Basic strength decreases

In period

$\ddot{N}H_2 \quad \ddot{O}H_2 \quad H-F$

→ Lewis Basic strength (Electronegativity increase)

PH_3 SH_2 $H-Cl$

Lewis basic strength decrease
(Electronegativity increases)

$PH_3 : H_2\ddot{S}$

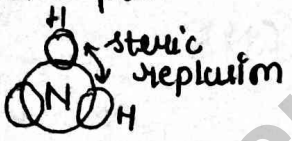
Dargo ability increases.
(Hybridisation decreases)

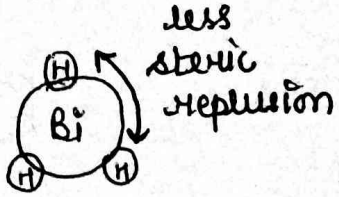
H_2O
H_2S
H_2Se
H_2Te

Dargo ability increases
hybrid ability decreases
(Parity of orbital in bond increases)

PH_3
less pure lone pair

H_2S
more pure lone pair





NH_3
PH_3
AsH_3
SbH_3
BiH_3

due to large size increases top to bottom then bond length increases, thermal stability decreases.

NF_3
NCl_3
NBr_3
NI_3

top to bottom size of sourrounding atom increases
∴ steric repulsion increases.
∴ thermal stability decreases.

Hybridisation :-

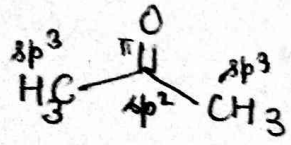
For second (2^{nd}) period element :-

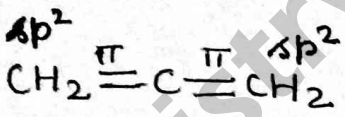
Especially C, N, O

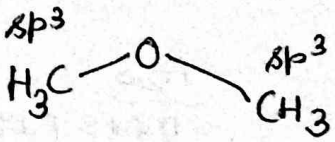
* Hybrid orbital forms σ-bond only, they donot form π-bond i.e., π-bond is formed unhybrid orbital.

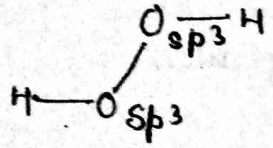
No. of π-bond	Hybridisation
0	sp^3
1	sp^2
2	sp

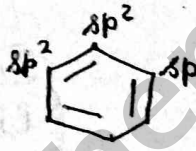
* It valid in absence of resonance and back-bonding.



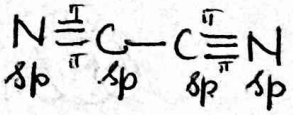


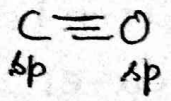


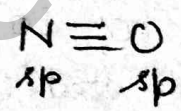




$(CN)_2$





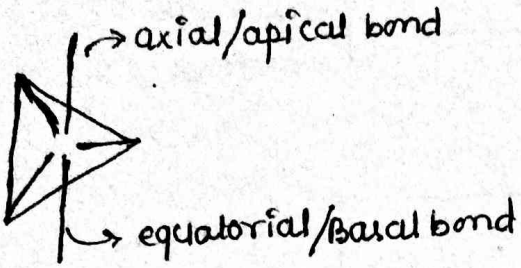


* Hybrid orbital only makes σ-bond unhybrid orbital makes both σ and π bond.
* π-bond formed by unhybrid orbital

Bent's Rule : (Not for coordination compound)

Electronegativity $\propto$ % s character $\propto \frac{1}{\theta}$

Trigonal bipyramidal Geometry

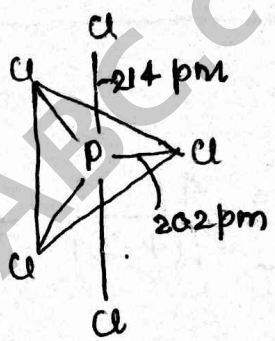


PCl_5 $P = 3s^2\ 3p^3\ 3d^0$

$P^* =$ ↑ (s) ↑ ↑ ↑ (p) ↑ (d) ----

Cl Cl Cl Cl Cl

sp^3d



Experimentally

Bond length of $(P-Cl)_{axial} > (P-Cl)_{equatorial}$

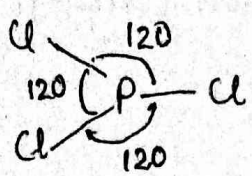
It is not necessary that a single hybridisation scheme can explain the properties completely some time single hybridisation scheme when broken into two section can explain more accurately such phenomenon is called Group hybridisation i.e., PCl_5 can be explained well $(sp^2 + pd)$ but not well by sp^3d collectively.

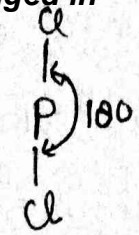
$P^* =$ ↑ ↑ ↑ ↑ ↑ ----

Cl Cl Cl Cl Cl

sp^2 pd

sp^2 pd





– In which % of s character is negligible therefore p-character is more that's why length is large

$$sp^2 + pd \longrightarrow sp^3d$$

Number of angles :–

$$\text{No. of angles } (\angle s) = \frac{n!}{2!(n-2)!}$$

where,
n = no. of surrounding atom.

① CH_4,
n = 4

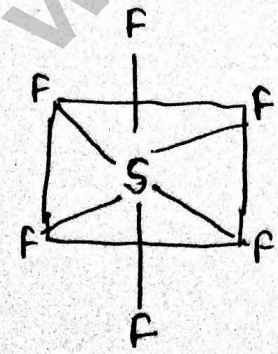
$$\angle s = \frac{4!}{2!(4-2)!} = \frac{4\times3\times2}{2\times2\times1\times1} = 6$$

② PCl_5
n = 5

$$\angle s = \frac{5!}{2!(5-2)!} = \frac{5\times4\times3!}{2\times1\times3!} = 10$$

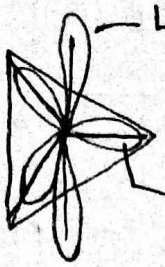
* Tetrahedral / Octahedral, cubic, isohahedral are spherical geometry i.e., they give same visualisation from different view i.e., bond length are same.

③ SF_6 sp^3d^2 In SF_6 all S–F bond length are same i.e., neither axial nor equitorial.

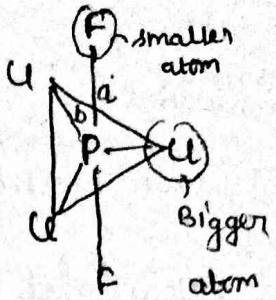


square bipyramidal (If all groups are not same)
or
Octahedral (when all groups are same)

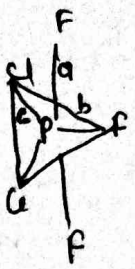
Trigonal bipyramidal



PCl_3F_2



PCl_2F_3



Bond length

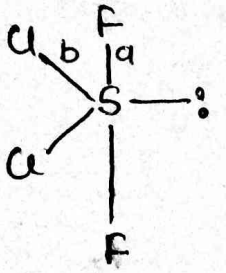
$a < b$

Bond length

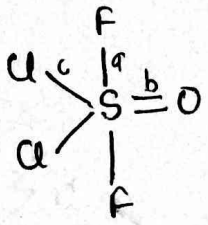
$c > a > b$

factor is size.

SF_2Cl_2 sp^3d



$b > a$



SOF_2Cl_2

sp^3d

$c > a > b$

due to double (=) bond

due to bigger size

Note a, b, c are bond length

Bent's Rule :-

For Trigonal bipyramidal, more electronegative atom prefere to join the axial (apical position) this is called it's Apicophilicity.

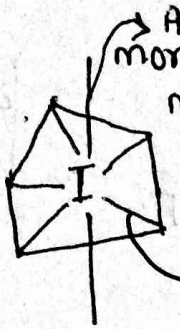
In short Bent's Rule says more electronegative atom prefere to joint the hybrid orbital which have less s-character.

* In PCl_5 bond length axial are large because bond-pair – bond-pair repulsion are more.

$P(CH_3)_2(CF_3)_2$ & $P(CF_3)(CH_3)_3$

Pentagonal Bipyramidal

IF_7



more angle
more %-S-character
more electronegativity

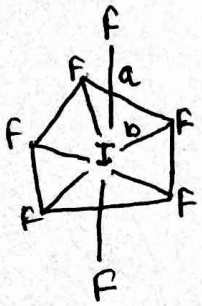
Equitorial
Less angle
less %-S-character
less electronegativity

Hybrid

Equivalent
All hybrid orbital have same % S-character

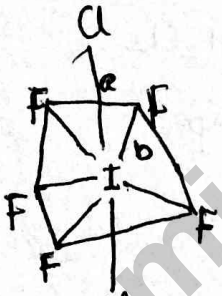
Non-equivalent
All hybrid orbital have different % of S-character

IF_7



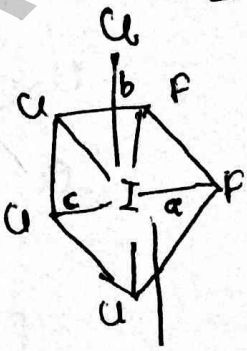
$(a)_{axial} < (b)_{equitorial}$

IF_5Cl_2



$\boxed{a>b}$

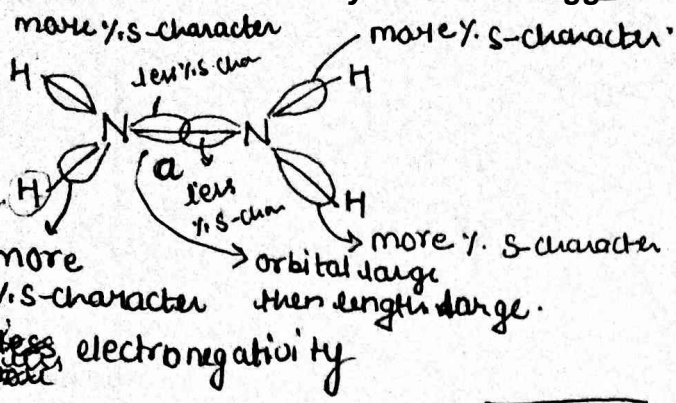
ICl_5F_2



$\boxed{c>b>a}$

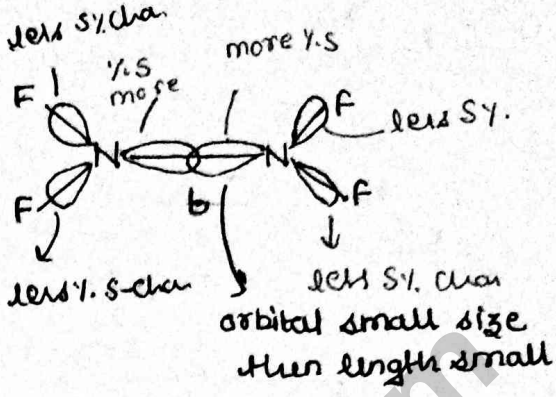
↳ Size factor

Bent Rule in Tetrahedral & Trigonal planar



$a > b$

$H_2N-_a^{}-NH_2$ $F_2N-_b^{}-NF_2$

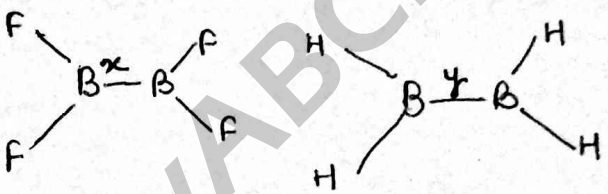


② $H_2P\underline{\ x\ }PH_2$

$F_2P\underline{\ y\ }PF_2$

$x > y$

③ B_2F_4 B_2H_4



$x < y$

④ $H_3C\underline{\ a\ }H$

$H_2F_3C\underline{\ b\ }H$

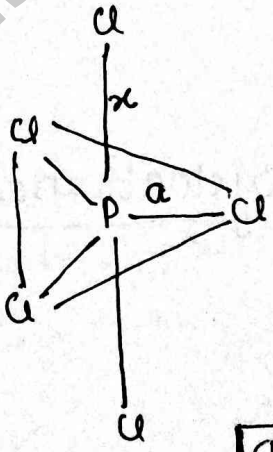
$HF_2C\underline{\ c\ }H$

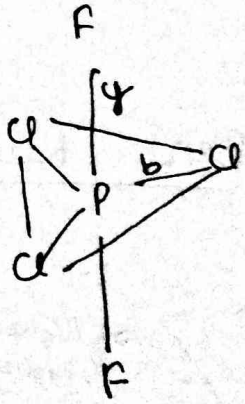
$F_3C\underline{\ d\ }H$

$a > b > c > d$

bond length

⑤





$a > b$

$x > a$

$x > y$

$y < b$

① Different atom is present size factor is effective.

② Same atom is present character factor is effective

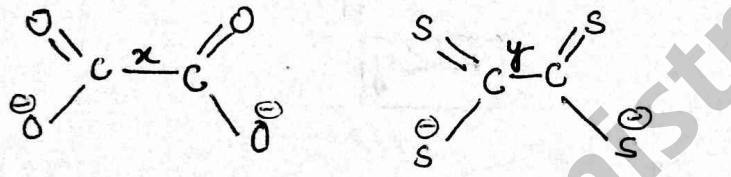
⑥ N_2O_3 N_2O_4

⑦

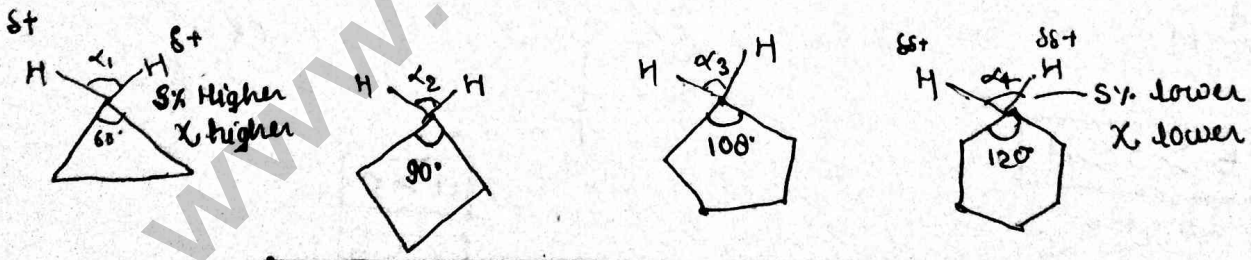
$x > y$

⑧

⑨



Bent Rule & cycloalkanes :- Electronegativity $\propto$ S% $\propto$ θ



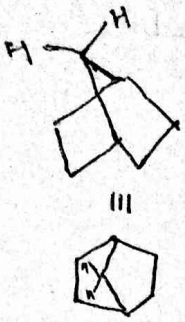
Internal Angle $= 100 - \frac{360°}{n}$ where, n = number of sides

∵ internal angle increases

∴ % S-character in internal bond increases and external angle decreases

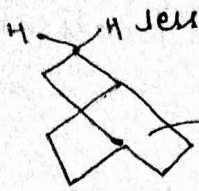
∴ % S-character in external bond decreases

Acidic strength decreases →

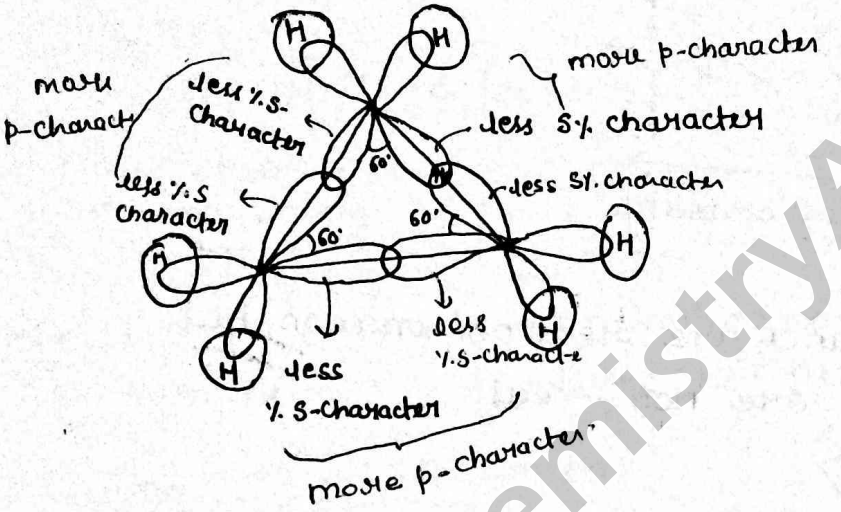


III

Five membered Ring
More acidic
(less pka)



III



① less internal angle (60°)

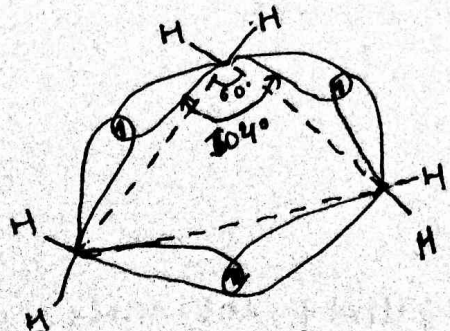
∴ More bond pair–bond pair repulsion

∴ expand outside

② Internal bond

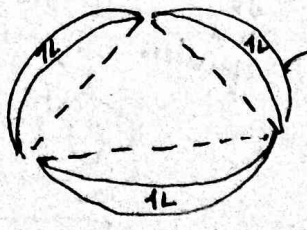
% p-character is more

∴ expand outside



B_2H_6

(3C–2e) banana

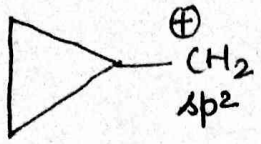


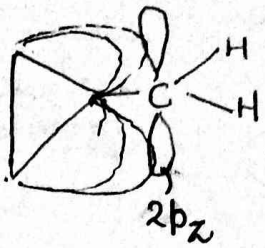
Banana bond
or
bent bond
or
Father bond
τ-bond

2 centre–2 electron

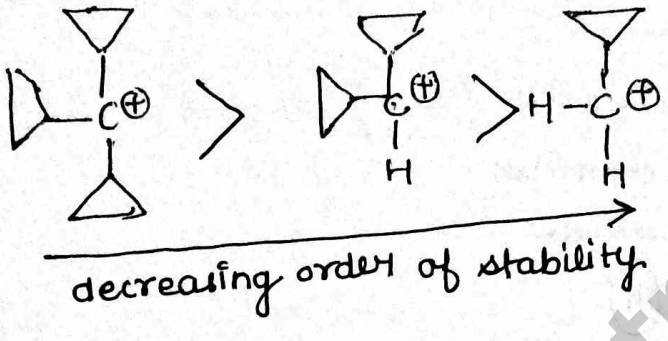
(2C–2e)

* In cyclopropane there are three banana bond in which the e's (σ-σ Electron) show delocalisation which is called dancing Resonance.

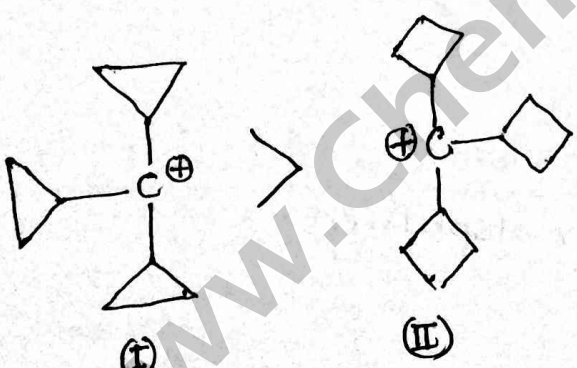




stable carbocation due to dancing Resonance



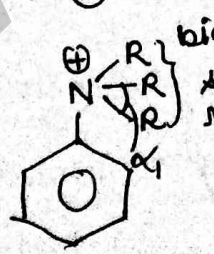
* Delocalisation, Resonance are real phenomenon but Resonance structure are non-real

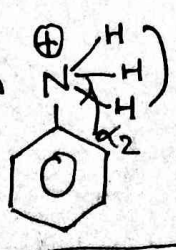


(I) is more stable than (II)

$\therefore$ $\boxed{-\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3}$

(-I- power.)





→ -I-effect power increase $\boxed{\alpha_1 > \alpha_2}$

→ Angle increases due to steric factor

$\therefore$ % S-Character increases therefore electronegativity increases (Attracting power increases)

* Bent rule apply on 2nd period but not apply on 3rd period.

HYBRIDISATION AND STEARIC NUMBER :-

Due to chelation stability increases w.r.to weak ligand.

$$[Co(H_2O)_6]^{+++} + 3en \longrightarrow [Co(en)_3]^{+++} + 6H_2O$$

$K_4[Fe(CN)_6]$ & $[Co(en)_3]^{3+}$

(more stable) due to strong ligand.

Note – Minimum no. of coordination no. may (1)
Minimum no. of steric no. may (2)

Resting Fe — Carbonate, Bicarbonate, Oxide

$V^{+5} = [Ar]\ 4s^0\ 3d^0$ → A/c to Afbau

↓

Afbau German language means "to built up"

↓

Given by Simmons.

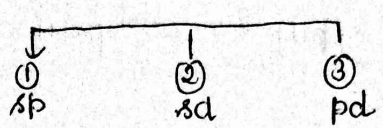
↓

based upon (n+l) Rule

↓

given by "Klechkowasky" (Cn+s) Rule

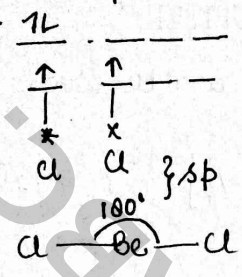
Stearic Number – 2
(No. of l.p. + No. of b.p.)



① sp

example – $BeCl_2$, CO_2, $CH \equiv CH$

$Be = 1s^2 2s^2 2p^0$

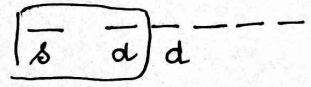


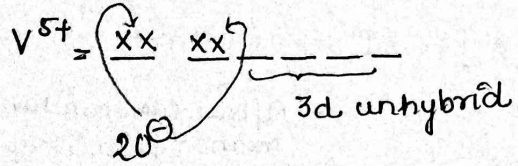
② sd → linear
→ Bent

example $VO_2^{\oplus}$

$V = [Ar]_{18}\ 3d^3\ 4s^2$

$V^{5+} = [Ar]_{18}\ 4s^0\ 3d^0$





⇒ VO_2^+ linear in shape

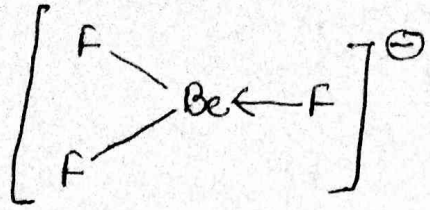
* Inner & outer complex are used octahedral & tetrahedral.

(Oxide are flexidentate ligands)

Stearic Number – 3

sp^2 (Trigonal Planar)

e.g ① $BeF_3^{\ominus}$



$Be = 1s^2 2s^2 2p^0$

$Be^* = 1s^2$ ↑x ↑x xx — — —

F F $F^{\ominus}$

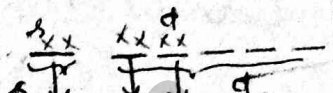
sp^2

Two covalent one coordination.

example ② CrO_3

$Cr = [Ar]\ 3d^5 4s^1$

$Cr^{+6} = [Ar]\ 4s^0\ 3d^0$



O O O

sd^2 hybridisation

Stearic Number – 4 (Tetrahedral (Td)) sp^3

example ① sd^3

$KMnO_4$ or $K^{\oplus}MnO_4^{\ominus}$

$Mn = [Ar]\ 3d^5 4s^2$

$Mn^{+7} = [Ar]\ 4s^0\ 3d^0$

$Mn^{+7} = [Ar]$ — — — — —

4s

sd^3

example ② sp^3

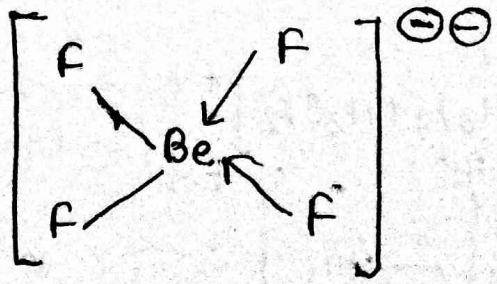
$BeF_4^{\ominus\ominus}$

$Be = 1s^2 2s^2 2p^0$

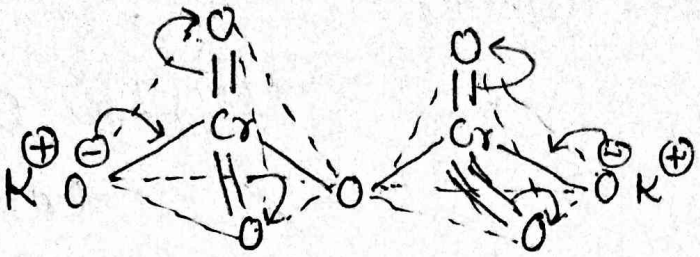
$Be = 1s^2$ ↑x ↑x xx xx

F F $F^{\ominus}$ $F^{\ominus}$

sp^3



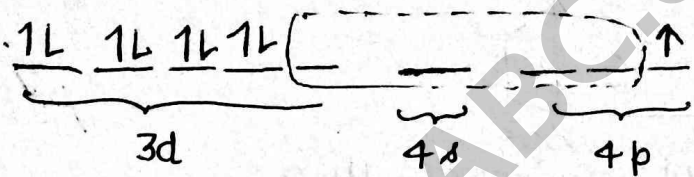
* sp^3 (tetrahedral) → $KMnO_4$, $K_2Cr_2O_7$, CrO_2Cl_2



Exam ③ dsp^2

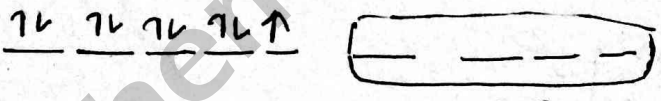
$[Cu(NH_3)_4]^{++}$ (square planar)

$Cu^{++} = 3d^9\ 4s^0\ 4p^1$

= 

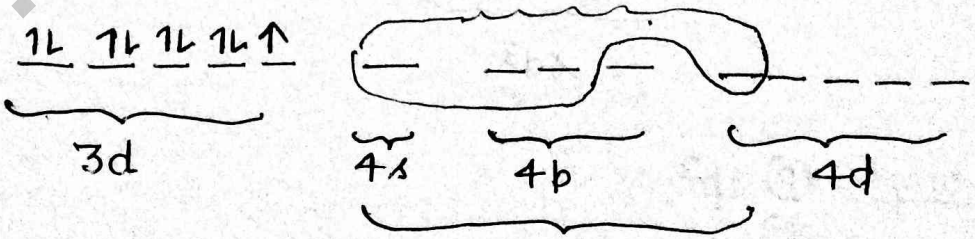
dsp^2

Note – By Orgel

Cu^{++} = 

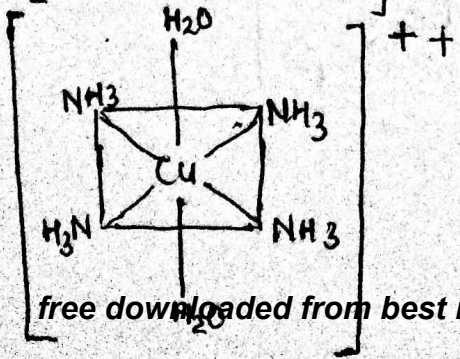
$sp3$

By Huggins

Cu^{++} = 

sp^2d hybridisation

$[Cu(NH_3)_4(H_2O)_2]^{++}$



++

* H_2O is very weakly attached with 'Cu'.

Note:- * Where there is strong John-Teller distortion hybridisation theory dosnot used.

* However if asked then sp^2d is quite reasonable.

Ques -

(a) $[Cu(en)_3]^{++}$

(b) $[Cu(H_2O)_6]^{++}$ sp^3d^2

(c) $[Cu(CN)_6]^{4\ominus}$

John teller distortion is more when strong ligands are attached.

ⓒ > ⓐ > ⓑ → weak hybridisation

↓

strong ligand

John Teller distortion.

Note:-

$[Ni(CN)_4]$

dsp^2

$NiBr_2 + 2PEt_2L \longrightarrow NiBr_2(PEt_2L)_2 \xrightarrow{\text{Isomerisation}} NiBr_2(PEt_2L)_2$

where, L = Ph, Me

C.N. = 4

Green

Paramagnetic

Tetrahedral

sp^3

Red

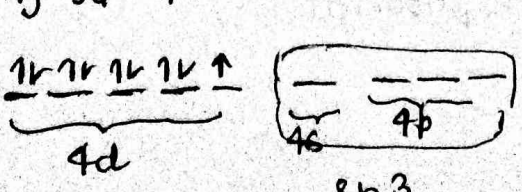
Diamagnetic

Square planar

d^2sp^2

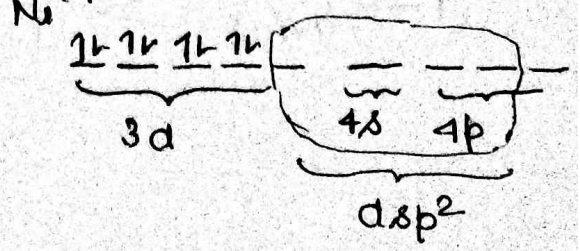
$Ni = [Ar]\ 3d^8\ 4s^2$

$Ni^{++} = [Ar]\ 3d^8\ 4s^0\ 4p^0$



sp^3

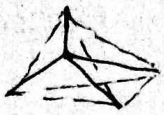
2 unpaired electron



dsp^2

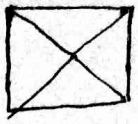
No unpaired electron

Tetrahedral ← Square planar



Paramagnetic

Polytopal isomer or (Allagon isomer) (Structure isomer)



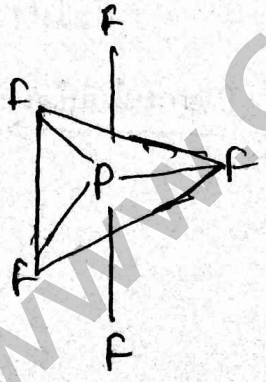
diamagnetic

Steric Number – 5 :–

- sp^3d (sp^2+pd) (Trigonal bipyramidal)
- Square pyramidal (sp^3d) or (dsp^3)

@ At Room temprature :–

PF_5 ↓ (Fluxonial compound)



Berry Pseudo Rotation

Speed fast

$(P-F)_{axial} = (P-F)_{equitorial}$

(bond length) (bond length)

(b) At low temprature :–

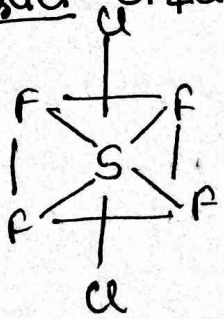
$(P-F)_{axial} > (P-F)_{equitorial}$

(apical)

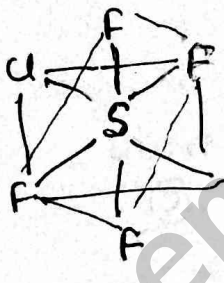
Qael $P(CH_3)_2(\bigcirc)_3$

Steric Number-6 :- sp^3d^2 / d^2sp^3
(Octahedral / Square pyramidal)

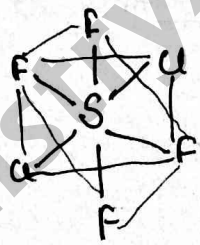
Qael SF_4Cl_2



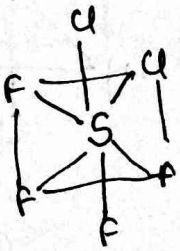
(A) trans



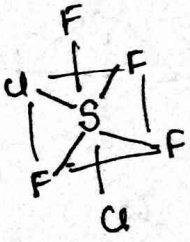
(B) Trans



(C) trans



(D) cis



(E) cis

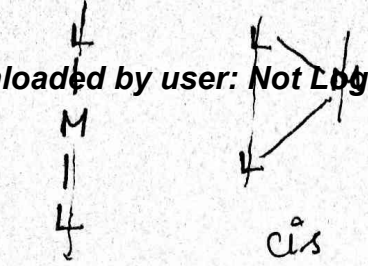
What are?

(a) Diastriomer
(b) Homomer
(c) Resonance structure
(d) Fluxonials

(A) & (B) (b)
(A) & (C) (b)
(A) & (D) (a)
(A) & (E) (a)
(B) & (C) (b)
(B) & (D) (a)
(B) & (E) (a)
(C) & (D) (a)
(C) & (E) (a)

* A, B, C are trans ⇒ Homomers.

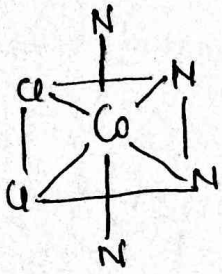
Note



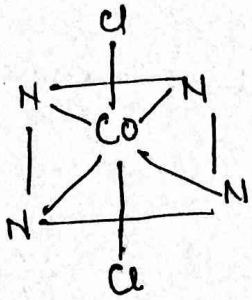
trans
(metal & ligand at a line)
(Straight line passing through metal)

cis

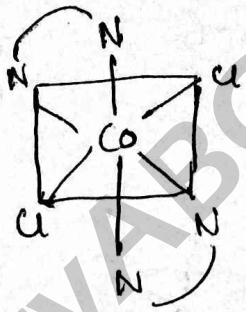
Ques $[Co(en)_2Cl_2]^{\oplus}$



cis
Ⓐ



trans
Ⓑ



trans
Ⓒ

⇒ Ⓐ & Ⓑ Diastereomer

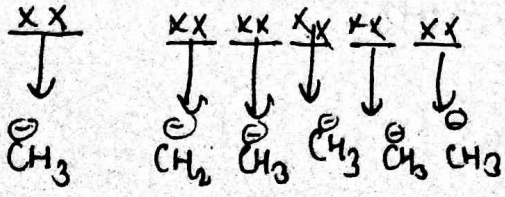
⇒ Ⓐ & Ⓒ Diastereomer

⇒ Ⓑ & Ⓒ Homomer.

⇒ $W(CH_3)_6$

$W = 5d^4\ 6s^2$

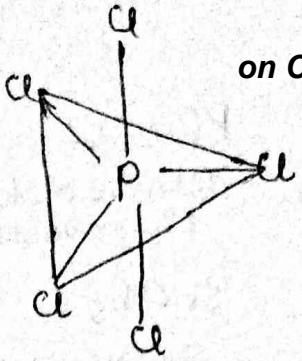
$W^{+6} = 6s^0\ 5d^0$



3d Cr $3d^5\ 4s^1$
4d Mo $4d^5\ 5s^1$
6d W $5d^4\ 6s^2$

⇒ All metal have less than 2.5 electronegative of carbon.

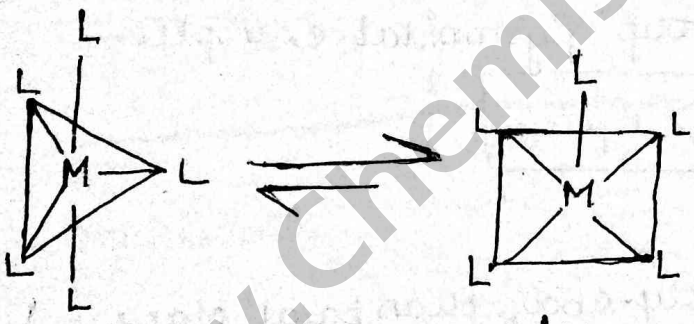
2. PCl_5



* At high temperature :-

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

* Fluxonial can not be separated } e.g - PF_5
* Geometry not change }
* Usually while Polytopal can be separated } e.g = $NiBr_2(PEt_2)_2$
* Geometry change



Bondpair – bond pair Repulsion at 90°

90°X8

More Repulsion

∴ less stable

Note :- For main Group Compound

to be square planar in SN = 5

→ ① Central Atom (C.A.) – Bigger = usually 4th, 5th, 6th

② Surrounding Atom (S.A) Bigger Ph, -CHPh, Mes (Mesityl gp)

$P(CH_2Ph)_5$ → Square planar (size factor effective)

$Sb(CH_2Ph)_5$ Square planar

PPh_5Cl_2 Tetrahedral bipyramidal

$SbCPh_5$ Square planar

PCl_5 (Tbp)

PF_5 (Tbp)

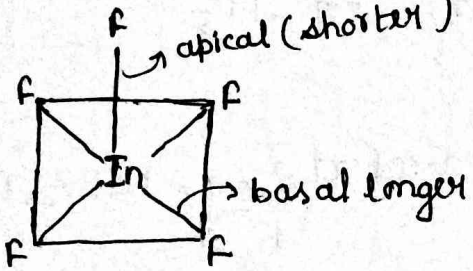
$P.Ph_5$ (Tbp)

AsF_5 (Tbp)

$AsPh_5$ (Square planar)

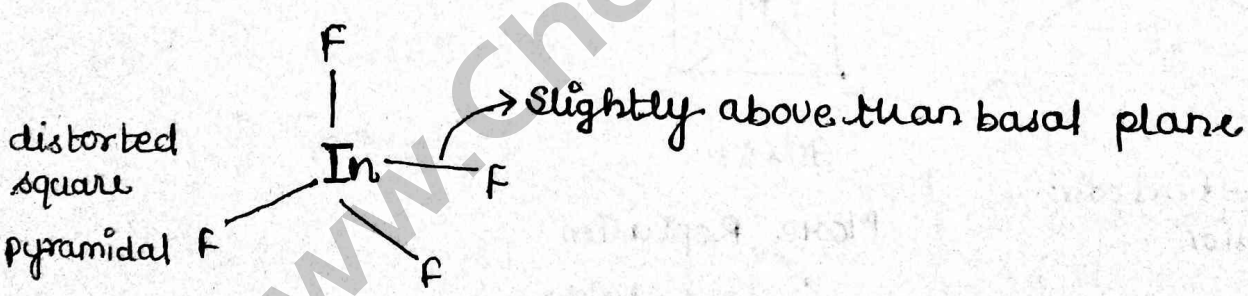
Abnormal Example :-

$InF_5^{\ominus\ominus}$ (Square pyramidal)



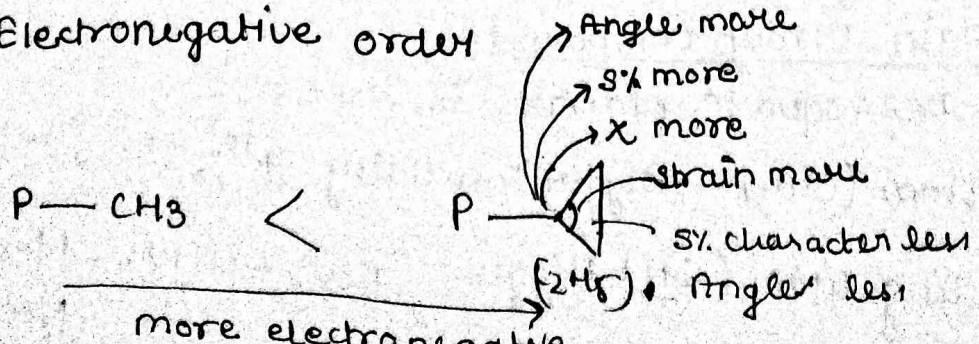
In most of main Group pyramidal examples —

Basal angle > Apical

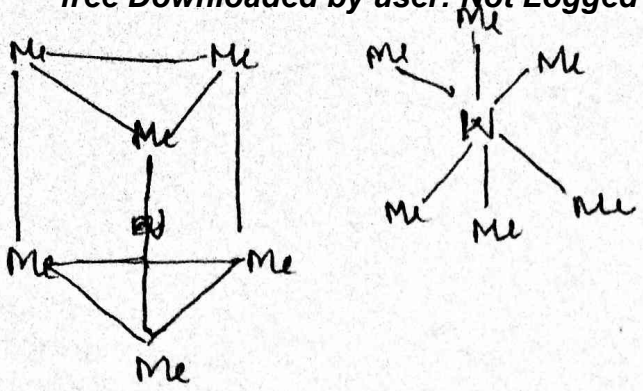


∴ Here no angles is of 90°

Ques Electronegative order



Geometry :- Trigonal prismatic

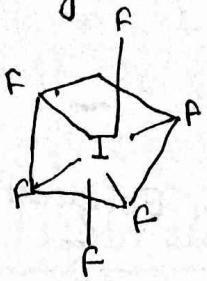


Steric No-7 :- ① sp^3d^3 / d^3sp^3

② sp^3d^3 / d^3sp^3 (Pentagonal bipyramidal)

eg IF_7

$[ReH_7]^{3-}$



Steric No-8

Square Antiprismatic
↓
(Most stable among three)
$IF_8^{\ominus}$

Hybridisation = sp^3d^4 / d^4sp^3 sp^3d^3f

Cubic
$[PaF_8]^{3-}$
$[UF_8]^{3-}$

Dodecahedral
↓
$[U(NCS)_8]^{3-}$
or
$[Cr(O_2)_4]^{3-}$
sp^3d^4 / d^4sp^3

Steric Number - 9 :-

Tricapped trigonal Prismatic Geometry

Hybridisation = sp^3d^5 / d^5sp^3

e.g $[ReH_9]^{3-}$ $[Sc(H_2O)_9]^{3+}$

Delta hedron :-

Δ^n = no. of Δ faces.

Δ^4 = Tetrahedron / hedral

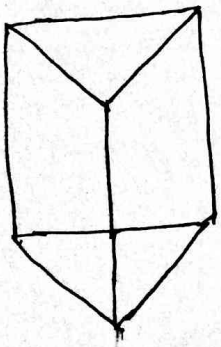
Δ^6 = Hexahedron

Δ^8 = Octahedron

Δ^{12} = Dodecahedron

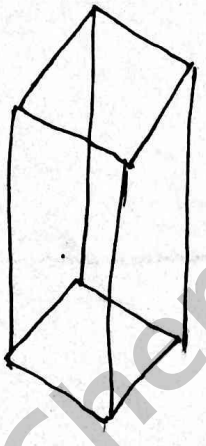
Δ^{20} = Icosahedron.

Prismatic :-



Base = triangle

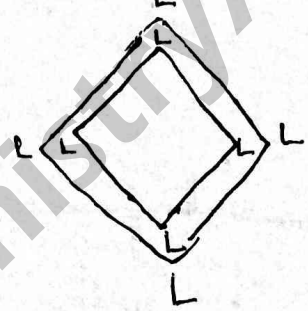
Trigonal prismatic



Box Square

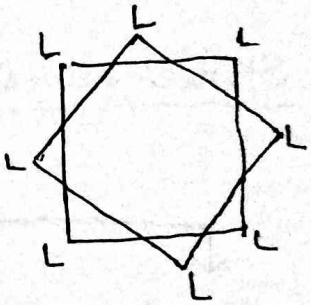
Square-prismatic

Eclipsed



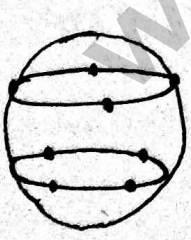
Square prismatic

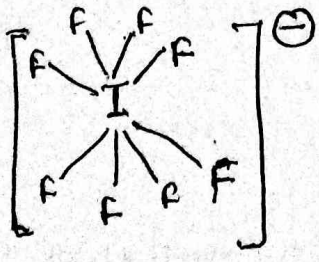
(More stable)
Staggered



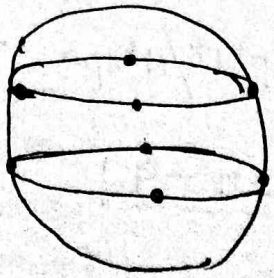
Square Antiprismatic

Eclipsed :-

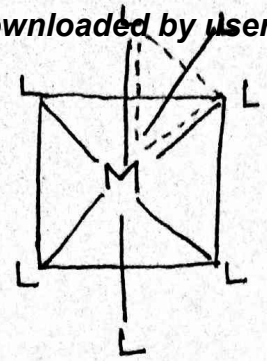




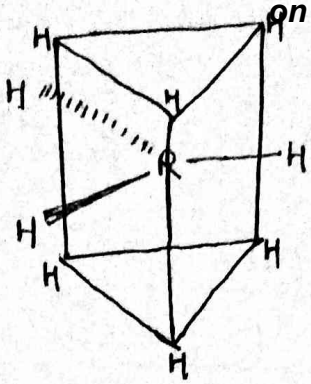
staggered



Square antiprismatic.



Mono capped Octahedral

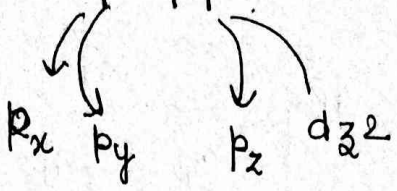


tricapped trigonal prismatic

* ReH_8^- not exist because two Hydrogen atom exist at 180° which is not possible because triangle base is small where replusion is more.
* Bicapped octahedral to get stability change into Dodecahedral or square prismatic.

Structure	Hybridisation	Orbital involved in hybrid^n
S.N.=2 ① Linear	sp / pd	p_z
S.N.=3 ② Trigonal Planar	sp^2	p_x, p_y
S.N.=4 ③ Tetrahedral	sp^3 / sd^3 / d^3s	p_x p_y p_z ; d_{xy}, d_{yz}
④ Square planar	sp^2d / dsp^2	$d_{x^2-y^2}$
S.N=5 ⑤ Trigonal bi-pyramidal	sp^3d / dsp^3	d_{z^2}
⑥ Square planar	sp^3d / dsp^3	$d_{x^2-y^2}$
S.N.=6 ⑦ Octahedral or squar pyramidal	sp^3d^2 / d^2sp^3	$d_{x^2-y^2}$ / d_{z^2}
⑧ Trigonal Prismatic	sd^5 / d^5s	d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}
S.N.=7 ⑨ Pentagonal Bipyramidal	sp^3d^3 / d^3sp^3	d_{z^2}, $d_{x^2-y^2}$, d_{xy}
S.N.=8 ⑩ Square anti prismatic	sp^3d^4 / d^4sp^3	d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$
⑪ Dodecahedron	sp^3d^4 / d^4sp^3	d_{xy}, d_{yz}, d_{zx}, d_{z^2}
⑫ cubic	sp^3d^3f	d_{xy}, d_{yz}, d_{zx}, f_{xyz}
S.N.=9 ⑬ Tricapped trigonal prismatic	sp^3d^5 / d^5sp^5	p_x, p_y, p_z d_{xy}, d_{yz}, d_{zx} $d_{x^2-y^2}$, d_{z^2}

$sp^3d^2 = sp^2 + pd$



Types of lone pair :-

(Stereochemically active lone pair)

→ lone-pair that cause distortion

→ Usually participate

(Stereochemically inactive lone pair)

→ lone pair → donot cause distortion

→ Usually remain deeply seated & hence don't take part in hybridisation

→ they are not involved in shape

Condition :-

① central atom (large)

② surrounding atom X, less

e.g.,

p^3d^3 Perfect Octahedral

- $[TeX_6]^{\ominus\ominus}$
- $[SeX_6]^{\ominus\ominus}$
- $[SnX_6]^{4\ominus}$
- $[BiX_6]^{\ominus\ominus\ominus}$
- $[SbX_6]^{\ominus\ominus\ominus}$

p^3d^3 Octahedral Perfect or

- $[BrF_6]^{\ominus}$
- $[ICl_6]^{\ominus}$
- $[XeF_8]^{\ominus\ominus}$
- $[XeF_7]^{\ominus}$

where X = Cl, Br

Important condition for

* Stereochemically inactivity usually takeplace in steric No > 7 always. (Greater than S.N. = 7).
* In steric No. 7 some time inactive.

$[SbCl_6]^{\ominus\ominus\ominus}$

S.N. = $\frac{5+6+3}{2} = 7$

∴ 6 ligand (b.p)

7 − 1 = 1 (lone pair)

↓

Stereochemically inactive

→ the lone-pair containing orbital will not participate in Hybrid.

∴ **Hybridisation p^3d^3 (Perfect octahedral)**

* $[XeF_8]^{\ominus\ominus}$

Steric No. = $\frac{8+8+2}{2} = \frac{18}{2} = 9$

Hybridisation = p^3d^5 (square antiprismatic)

* $[XeF_7]^{\ominus}$

S.N. $\frac{8+7+1}{2} = \frac{16}{2} = 8$ (sp^3d^4)

Hybridisation = sp^3d^4

S.N = 8 → Bond pair = 7

lone pair = 1 (Inactive lone pair)

∴ hybridisation = p^3d^4

Geometry – Monocapped Octahedral

$[XeF_6]$

Expectation

$\vec{\mu} = 0$

$\frac{8+6}{2} = \frac{14}{2} = 7$

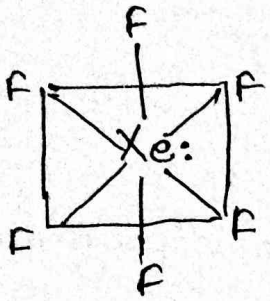
But experimental

$\vec{\mu} \neq 0$

Hence it is not of perfect shape.

B.p = 6

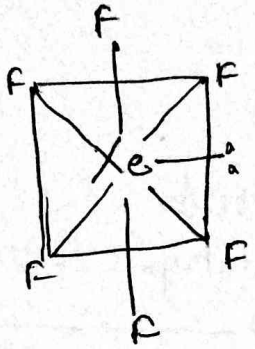
l.p = 1



Stereochemically inactive

40%.

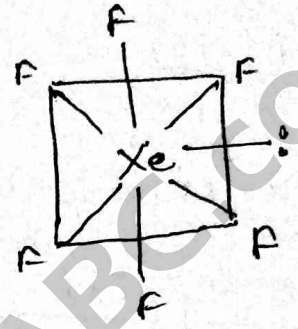
Perfect octahedral



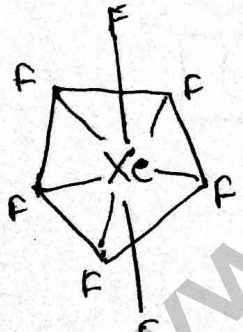
Active

60%.

sp^3d^3 distorted ochahedral (Monocapped octahedral)



Borderline activity



Distorted Pentagonal Bipyramidal

* XeF_6 is very special where due to fluxonality the lone pair more inside & outside the sphere (face). At agiven time maximum molecules of XeF_6 is in gas exist in distorted octahedral from sp^3d^3.

* XeF_6 covalent

↓ cooling

Polymeric solid

Tetramer, Pentamer

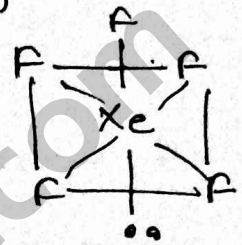
major ↓

$[[XeF_5]^+F^-]_4$ ionic form

$[XeF_5]^{\oplus}$ b.p = 5, l.p = 1

$S.N = \frac{0+5-1}{2} = 6$

$[XeF_5]^{\oplus}$ Hybridisation



sp^3d^2

$[XeF_5]^{\oplus}$ → Hybridisation = sp^3d^2

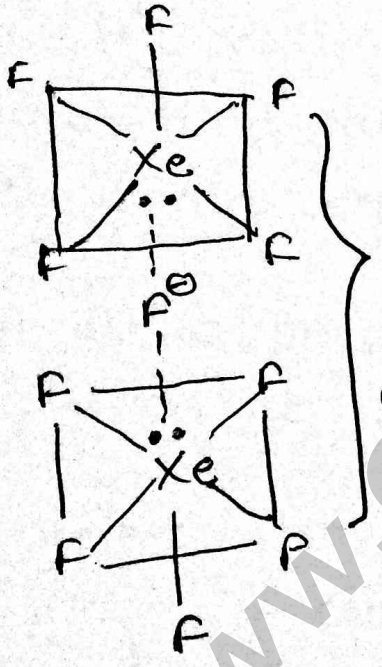
→ Shape = Square pyramidal

Square Pyramidal

↓ with $F^{\ominus}$

↓

Octahedral



octahedral.

VSEPR MODEL :-

(Valence shell electron pair Repulsion Model) :-

Given by "Gillespie & Nyholm"

* Valid ~~for~~ only for main groups
* VSEPR theory not valid for coordination / d-block
* Based upon electronic repulsion

A compound exist in that structure where it's repulsion are minimised (i.e maximum stability.

Q<u>yes</u> At 105° in Water ?

(I) l.p − l.p = l.p − b.p = b.p − b.p

(II) l.p − l.p > l.p − b.p > b.p − b.p

(III) l.p − l.p < l.p − b.p < b.p − b.p

<u>Types of electron</u> :-

(I) lone-pair

(II) π

(III) bond-pair (σ-bond)

(IV) odd e⁻

<u>Types of repulsion</u> :-

(1) l.p − l.p (2+2=4)

(2) l.p − π (2+2=4)

(3) l.p − b.p (2+2=4)

(4) l.p − Odd (2+1=3)

(5) π − π (2+2=4)

(6) π − b.p (2+2=4)

(7) π − odd (2+1=3)

(8) b.p − b.p (2+2=4)

(9) b.p − odd (2+1=3)

(10) odd − odd (1+1=2)

* lone-pair influence of one nucleus so that l.p. e's cloud is fatty.

$$\text{lone-pair} \geqslant \pi > \text{b.p} > \text{odd } e^-$$

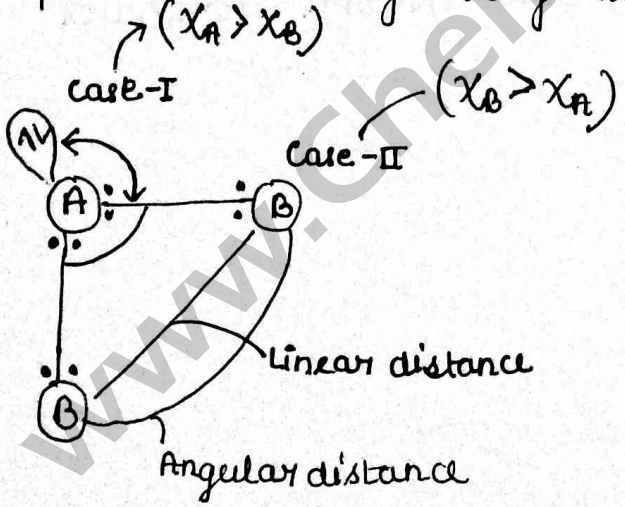
① > ② > ⑤ > ③ > ⑥ > ⑧ > ④ > ⑦ > ⑨ > ⑩

decreasing order of repulsion

Note:-

Infact the repulsion power of π electrons cloud depends upon the position of it if it is in the same plane where bond pair is present then it will show very strong repulsion on even greater than l.p.

⇒ If it is present in 1^{st} plane of b.p. than its repulsion it very-very low even less than b.p.



Postulates:-

① If the central atom (C.A) of a molecule has only bond pair then shape equal to geometry i.e., No distortion take place, called as Regular geometry (Ideal angle).

2. If the central atom (C.A.) of molecules has both lone pair & bond pair then, due to repulsion shape will be different from geometry i.e., irregular or distorted shape i.e., angle gets change from ideal values.

3. If the electron negativity of C.A. decreases (size of C.A. increases), bond angle decreases.

4. If the electronegativity of surrounding atom (S.A.) is decreases (size increases), bond angle increases.

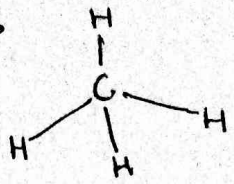
⑤ Notes:- Bargo compounds have angle around $90° \pm 5$

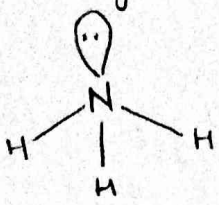
⑥ π-bond behave like lone pair.

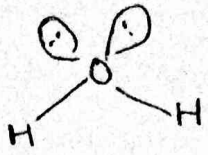
⑦ VSEPR Vs NBEPR (Non-bonded electron pair repulsion):-
NBEPR deals with surrounding & it is usually a type of steric repulsion or lone-pair - lone pair repulsion of ∅ S.A. and in maximum cases NBEPR dominates over VSEPR.

Note VSEPR doesnot have any relationship with hybridisation.

① & ② postulates examples





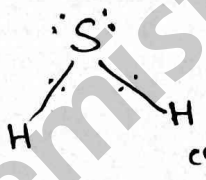


b.p.	4	3	2
l.p.	0	1	2
Steric No.	4	4	4
Geometry -	Tetrahedral	Td	Td
Angle	109°28'30''	107°	105°
Shape	Tetrahedral	Trigonal pyramidal	Bent / Angular.

Examples of ③

χ of C.A ↓ → angles ↓

case I



case II

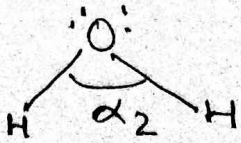
b.p =	2	2
l.p. =	2	2
S.N. =	4	4
Geometry -	Td	Td
Angle / Shape	Angular	Angular

$\alpha_1 > \alpha_2$

④

case II

case I



$\alpha_1 < \alpha_2$

χ of C.A ↓

Bond angle ↑

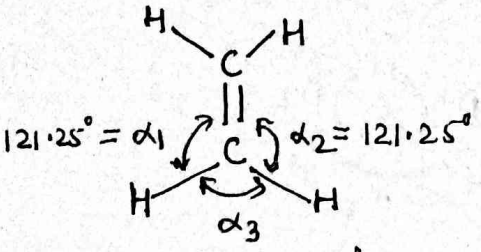
Ques. Arrange angles -

NF_3 NH_3

$NF_3 < NH_3$

Ques SH_2 SF_2

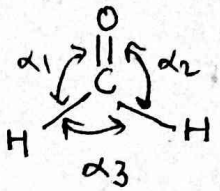
$SH_2 < SF_2$

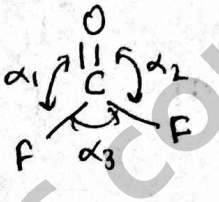


$\alpha_3 = 117.5°$

$\alpha_3 < 120°$

$(\alpha_1 = \alpha_2) > 120°$





$\alpha_1 = \alpha_2 > \alpha_3$

* Multiple bond have larger angle.

$H_3C - CH_3$ $H_2C = CH_2$ $HC \equiv CH$

sp^3 sp^2 sp

no. of π increases (↑el)

NBESPR

* χ factor: $NH_3 > NF_3$; size factor: $NCl_3 < NBr_3$

$NF_3 < NH_3 < NCl_3 < NBr_3$

* PH_2 PF_3 PCl_3 PBr_3

Drago → $PH_2 < PF_3 < PCl_3 < PBr_3$

* H_2S SF_2 SCl_2

Drago → $H_2S < SF_2 < SCl_2$

* OH_2 OF_2 OCl_2 OBr_2

χ factor → OH_2 ; $OF_2 < OH_2 < OCl_2 < OBr_2$

Bent's Rule

* AsH_3 AsF_3 $AsCl_3$

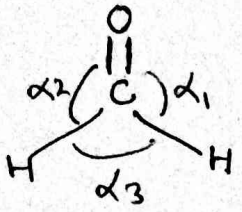
Drago $AsH_3 < AsF_3 < AsCl_3$

* $SbH_3 < SbF_3 < SbCl_3$

Drago

* $SeH_3 < SeF_3 < SeCl_3$

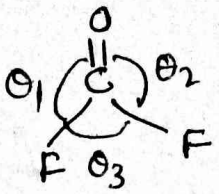
Drago



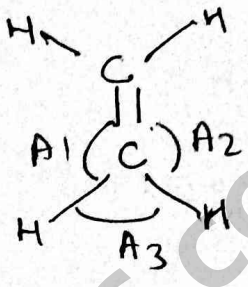
$\alpha_1 = \alpha_2 > \alpha_3$

$\alpha_1 < \theta_1$

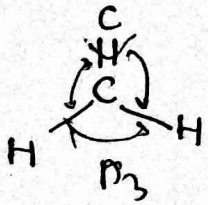
$\alpha_3 > \theta_3$

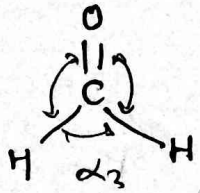


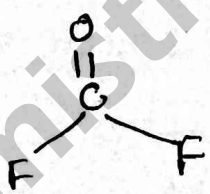
$\theta_1 = \theta_2 > \theta_3$



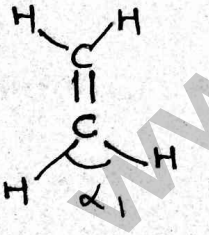
$A_1 = A_2 > A_3$



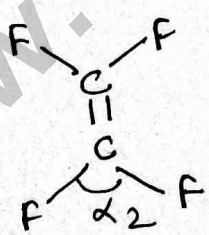




$\alpha_3 > A_3$

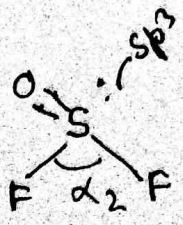


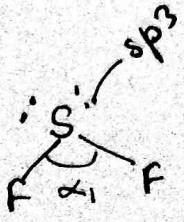
case I



case II

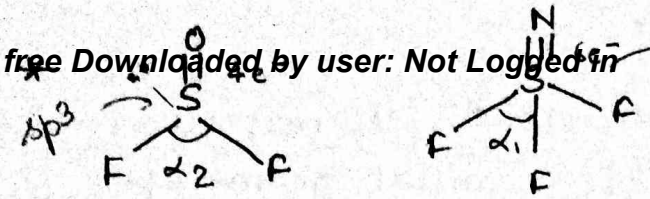
$\alpha_1 > \alpha_2$





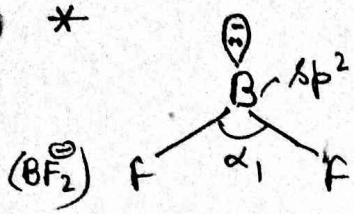
$\alpha_2 > \alpha_1$

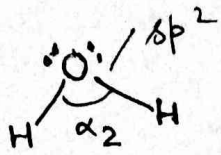
* Fristly drago then hybridisation

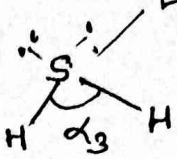


$\alpha_2 > \alpha_1$

*







$\alpha_1 > \alpha_2 > \alpha_3$

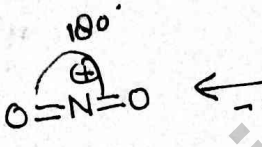
Example

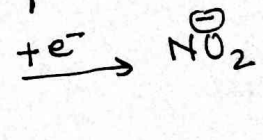
(1) NO_2 (134°)

sp^2 $\overset{+}{N}O_2$ (117) $\frac{5+1}{2} = 3\ sp^2$

sp $\overset{+}{N}O_2$ (180) $\frac{5-1}{2} = 2\ sp$

sp^2 $\bar{N}O_3$ (120) $\frac{5+1}{2} = 3\ sp^2$





$-e$ $\quad +e^- \rightarrow \ \bar{N}O_2$

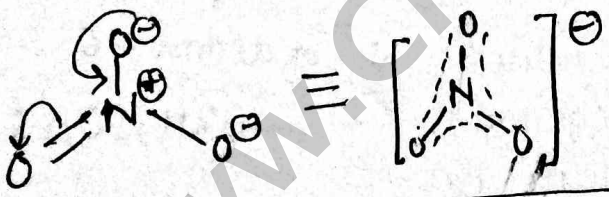
No. of σ-bond = 2

lp = 1

Hybrid = 2+1 = 3 sp^2

More than 120°

less than 120° (117°)

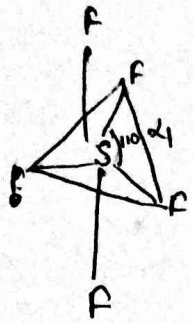


$\overset{+}{N}O_2 > NO_2 > \bar{N}O_3 > \bar{N}O_2$

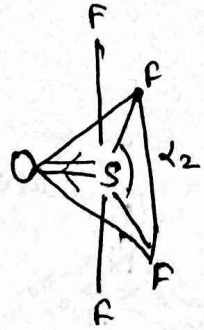
(2)

The repulsion of π-electron cloud depends on position of it in trigonal bipyramidal geometry, if the π e's density lies equitorial plane then it will be show very powerful repulsion even more than l·p. of the π e's density is present in axial plane than equitorial bonds are repel only a little.

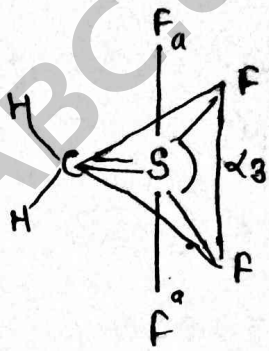
sp^3d
SF_4



sp^3d
OSF_4



sp^3d
$H_2C{=}SF_4$



in which most EN atom 'O' directly attached which attack the π-e's toward itself.

$\alpha_1 > \alpha_2 > \alpha_3$

Maximum atoms in a axial plane.

π-e's cloud in equitorial plane. The repulsion of π-bond > l·p.

No. of atoms = 6
(2H, 1C, 1S, 2Fa)

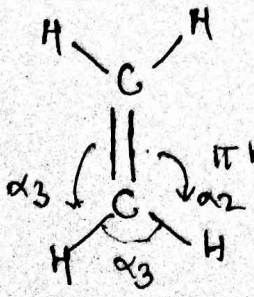
VSEPR Vs NBEPR (Steric Repulsion)

Central Atom = 2nd period

Side atom group = bigger

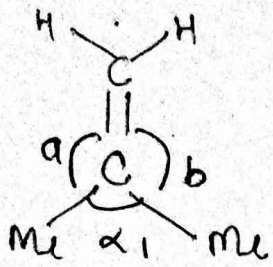
Angle should be less than 120°

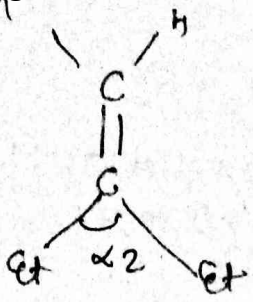
$\theta < 120°$

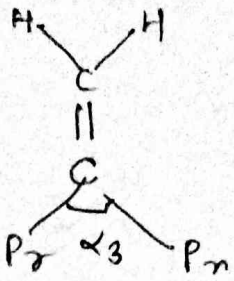


$\alpha_3 < \alpha_1 = \alpha_2$

121.25°







$a = b > \alpha_1$

$\downarrow$

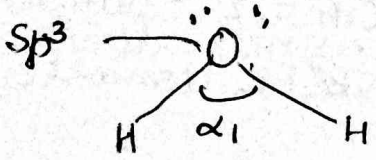
114.5°

$\alpha_1 < \alpha_2 \; \alpha_3$

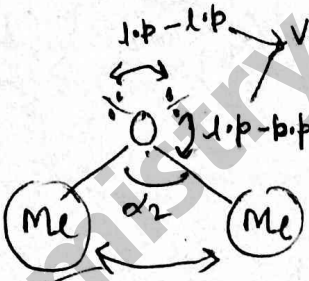
Steric repulsion increases.

Size of side gp incres.

∴ Angles increase



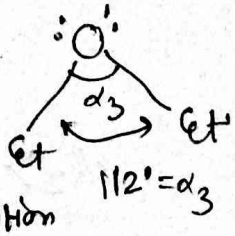
$\sim 105^\circ$



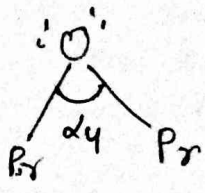
Hence $\alpha_2 > 109^\circ$

steric repulsion NBEPR

NBEPR > VSEPR



$112^\circ = \alpha_3$



Experimentally $= 110 = \alpha_2$

Size of side group increases

∴ Steric repulsion ↑es.

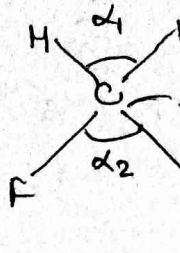
∴ angle increases

(standard angle)

When angle is less than or equal to 109° then NBEPR is dominate on VSEPR.

Bent Rule Vs VSEPR :-

CH_2F_2



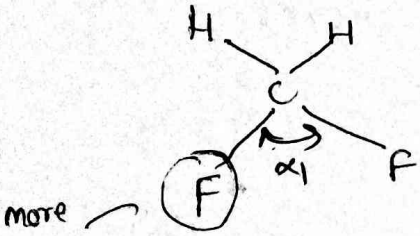
more S% character
∴ θ more

less S%

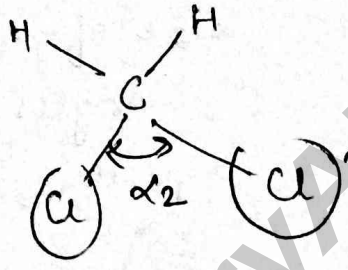
↓

more χ-atom
more S% chara

In case of HfF
Bent's Rule



more EN Atom
More S% char



standard angle 109°

bigger

C.A = 2nd period
NBEPR dominate

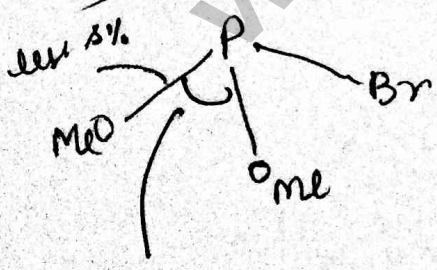
$\alpha_2 > \alpha_1$

Abnormality of Bent's Rule :-

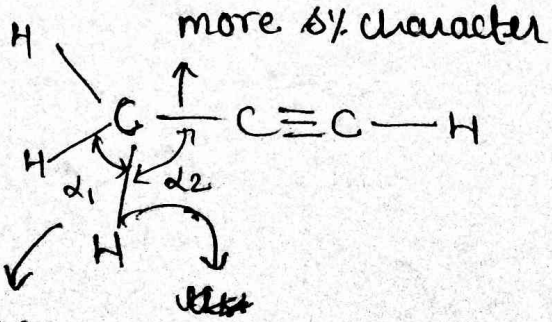
Some times Bent's Rule i.e., % S-character does not work specially in multiple bond P=O, C≡C.

(Reverse of Bent rule)

O → more EN atom
|| → more S%



α = less than 109°

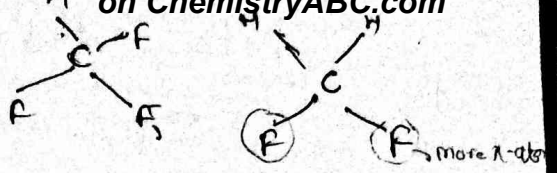


less S% character
(less than 109° angle)

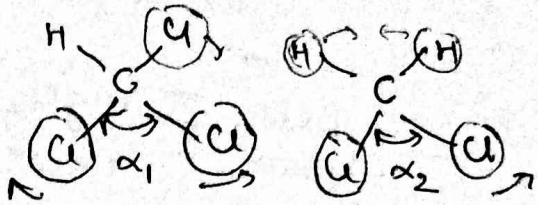
Bent Rule is Not applicable / Neither VSPER Nor NBPER (C≡N)

Other example

Q.1 $\angle FCF$ CHF_3 CH_2F_2



Q.2 $\angle ClCCl$ $CHCl_3$ CH_2Cl_2



Ans - $\alpha_2 > \alpha_1$

$\alpha_2 > \alpha_1$ Steric repulsion

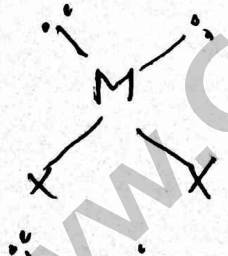
NBPER

Cation polarisation Vs VSEPR :-

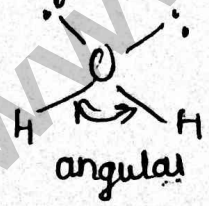
~~Some~~ time $\theta \propto s\%$

$\theta \propto \frac{1}{p\%}$

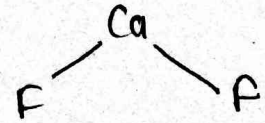
① For MX_2 types — two probable shape → Linear 180° exact; Angular less than 180°



e.g



CaF_2



Bent & Angular terms are usually used when l·p are present. otherwise then we quasi linear.

Note Alkaline earth metal

Be Mg Ca Sr Ba

Be → covalent in all state.

Mg Ca Sr Ba → Ionic in solid state → But covalent in vapour state

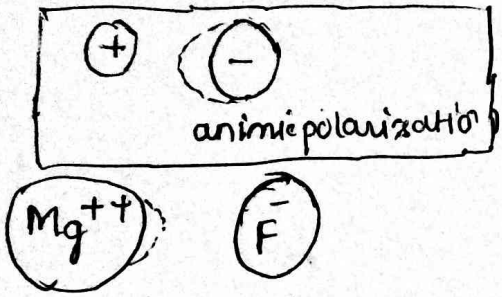
→ $F^{\ominus}$ $BeF_2 > MgF_2 > CaF_2 > SrF_2 > BaF_2$ angle decreases
Linear

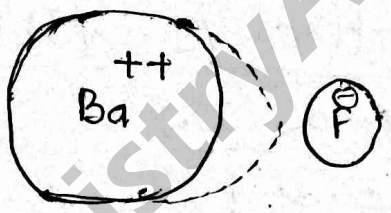
∵ p% increases ; size of alkine earth metal ↑es
∴ angle decreases ; ∴ cation Pol. ↑es ∴
∴ CVC ↑es

→ $Cl^{\ominus}$ $BeCl_2 \geq MgCl_2 = CaCl_2 > SrCl_2 > BaCl_2$
Linear Linear Linear quasi linear quasi linear

→ $X = Br^{\ominus}, I^{\ominus}$ $BeX_2 = MgX_2 = CaX_2 = SrX_2 > BaX_2$
linear linear linear quasi linear quasi linear

Normal Polarisation





p% ∝ covalent character ∝ Polarisation

$\theta \propto \frac{1}{\text{Cation Polarisation}}$

Shapes of Molecules

lone pair – lone pair
l·p – b·p

Supposed to be active (effective) When $\theta \leq 90^\circ$ in deciding shape.

Geometry → (Use l·p & b·p both) Non observed (assumed)

Shape → (Use only b·p) observed.

① SF_4

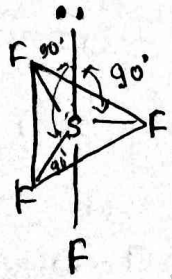
Hybridisation = $\frac{6+4}{2} = 5$

→ σ-bond pair = 4

→ l·p. 5 − 4 = 1

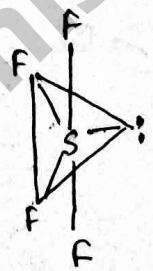
→ Hybridisation sp^3d

Geometry – trigonal bipyramidal



(I)

l·p – b·p = 90° × 3



(II)

Q. (I) + (II) ?

a.) Resonance structure
b.) Structural
c) Conformation
d. Homomers

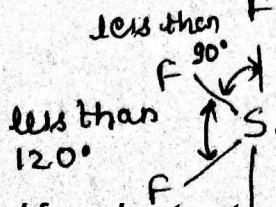
l·p – b·p = 90° × 2

l·p – b·p = 120° × 2

↓

can be tolerated
i.e., can be neglected

Shape is decided by more stable II structure without lone pair ~~less th~~

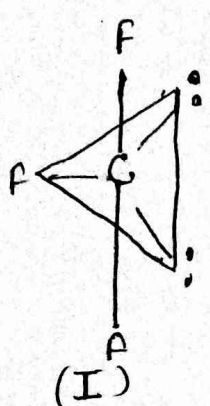


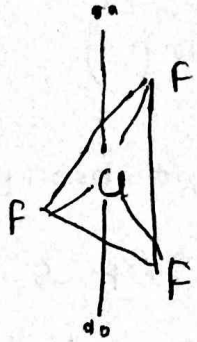
→ see-saw shaped
→ distorted tetrahedral
F → Sphenoidal structure

② ClF_3 $H = \frac{7+3}{2} = 5$ → b.p = 3, l.p = 5 − 3 = 2

Geometry – (tbp)

Q. How many tbp structural isomers are possible for ClF_3 = 3


(I)

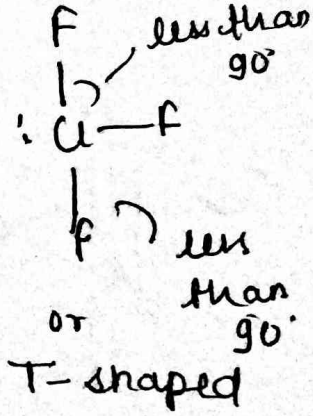

II


III

l.p – b.p = 90 × 2 = 180

l.p – b.p = 90 × 4

Stability (I) > II > III



T-shaped

③ XeO_2F_2

$H = \frac{8+2}{2} = 5$ → σ/b.p = 4, l.p = 1

Same as in SF_4

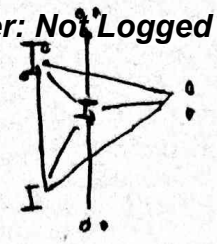
∴ Shape of XeO_2F_2 ⇒ See-saw

④ $[I_3]^{\ominus}$ $I-I_2^{\ominus}$ $H = \frac{7+2-1}{2} = 5$ → b.p = 2, l.p = 5 − 2 = 3

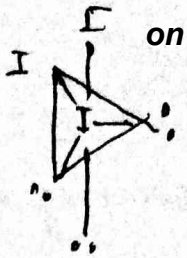
Geometry – tbp

How many str. isomers are possible for $I_3^{\ominus}$ = 3

I



II



III

l.p − l.p = 90 × zero

l.p − b.p =

90°×2

90°×4

90°×2

90°×2

shaped ⇒ Linear

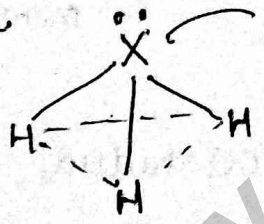
stability (I) > (III) > (II)

(*) NH_3 , l.p = 1

b.p = 3

s = 4

CHO = Td

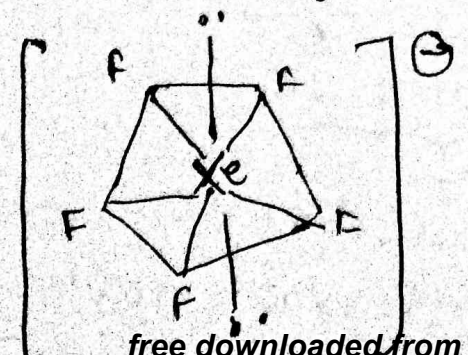
shape  N, P, As, Sb, Bi - 1

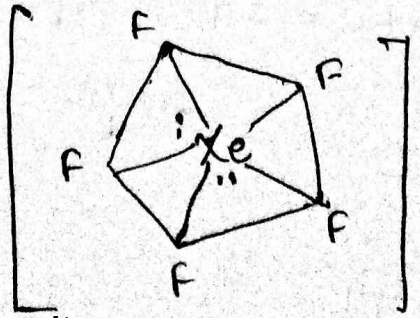
Trigonal pyramidal — shape

ionic

(6) $[XeF_5]^{\ominus}$ $H = \frac{8+5+1}{2} = 7$ → b.p = 5, l.p = 2

ionic Geometry = Pbp





Pentagonal Planar

I st example of Pentagonal planar in [gg]

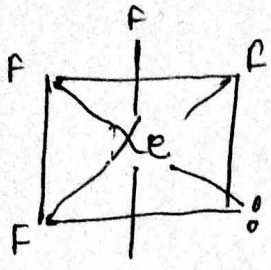
(I), (II) = Structural Isomers

(I), (III) = "

II, III = Homomers

XeF_4 $H = \frac{8+4}{2} = 6$ — b.p = 4, l.p = 2

Geometry = Octahedral

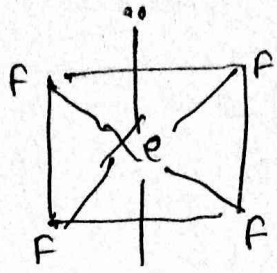


(I)

l.p - l.p = 90

cannot be tolerate

∴ less stable

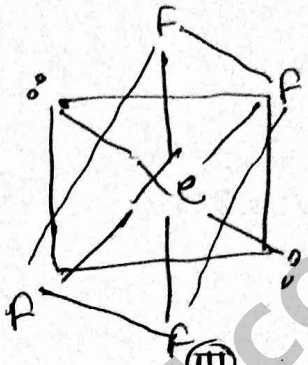


(II)

∵ l.p - l.p = 180

good ; No repulsion

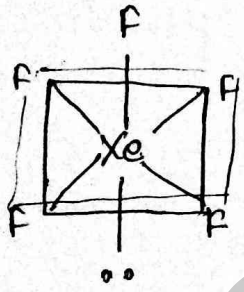
∴ stable



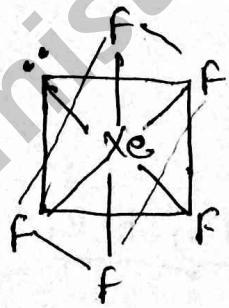
(III)

Shape ⇒ square planar

$[XeF_5]^{\oplus}$ $\frac{8+5-1}{2} = 6$ — b.p = 5, l.p = 1

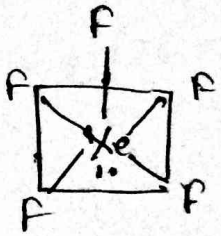


I



II

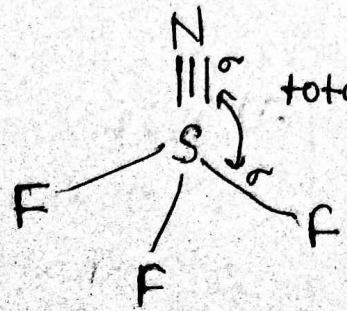
Homomers (Identical)

Shape = 

square monopyramidal

In Octahedral

⇒ NSF_3

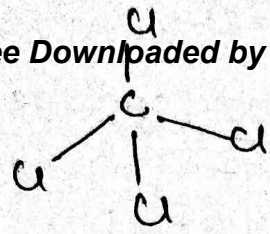


total σ = 4 ∴ sp^3

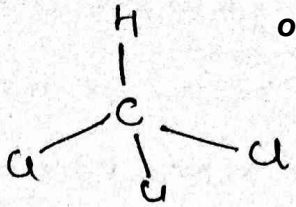
Shape = Distorted Td

↓

Because angle is not exact 109°



(Tetrahedral)



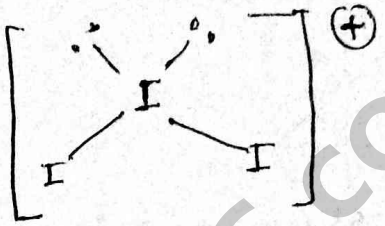
(distorted Td)

* $I_3^{\oplus}$

$[I-I_2]^{\oplus}$

$H = \frac{7+2-1}{2} = 4$ — b.p = 2, l.p = 2

Geometry = Td



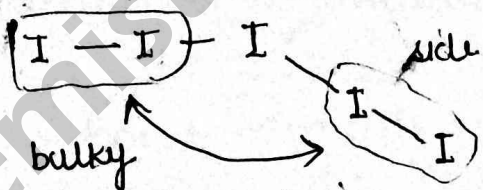
Shape = Bent

* $I_2 + I^{\ominus} \longrightarrow I_3^{\ominus}$

linear

$I_5^{\ominus} = I^{\ominus} + 2I_2 = I_8^{\ominus} + I_2$

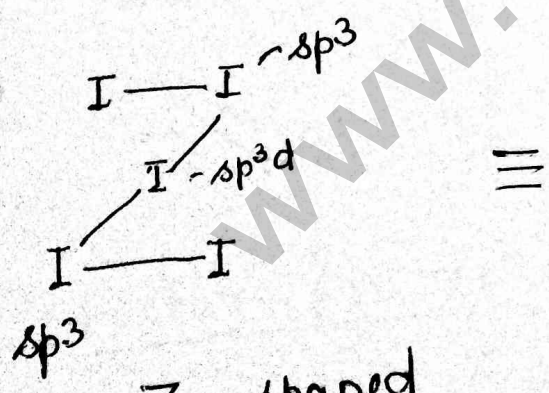
side gp



bulky

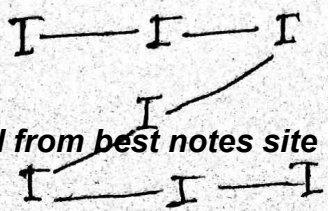
∴ high repulsion

|||



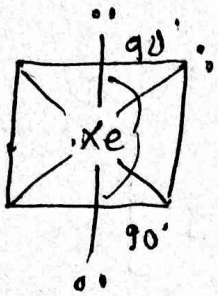
Z-shaped

* $I_7^{\ominus}$



Z-shaped.

Octahedral
- One-l.p. — XeF_5 — l.p. any position
- two-l.p — XeF_4 — at 180° (opposite)
- three l.p. — $XeF_3^{\ominus}$ → $H = \frac{8+3+1}{2} = 6$ (bp = 3, l.p = 3)
  - → ∴ does not exist
  - ∴ $XeF^{\ominus}$ does not exist



Now l.p − l.p = (90°) × 2 very powerful ∴ less stable.
repulsion

* e' make by combination of 6 particle (quark)

Dipole Moment :-

It is magnitude of charge separation.

$$\vec{\mu} \Rightarrow |q| l$$

$|q|$ = charge

l = Bond length

Dipole Moment → vectro quantity (direction)

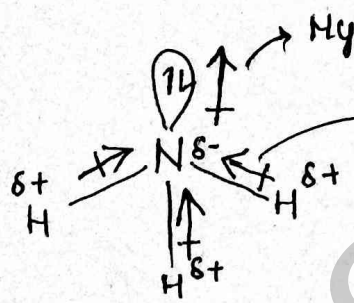
$q+$ $q-$

H → Cl

← + IUPAC

+ → old concept (we use this)

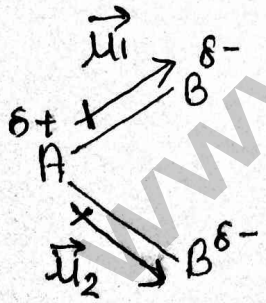
* Type of dipole Moment :-



Dipole Moment of individual bond

↓

Bond Moment



$$\vec{\mu}_{Net} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

$$\vec{\mu}_{Net} \propto \sqrt{\cos\theta}$$

$$\boxed{\vec{\mu}_{Net} \propto \frac{1}{\sqrt{\theta}}}$$

Factor for $\vec{\mu}$ (D.M) →

① $\vec{\mu} \propto q \propto (\chi_A - \chi_B)$ (electronegative difference)

② $\vec{\mu} \propto l$

③ $\vec{\mu} \propto \sqrt{\theta}$

Unit of Dipole moment ($\vec{\mu}$)

(1) S.I unit

$\vec{\mu} = q \times l$ = coulomb × meter = C.m

$1.6 \times 10^{-19} C = 4.8 \times 10^{-10}$ esu

$1\ C = \frac{4.8 \times 10^{-10}}{1.6 \times 10^{-19}}$ esu

$\boxed{1\ C = 3 \times 10^{9}\ esu}$

(2) Nm S.I unit

Debye

$\boxed{1D = 4.8 \times 10^{-18}\ esu \times cm}$

(electrostatic unit)

Let $l = 1A^\circ = 10^{-10}\ m = 10^{-8}\ cm$

$\vec{\mu} = q \times l$

$= 4.8 \times 10^{-10}\ esu \times 10^{-8}\ cm$

$\boxed{\vec{\mu} = 4.8 \times 10^{-18}\ esu \cdot cm}$

$\boxed{\vec{\mu} = 4.8D}$

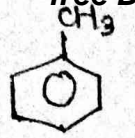
Q. Dipole Moment in NaCl & HCl

$\overset{+}{Na}\overset{-}{Cl}$ $\quad$ $H\overset{\delta+}{-}Cl^{\delta-}$

$\vec{\mu}$: NaCl > HCl

In ionic compound dipole moment is high due to more charge separation.

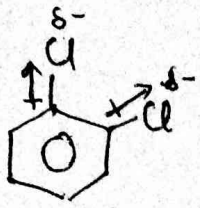
Orientation of dipole moment :-



$\vec{\mu} = 0.4D$

$\vec{\mu} = 1.7D$

$\vec{\mu} = 2.8D$



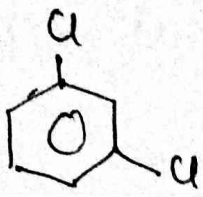
$$\vec{\mu} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

$$\vec{\mu} = \sqrt{x^2 + x^2 + 2x \cdot x \cos 60}$$

$$\vec{\mu} = \sqrt{2x^2 + 2x^2 \cdot \tfrac{1}{2}}$$

$$\vec{\mu} = x\sqrt{3}$$

$$\boxed{\vec{\mu} = 1.7\sqrt{3}\,D}$$

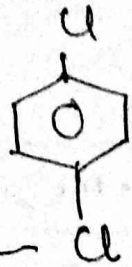


$$\vec{\mu} = \sqrt{x^2 + x^2 + 2x \cdot x \cos 120}$$

$$\vec{\mu} = \sqrt{2x^2 + 2x^2 \cdot (-\tfrac{1}{2})}$$

$$\vec{\mu} = \sqrt{x^2} = x$$

$$\boxed{\vec{\mu} = 1.7}$$



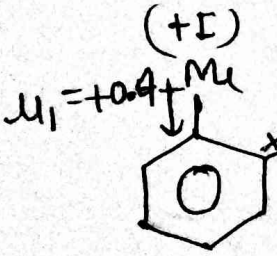
$$\vec{\mu_1} = \sqrt{x^2 + x^2 + 2x \cdot x \cos 180^\circ}$$

$$\vec{\mu} = \sqrt{2x^2 + 2x^2 \cos(-1)}$$

$$\boxed{\vec{\mu} = 0}$$

So, μ_{net} of para < μ_{net} of meta < μ_{net} of ortho

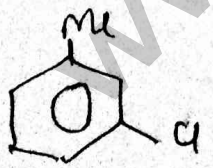
$$\boxed{D.M. = \frac{1}{\theta}} \quad (\theta = \text{direction})$$

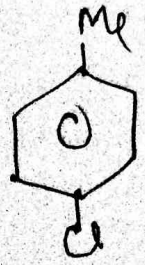


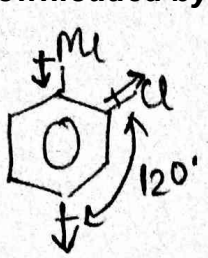
$\mu_1 = +0.4$ (+I) Me

Cl (−I) $(\vec{\mu_2} = -1.7)$

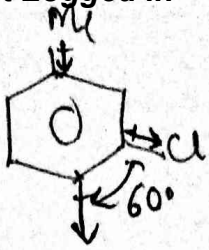
$$\vec{\mu}_{net} = \sqrt{(+0.4)^2 + (-1.7)^2 + 2(+0.4)(-1.7)\cos 60^\circ}$$







$\theta = 120°$



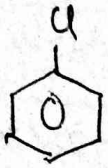
$\theta = 60°$

$\theta = 0°$

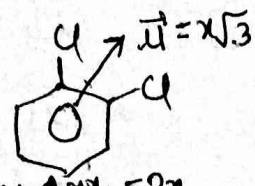
$\therefore \vec{\mu} \propto \sqrt{\frac{1}{\theta}}$

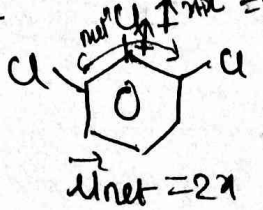
$\therefore$ order

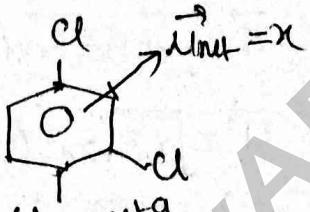
$$\boxed{p > m > 0}$$

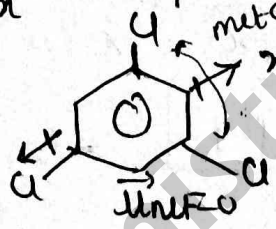


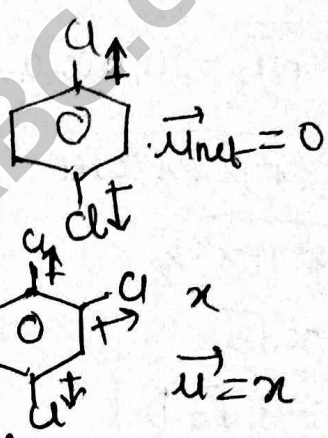
$x = 1.7$



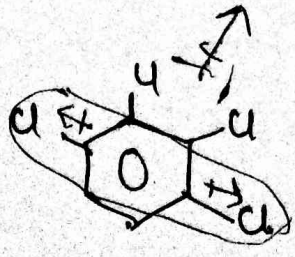




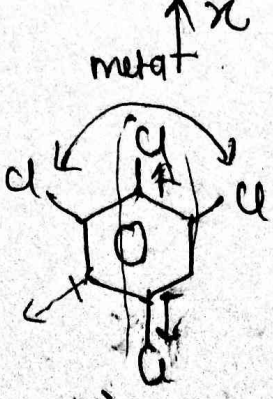


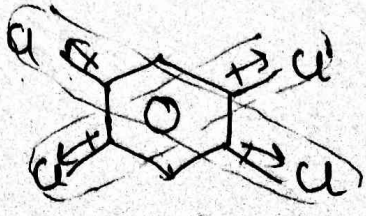


Substituent in Benzene	No. of Isomers
Mono sub	1
Di substituted — both are same	3
Di substituted — both are different	
tri — Three are same	3
tri — 2A + B	6
tri — A + B + C	10



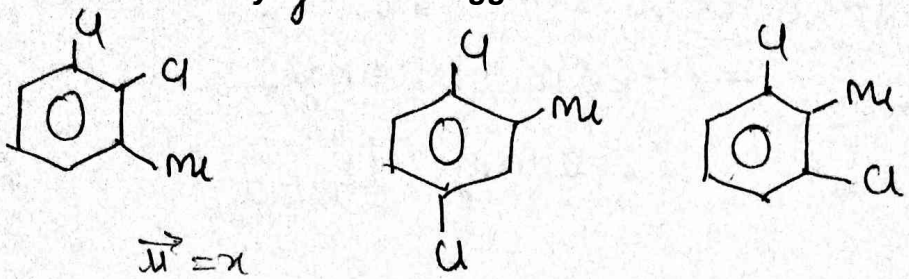
$\vec{\mu}_{net} = x\sqrt{3}$



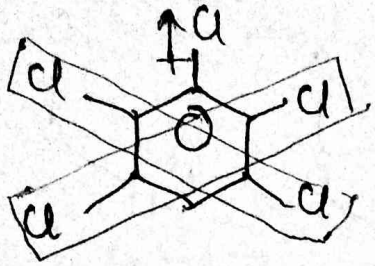


$\vec{\mu}_{net} = 0$

Que Arrange $\vec{\mu}$

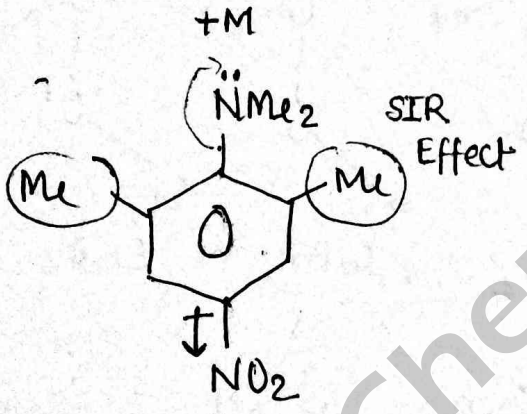


$\vec{\mu} = x$

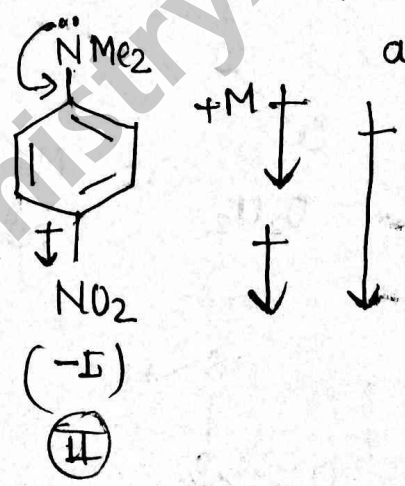


$\vec{\mu} = x$

* -



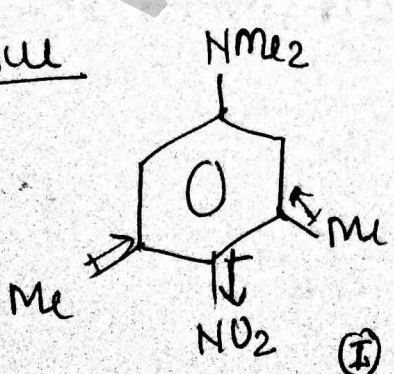
substrat (I)

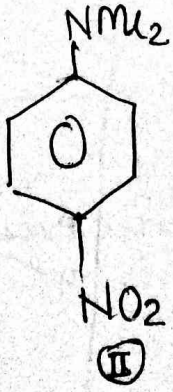


addition of vector

$\vec{\mu}_{(II)} > \vec{\mu}_{(I)}$

Que





Arrange $\vec{\mu}$

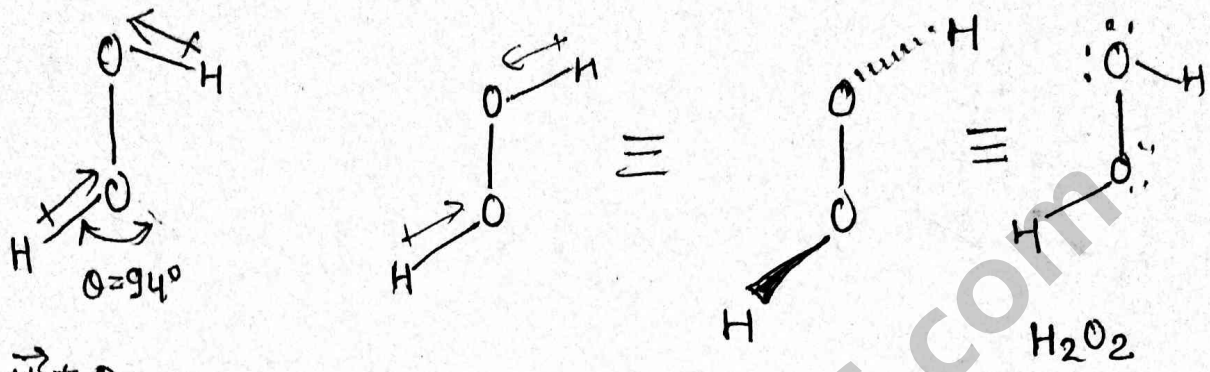
Gauche structure (driven by Bloom strain)

* Open book structure

↳ θ = Dihedral angle < 180°

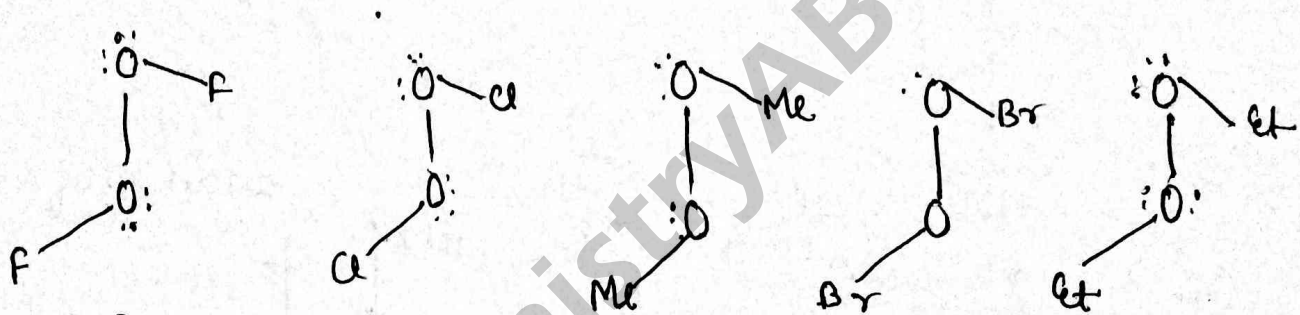
Best example H_2O_2

∴ always $\vec{\mu}_{net} \neq 0$

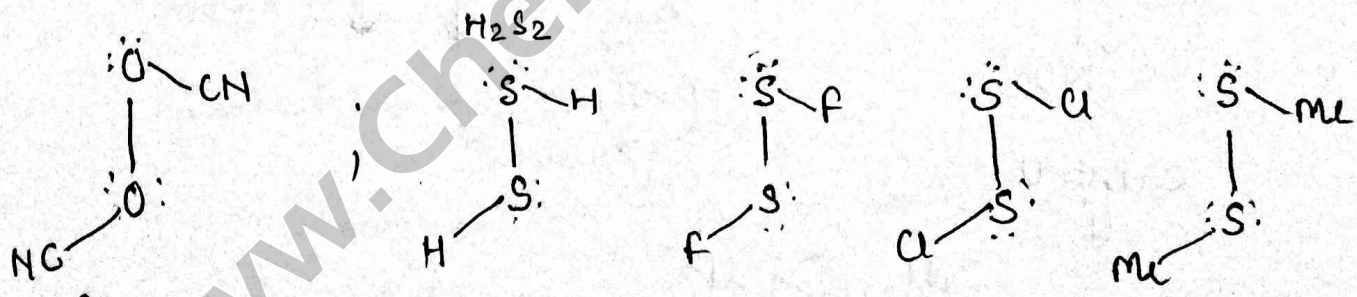


$\vec{\mu} \neq 0$

H_2O_2

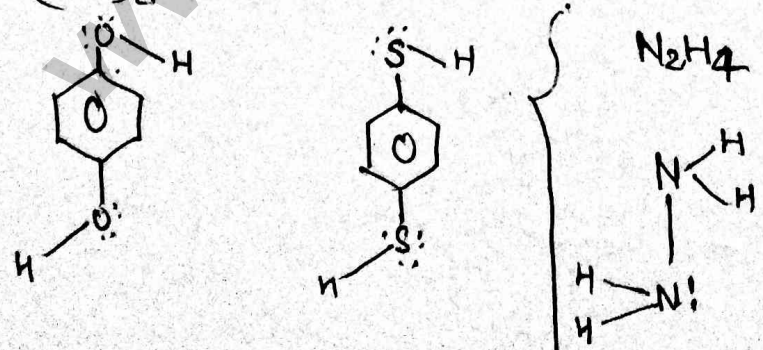


O_2F_2 O_2Cl_2 Me_2O_2 O_2Br_2 Et_2O_2



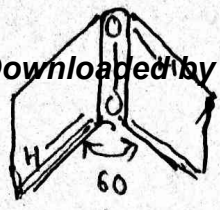
H_2S_2

or $(OCN)_2$



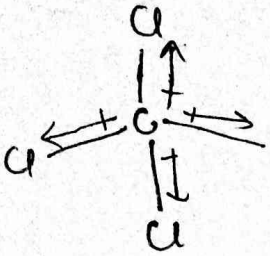
N_2H_4 , P_2H_4, N_2F_4, P_2F_4

In all open books structure $\vec{\mu} \neq 0$



$\vec{\mu} \neq 0$

* CH_4 , CCl_4 , CBr_4 , CI_4 (All have $\vec{\mu} \neq 0$)



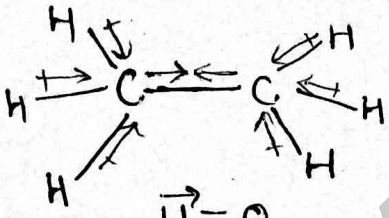
$\vec{\mu} = 0$

CH_3-CH_3

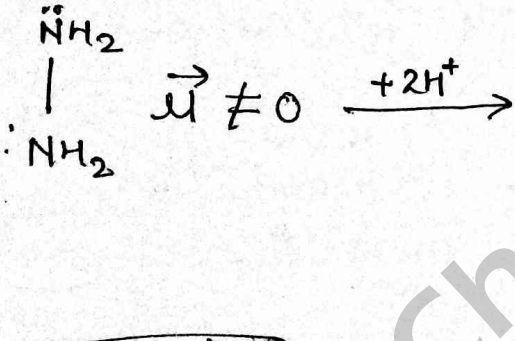
$\vec{\mu} = 0$

Cl_3C-CCl_3

$\vec{\mu} = 0$



$\vec{\mu} = 0$



$\therefore \vec{\mu} = 0$

Learn it

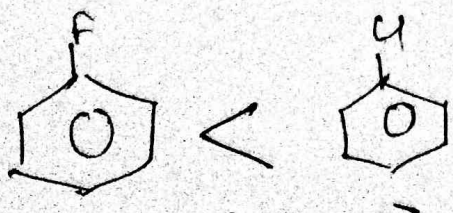
* Abnormal Order

$CHCl_3 < CH_2Cl_2 < CH_3Cl$

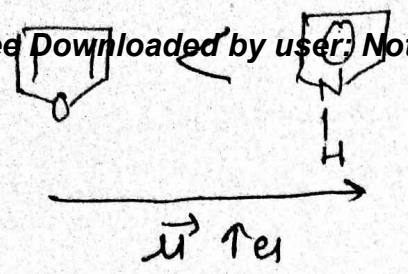
$\vec{\mu}$ ↑el

$CH_3F < CH_3Cl$ Bond length factor with

$\vec{\mu}$ ↑el



$\vec{\mu}$ ↑el



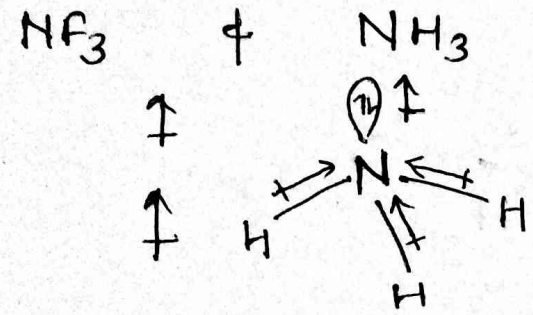
$\vec{\mu}$ ↑ei

Normal

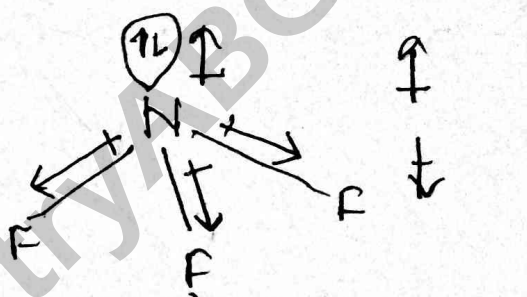
$CH_2F_2 > CH_2Cl_2$

$CHF_3 > CHCl_3$

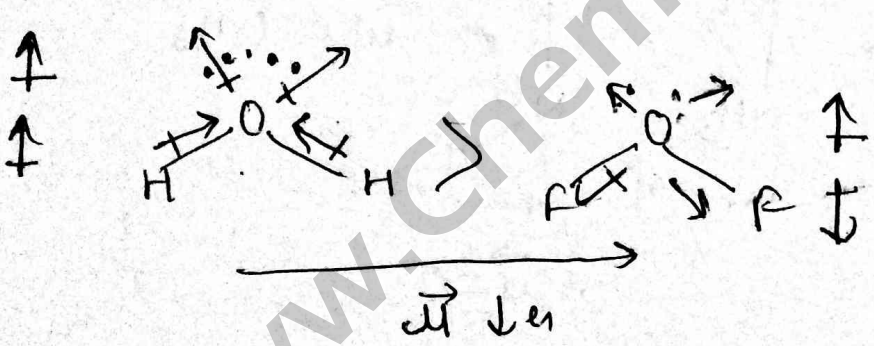
*



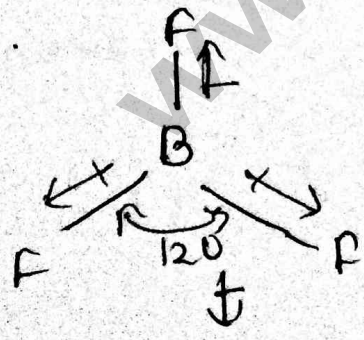
$\vec{\mu}$ = additive



$\vec{\mu}$ = substrative

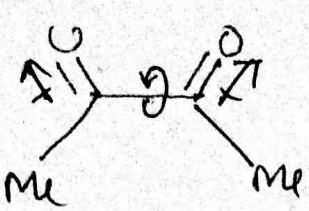


$\vec{\mu}$ ↓ei

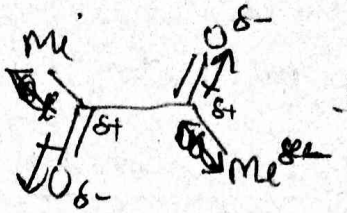


$\vec{\mu} = 0$

* Dipolar Interaction — Should be minised for stability



more dipole moment



less dipole moment

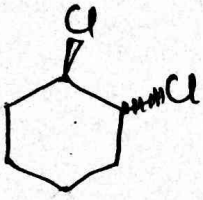
s-cis
cisoid

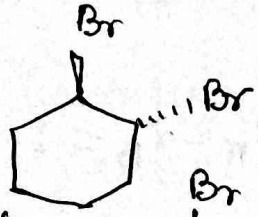
conformation

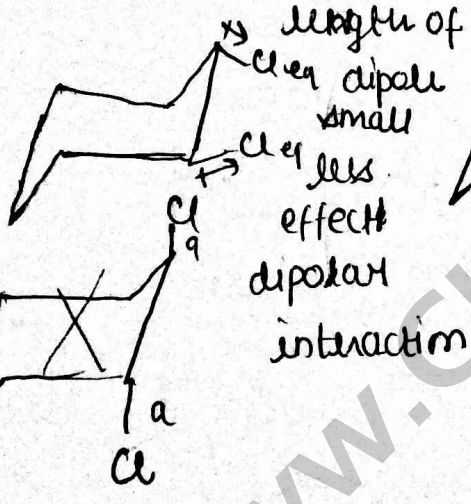
s-trans
transoid

more stabl

exist in transoid form

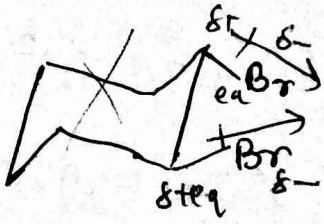




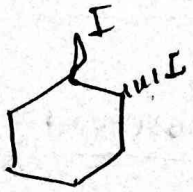


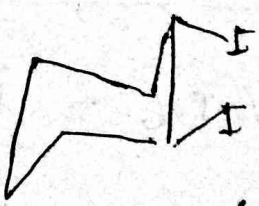
length of Cl eq dipole small
less effect dipolar interaction

more stabl



dipolar repulsion





Highly unstable

x-less
∴ dipole less effective

∴ No question of dipolar repulsion

% Ionic character

- two methods
  - ① Hanny-Smidth eqⁿ (electronegativity ↑)
    - when χ are give

$$\% \text{ Ionic Character} = 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2$$

Ques Find % I.C. in Cl–F

Cl – F

$\chi = 3$ $\chi = 4$ $\chi_A - \chi_B = 1$

$$\% \text{ I.C} = 16(1) + 3.5(1)^2 = 19.5\%$$

$$\% \text{ I.C} = 19.5\%$$

② Dipole moment method :–

$$\% \text{ I.C} = \frac{\vec{\mu}_{observed}}{\vec{\mu}_{calculate}} \times 100$$

Ques The Dipole moment of HCl is 2.03D if its bond length is 1.27 A° % Find % I.C in H–Cl

$\vec{\mu}_{obs} = 2.03D$, $l = 1.27\text{Å} = 1.27 \times 10^{-8}$ cm

$\vec{\mu}_{calculate} = q \cdot l$

$= 4.8 \times 10^{-10}$ esu $\times 1.27 \times 10^{-8}$ cm

$= 4.8 \times 1.27 \times 10^{-18}$ esu cm

$= 4.8 \times 1.27$ D

$$\% IC = \frac{2.88 D \times 100}{4.8 \times 1.27 D}$$

$$= 33.$$

Qu Find value of charge

$\vec{\mu}_{observed} = 4.8 \times 10^{-18}$ esu x cm $= 4.8$ D

$\overset{\delta+}{A} \rightarrow \overset{\delta-}{B}$

$l = 1 A^\circ = 10^{-8}$ cm

$\vec{\mu} = q \cdot l$

$$q = \frac{\vec{\mu}}{l} = \frac{4.8 \times 10^{-18} \text{ esu x cm}}{10^{-8} \text{ cm}} = 4.8 \times 10^{-10} \text{ esu}$$

It means practically charge is ~~4.8~~

4.8×10^{-10} esu $= 1.6 \times 10^{-19}$ coulomb

$=$ one unit charge

Hence,

$\overset{+1}{A} \cdots \overset{-1}{B}$

Hence compound is ionic

Qu $\overset{\delta+}{A} - \overset{\delta-}{B}$

$\vec{\mu}_{observed} = 1.6 \times 10^{-18}$ esu x cm

$l = 1 A^\circ = 10^{-8}$ cm

$$q = \frac{\vec{\mu}}{l} = \frac{1.6 \times 10^{-18} \text{ esu x cm}}{10^{-8} \text{ cm}} = 1.6 \times 10^{-10} \text{ esu}$$

4.8×10^{-10} esu $= 1.6 \times 10^{-19}$ coulomb $=$ one unit charge

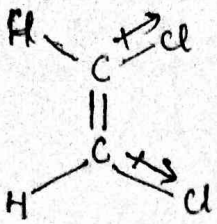
$$1.6 \times 10^{-10} = \frac{1.6 \times 10^{-19}}{4.8 \times 10^{-10}} \times 1.6 \times 10^{-10} = \frac{1}{3} \times 1.6 \times 10^{-19} \text{ coulomb}$$

$= \frac{1}{3}$ one unit of charge

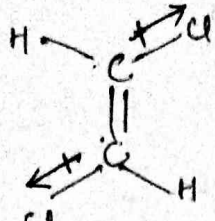
$\overset{\delta+}{A} - \overset{\delta-}{B}$

$\downarrow +1/3 \quad \downarrow -1/3$

* Cis -isomer trans isomer

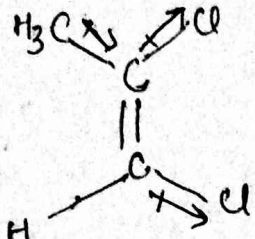


$\vec{\mu} \neq 0$



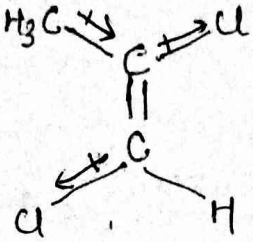
$\vec{\mu} = 0$

*



cis

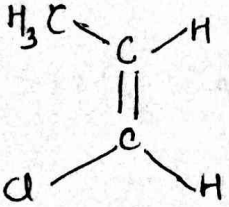
$\vec{\mu} \neq 0$



trans

$\vec{\mu} \neq 0$

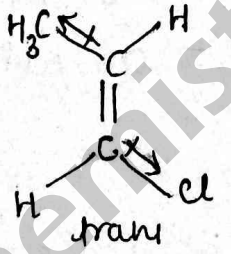
*



cis

$\vec{\mu} \neq 0$

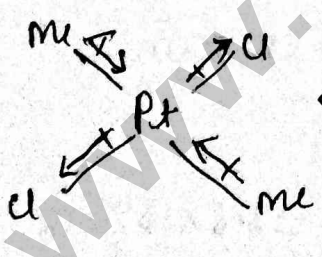
<



trans

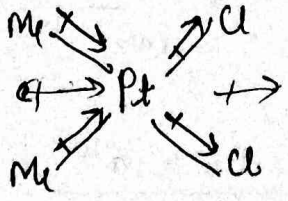
$\vec{\mu} \neq 0$

*



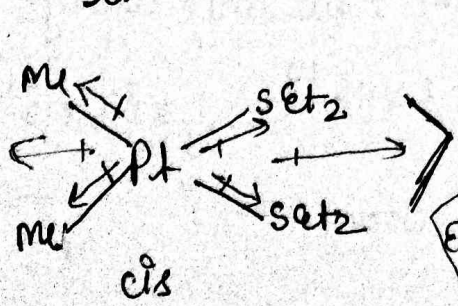
$\vec{\mu} = 0$

<

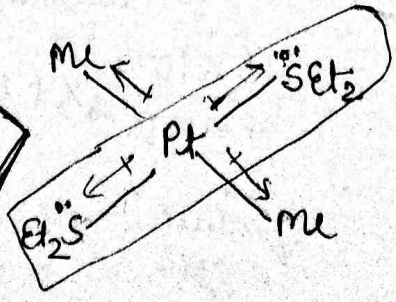


$\vec{\mu} \neq 0$

additive



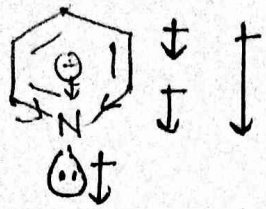
cis



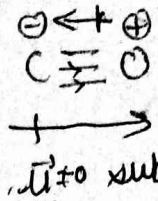
(Not exactly linear (as not cancelled completely)

(Carbon can't bond with metal then behave like (−I) (electronegative atom)

Direction of dipole moment :-

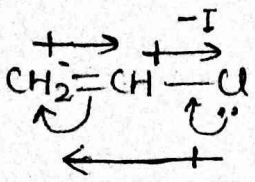


$\vec{\mu} \neq 0$



$\vec{\mu} \neq 0$ substractive

$\therefore \vec{\mu}$ of CO is very very low.

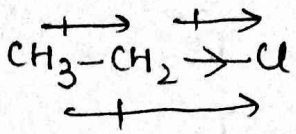


In halogen -I is powerful than +M.

$-I > +M$

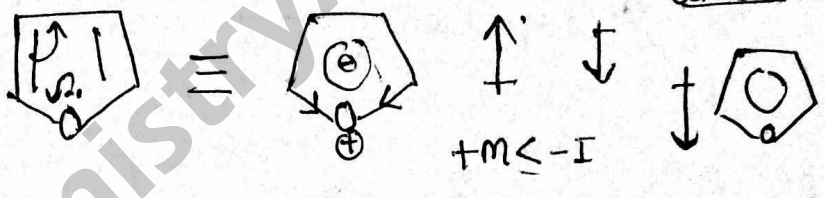
substractive

$\vec{\mu} \neq 0$



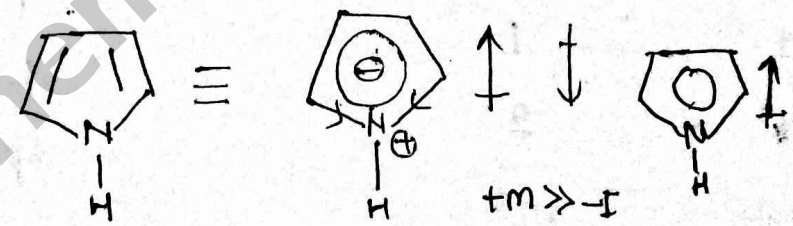
additative

$\vec{\mu} \neq 0$

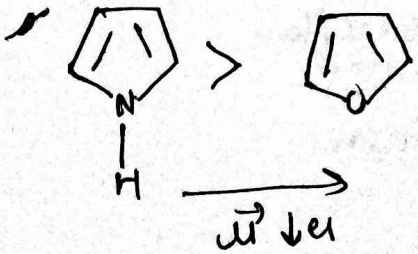


Net D.M. direction

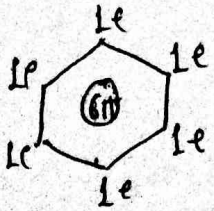
$+M \leq -I$

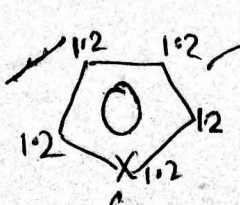


$+M \gg -I$



$\vec{\mu}$ ↓el



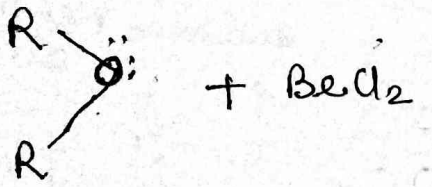


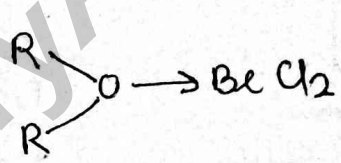
- More electron density in ring than benzene so more reactive towards $E^{\oplus}$ than benzene ring
- Pyrrole is super aromatic compound

O, N, S

Hybridisation in adduct :-

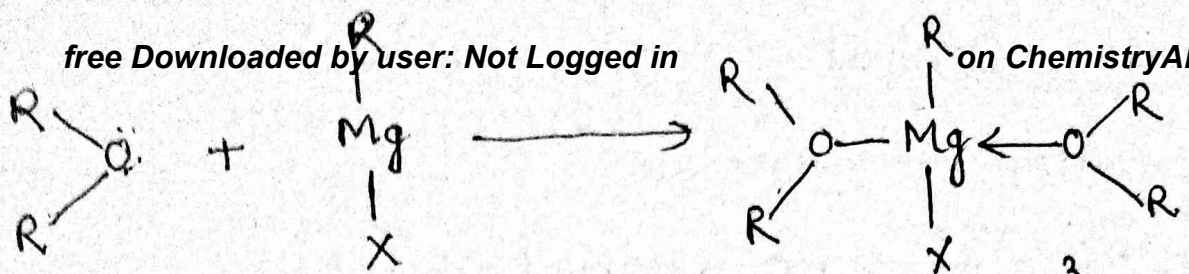
	H_3N :	BF_3	$\rightarrow$	$[H_3N \rightarrow BF_3]$ (Lewis acid - base adduct)
b.p	3	3		4
l.p	1	0		0
Steric No.	4	3		4
Hybri	sp^3	sp^2		sp^3
Geo	Td	Trigonal Planar		Td
Shape	Trigonal ~~Planar~~ Pyramidal			Td





(Change in Lewis acid)

b.p.	2	2	3 3
l.p.	1	0	1 0
S.No. =	4	2	4 3
Hybr =	sp^3	sp^2	sp^3 sp^2
Geo =	Td	Trigonal Planar ~~Trigonal Planar~~ Linear	Td Trigonal Planar
Shape =	Angular/ Bent	linear	Trigonal Pyramidal Trigonal Planar



b.p.	2	2		3	3
l.p.	2	0		1	i
S.N.	4	2		4	4
hybr.	sp^3	sp		sp^3	sp^3
Geo	Td	linear		Td	Td
shape	~~Trigonal~~ Bent	linear			

Molecular Orbital theory :-

Atom + Atom ⟶ Molecule

A.O. + A.O. $\xrightarrow{VBT}$ H.O. (Hybrid orbital)

A.O + A.O $\xrightarrow{MOT}$ M.O

A.O	Non-Real	Mono centric
H.O	Non-Real	Mono centric
M.O	Non-Real	Poly centric

Monocentric :- (e's are in influence of one nucleus)

* x A.O + x A.O ⟶ 2x M.O

↓

Law conservative of Orbital

* A.O + A.O ⟶ M.O

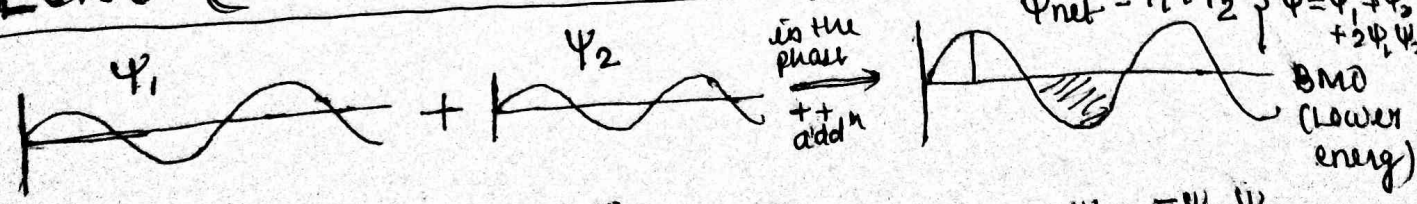
↓

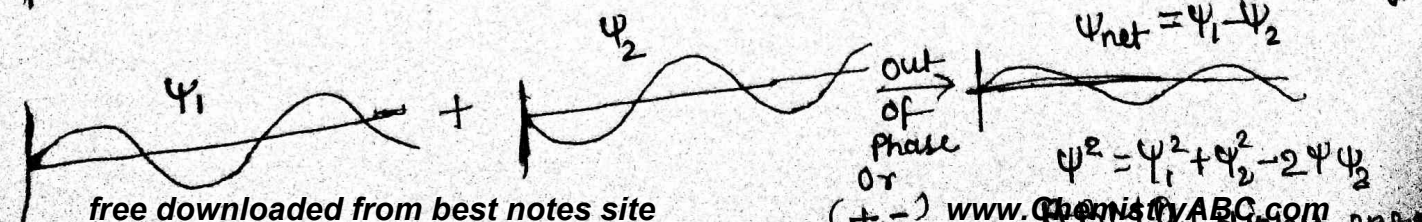
mathematical approach

↓ United atom method

↓ LCAO method

LCAO (Linear combination of atomic orbital) :-

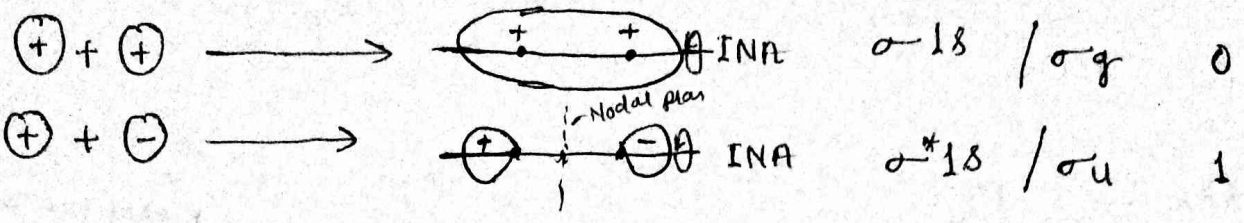




When Inter nuclear axis rotate 180° if sign change then π-bond formed if not then σ-bond.

(1) 1s + 1s —

Nodal plane



σ 1s / σ_g 0

σ^* 1s / σ_u 1

i — Present — centrosymmetric — Gerade ⇒ g

centre of symmetry

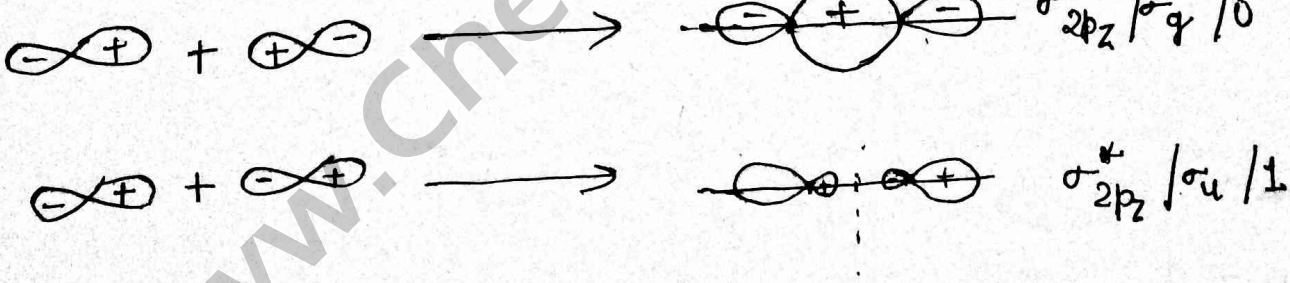
Absent — Non-centrosymmetric — Ungerade ⇒ u

(2) 2s + 2s

- σ_{2s} / σ_g / 0
- σ^*_{2s} / σ_u / 1

(3) $2p_z + 2p_z$

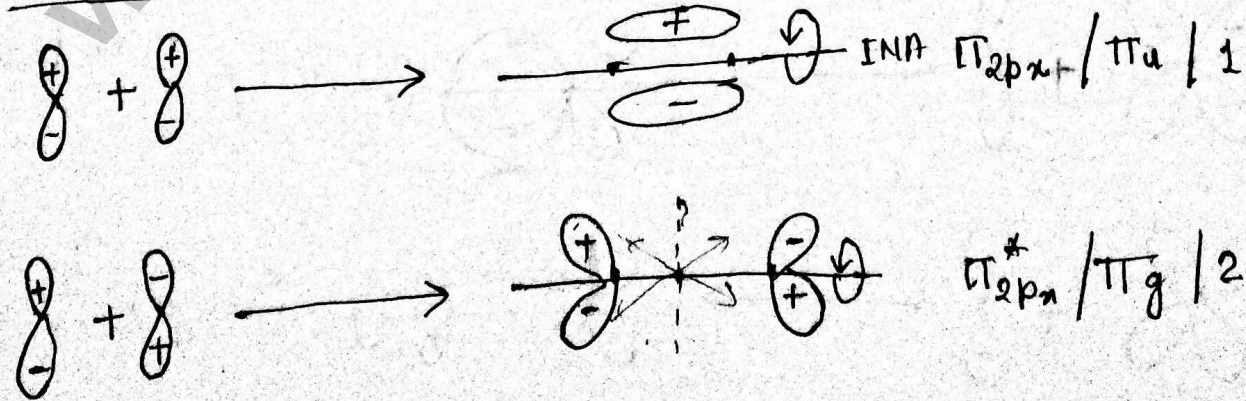
Nodal plane



σ_{2p_z} / σ_g / 0

$\sigma^*_{2p_z}$ / σ_u / 1

(4) $2p_x + 2p_x$ —



INA π_{2p_x} / π_u / 1

$\pi^*_{2p_x}$ / π_g / 2

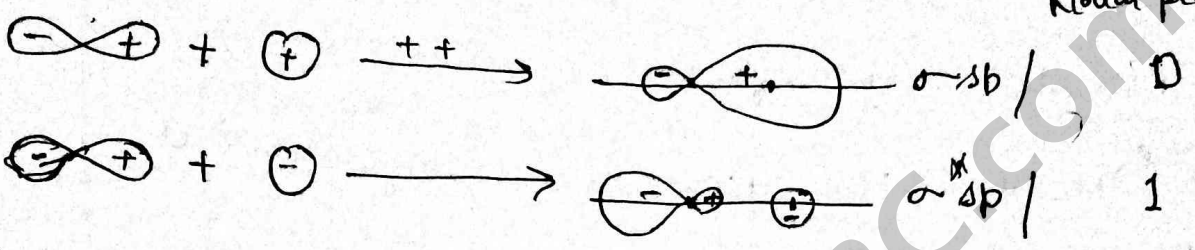
(5) $2p_y + 2p_y \rightarrow \pi_{2py}/\pi_u/1$

$\pi^*_{2py}/\pi_g/2$

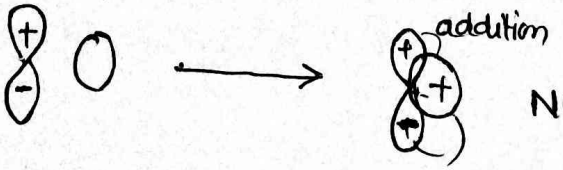
Ques- No. of Nodal plane in π^* of Ethylene.

Ans- Two

(6) ~~2p~~ $2s + 2p_z$



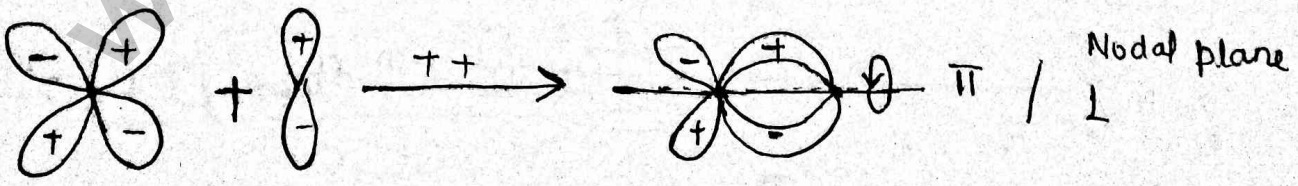
(7) $2s + 2p_x$

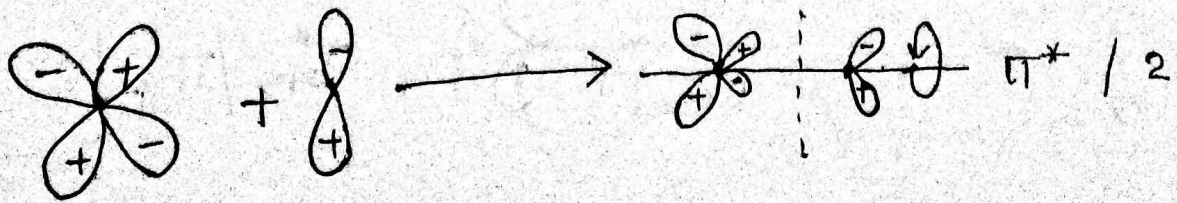


Substraction, called Non-Bonding.

(8) $2s + 2p_y$

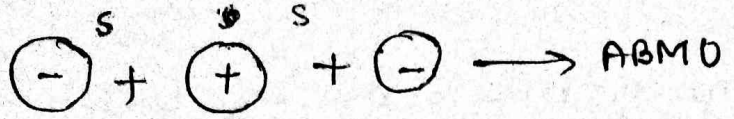
(9) $2p + d$

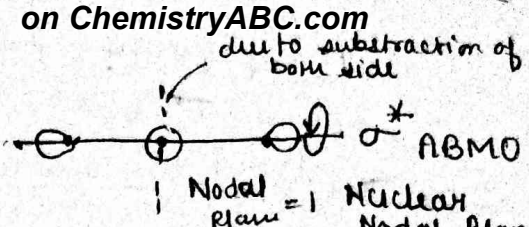


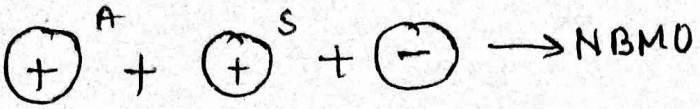


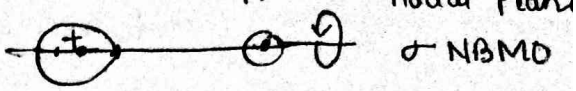
Nuclear Nodal Plane different in atomic structure

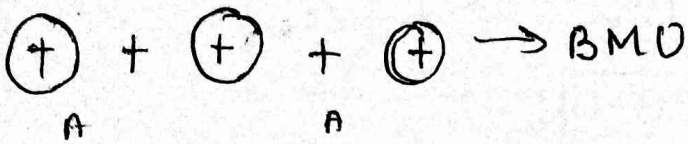
(10)



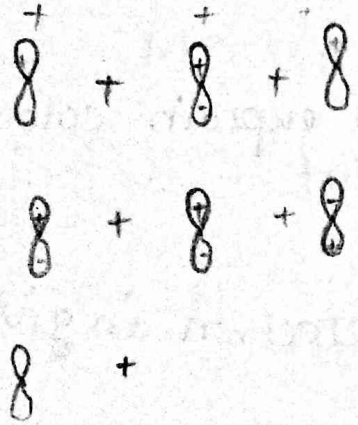








(11) $2p_z + 2p_z + 2p_z$



Bond order $= \frac{n_b - n_a}{2}$

(Bond dissociation energy) BDE or BE $\propto$ B.O.

Bond length $\propto \frac{1}{B.O}$

wave no
(stretching frequency) $\bar{\nu} \propto$ B.O.

$\boxed{T.S \propto B.O}$

Thermal stability

Term Symbal :— (It is use to explain colour spectra)

Name of energy levels.

* Microstate :—

The no. of probable arrangement of electron in given energy level is called Microstate.

$$M_s = \frac{n!}{r!\,\lfloor n-r}$$

n = 2 × no. of orbital

r = no. of e's.

p^1

$n = 2 \times 3 = 6$

$r = 1$

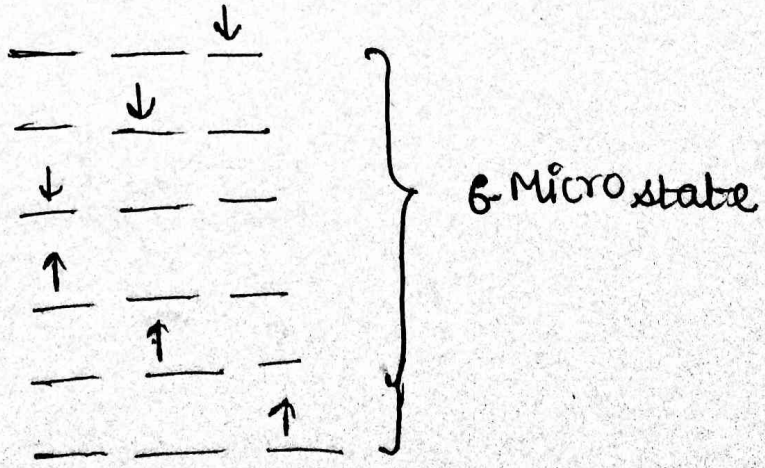
$$M_s = \frac{6!}{1 \cdot (6-1)!}$$

$M_s = 6$

2 × no. of orbital

$p^1 = 2 \times 3$

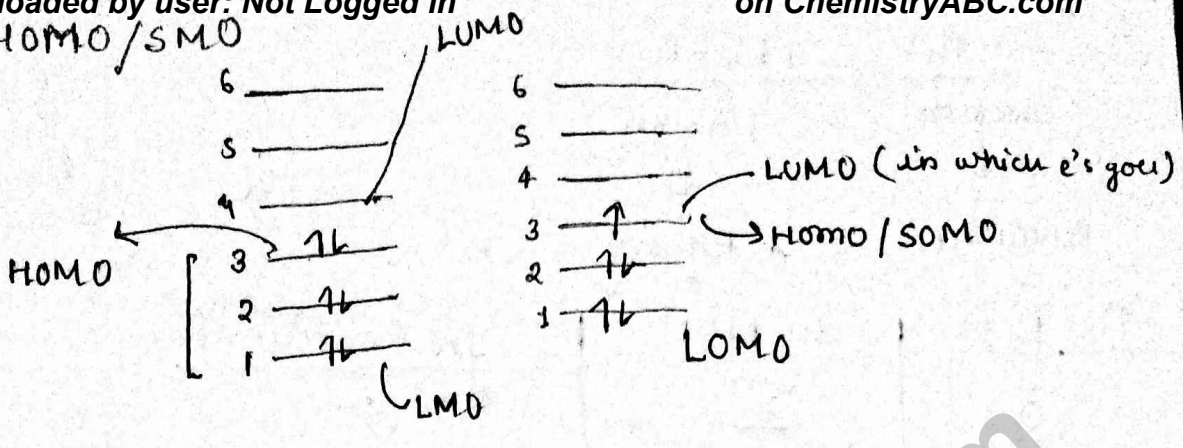
$= 6$



6 Microstate

Rules :-

① Find HOMO/SMO



② Find Spin Multiplicity :-

$M = 2S + 1$

③ Find L - total orbital angular momentum

N $\frac{\uparrow\downarrow}{1s}$ $\frac{\uparrow\downarrow}{2s}$ $\frac{\uparrow}{}$ $\frac{\uparrow}{}$ $\frac{\uparrow}{}$ (2p)

3 $n = 2$ 6 $n = 2$ 2

$l = 0$ $l = 1$

$m = 0$ $m = 0$

$s = +\frac{1}{2}$ $s = +\frac{1}{2}$

$l =$ — — (+1, −1)

$l =$ — — — (+1, 0, −1)

$l =$ — — — — — (+2, +1, −1, −2)

Pauli Rule

→

→ No two e's of same orbital have same energy

→

Exclusion → set of 4 q.N.

↿⇂	↑↑↑↑
electron	Photon
↓	↓
fermions	Boson

↿⇂	↑↑
S	T
α	A
β	B
θ	H
K	K

④

L ⇒	In MOT	In Coordination
0	Σ	S
1	Π	P
2	Δ	D
3	Φ	F

⑥ Term Symbol

$^{M}L_{g/u}$

⑦ If Term Σ

$^{M}\Sigma^{+/-}_{g/u}$ Parity sign

⑧ For +/-

↓

Look

HOMO

If σ-MO → ↓ → (+)

If π-MO → M = 3 ↓ ; M = 1 ↓ (+)

Selection Rule :-

① Spin selection Rule :-

$\Delta S = 0$ allowed

$\Delta S \neq 0$ forbidden

C = $\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$ —

$S_1 = 1$

① C* $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$

$S_2 = 2$

$\Delta S = S_2 - S_1 = 2 - 1 = 1$

(forbidden)

② C* $\underline{\downarrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$

$S_2 = 1$

$S_2 - S_1 = 1 - 1 = 0$

(allowed)

Energy of Photon can not be change spin of electron because very low energy via thermal energy of photon can be change spin

$\underline{\downarrow}$ — $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$

$\Delta S = 1$ ✓

$h\nu$ ←

— — e_g

$\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$ t_{2g}

$S = 1$

$h\nu$ ↛

$\underline{\uparrow}$ —

$\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$

$\Delta S = 2$

↓ $h\nu$

$\underline{\uparrow}$ —

$\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$

$\Delta S = 1$

an Green light rate of Photosynthesis is very low but in red & blue rate of photosynthesis

14/08/2018

2. Laporte Selection Rule

↓

For molecular spectro (in MOT) of diatomic species (Homodiatomic)

$\Sigma^{L=0} \longrightarrow \Sigma^{L=0}$ $\Delta L = 0$ allowed

$\Sigma^{L=0} \longrightarrow \Pi^{L=1}$ $\Delta L = 1$ Allowed

$\Sigma^{L=0} \longrightarrow \Delta^{L=2}$ $\Delta L = 2$ forbidden

$\Pi^{L=1} \longrightarrow \Phi^{L=3}$ $\Delta L = 2$ forbidden

$\Pi^{L=1} \longrightarrow \Delta^{L=2}$ $\Delta L = 1$ Allowed

$\Pi^{L=1} \longrightarrow \Pi^{L=1}$ $\Delta L = 0$ Allowed

$\Phi^{L=3} \longrightarrow \Delta^{L=2}$ $\Delta L = 1$ Allowed

For Atomic orbital :- $\Delta L = \pm 1$ allowed

$\Delta L = 0$ & other forbidden

	s	p	d	f
l	0	1	2	3

$s^0 \longrightarrow s^0$ $\Delta L = 0$ forbidden

$p^1 \longrightarrow s^0$ $\Delta L = 1$ Allowed

$p^1 \longrightarrow d^2$ $\Delta L = 1$ Allowed

3. Symmetry Rule :-

s	p	d	f
(g)	(u)	(g)	(u)

$g \longrightarrow g$, $u \longrightarrow u$] forbidden

$g \longrightarrow u$, $u \longrightarrow g$] allowed.

$d - d$ $(g \longrightarrow g)$ forbidden

$s - s$ $(g \longrightarrow g)$ Forbidden

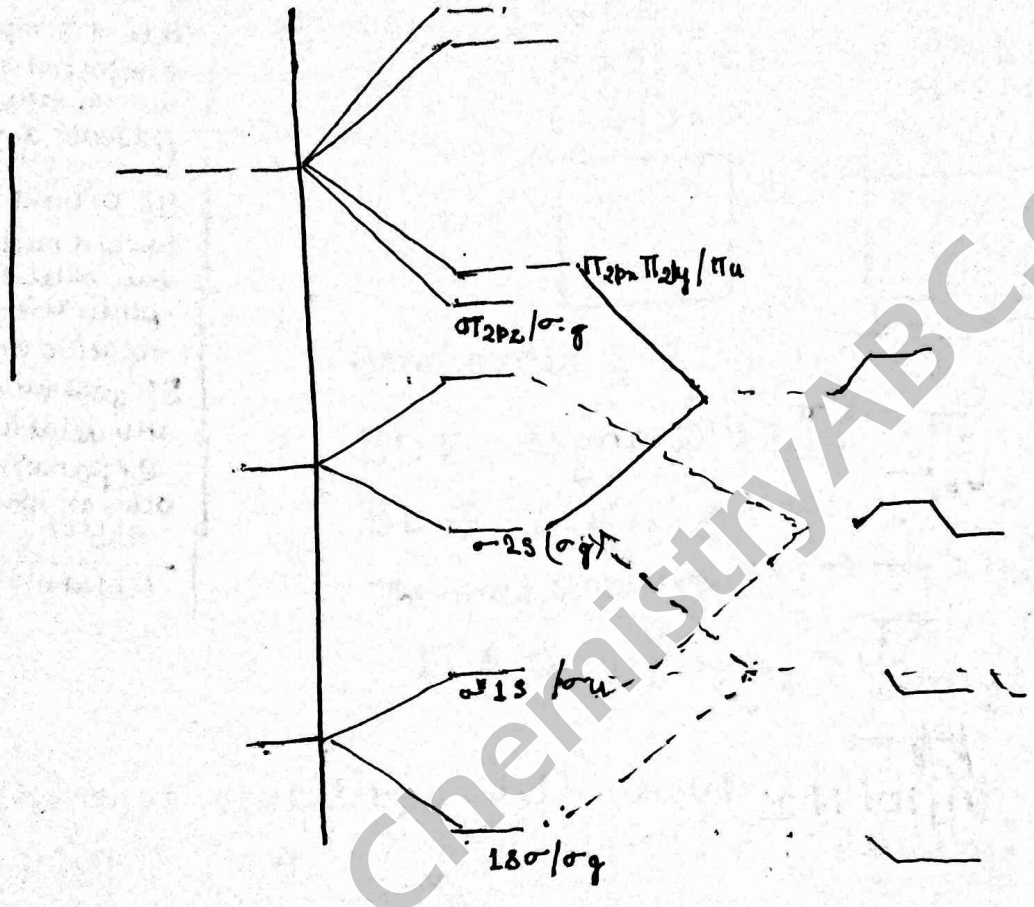
$p \longrightarrow d$ $(u \longrightarrow g)$ Allowed

④ Parity Rule —

⊕ → ⊕
⊖ → ⊖
} Allowed

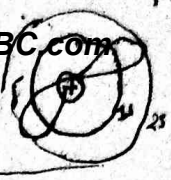
⊕ → ⊖
⊖ → ⊕
} forbidden

For Homodiatomic molecule! — Energy distribution in same symmetry & low energy gap



Configuration of single electron system H = 1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < 5s ...

Li Be B C N O F →



Energy gap b/w 2s–2p are increased

For more than one electron system

1s / 2s < 2p < 3s < 3p < 4s < 4d ...

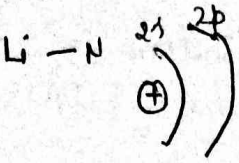
due to repulsion & attraction both occur due to present of e's.

If orbitals goes toward nucleus then called penitration or relative contract

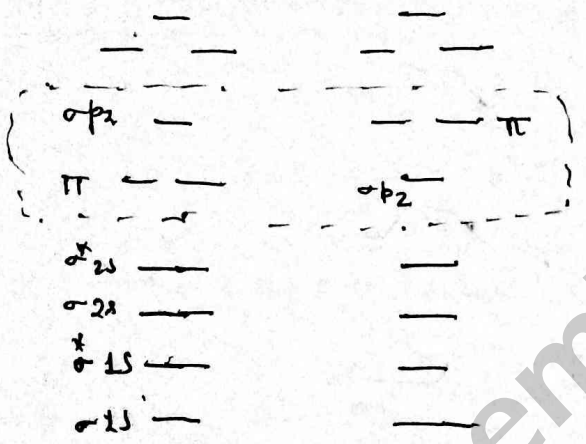
If goes outwards then relative expansion occur or shielding effect

Relative effect

Li – N

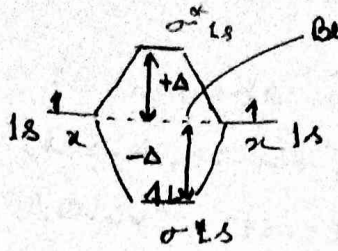


F, O



Bond is force of attraction. To gain stability atom form bond by lowering the P.E.

① He₂



Energy of H = x

Energy of H_2 = 2x − 2Δ

∴ BDE / BE = 2Δ

H_2	$H_2^{\oplus}$	$H_2^{\ominus}$
σ^*_{1s}/σ_g — LOMO	—	↑ HOMO/SOMO/LOMO ($l=2$, $l=0$)
σ_{1s}/σ_g ↿⇂ HOMO ($l=0$) LOMO	↑ LOMO ($l=0$) HOMO SOMO LOMO	↿⇂ LOMO
S = 0	S = ½	S = ½
M = 2S+1 = 1	M = 2S+1 = 2	M = 2
L = 0+0 = 0	L = 0	L = 0
$^1\Sigma_g^+$	$^2\Sigma_g^+$	$^2\Sigma_u^+$
Bond order ⇒ $\frac{2-0}{2}=1$	$\frac{1-0}{2}=\frac{1}{2}$	$\frac{1-0}{2}=\frac{1}{2}$

BDE ⇒ $H_2 > H_2^{\oplus} = H_2^{\ominus}$

BL ⇒ $H_2 < H_2^{\oplus} < H_2^{\ominus}$

Thermal stability (T.S) ⇒ $H_2 > H_2^{\oplus} > H_2^{\ominus}$

IES ⇒ $H_2^{\oplus} > H_2 > H_2^{\ominus}$

* Thermal stability tell about ideality of bond
* Kinetic " " " reality of reactivity

* No relation of ionisation energy to bond order. For ionisation energy we consider attraction.

H_2^+, H_2^-, H_2 } isostoichiometric
O_2, O_2^+, O_2^-, O_2^{2+}, O_2^{--} } speciel

$H_2^{\ominus}$: ↑ (1L) → ↑ (1L)

B.O = $\frac{2-1}{2}=\frac{1}{2}$

$H_2^{\oplus}$: ↑ (1L)

B.O = $\frac{1-2}{2}=-\frac{1}{2}$

$H_2^{\oplus}$ B.O = ½ $[H-H]^{\oplus}$

(2C−1e) (bond)

Minimum bonding condition

$\nu \propto \sqrt{\frac{K}{\mu}}$ only K = force constant

from this we calculate force in Newton

* Bond order just represent the force of attraction between atom.
* If bond order is zero, it means, there is absence of covalent bonding but physical bonding (vander Waal) may be present i.e, He_2, dounot exist covalentally but may exist physical bonding.
* Fraction bond order means bonding is complete but magnitude of force of attraction is low i.e, $H_2^{\oplus}$, B.O = 1/2, means their is half force of attraction b/w H^+-atom as compare to force of attraction in H_2 molecule.

$$He_2 \longrightarrow He_2^{\oplus}$$

σ^*_{1s} ↑↓ ↑

σ_{1s} ↑↓ ↑↓

Bond Order = 0 B.O = 1/2

$\Rightarrow$ $He_2^{\oplus}$ $H_2^{\ominus}$

B.O = 1/2 B.O = 1/2

T.S $\Rightarrow$ $He_2^{\oplus} > H_2^{\oplus}$

I.E $\Rightarrow$ $He_2^{\oplus} > He_2^{\ominus}$

BDE $\Rightarrow$ $He_2^{\oplus} > H_2^{\ominus}$

BL $\Rightarrow$ $He_2^{\oplus} < H_2^{\ominus}$

Condition for Minimum bonding condition

2C−1e

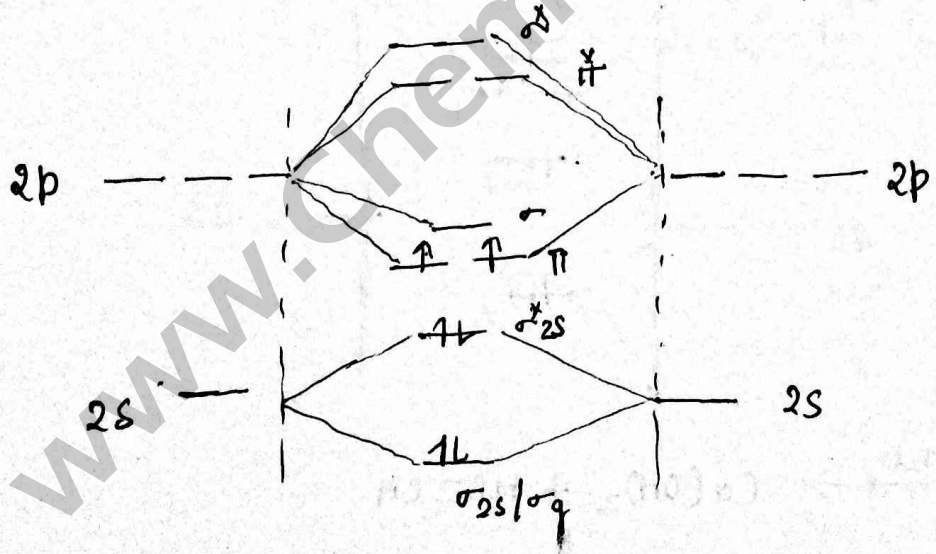
* Li_2 $Li_2^{\oplus}$ $Li_2^{\ominus}$

*Negative bond order in ground state is not possible but in case of having atoms and in photochemical excitation it may be possible but the molecule should be Photo sensitive.

* Photo sensitizer for Hydrogen is Mercury (Hg)

* B_2 $B = 1s^2\ 2s^2\ 2p^1$

$= K\ 2s^2\ 2p^1$



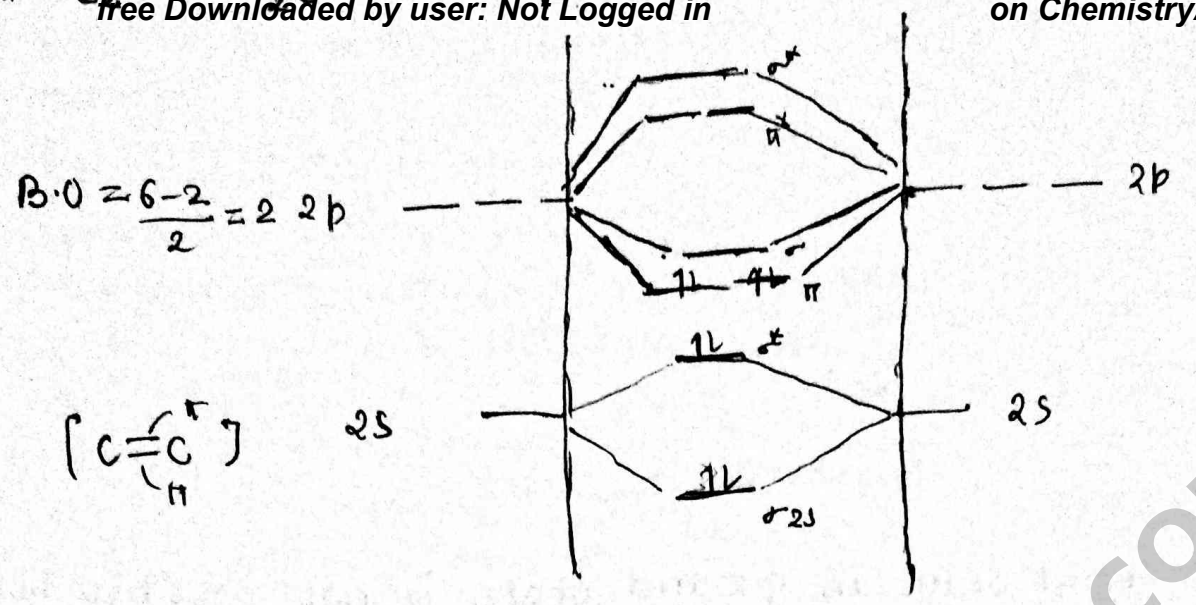
$B.O = \frac{4-2}{2} = \frac{2}{2} = 1$

B — B

↓

2e (Both e's are unpaired and exist in π that's why it which 1-π-bond so it highly unstable)

* C_2 ${}_6C = K^2 2s^2 2p^2$



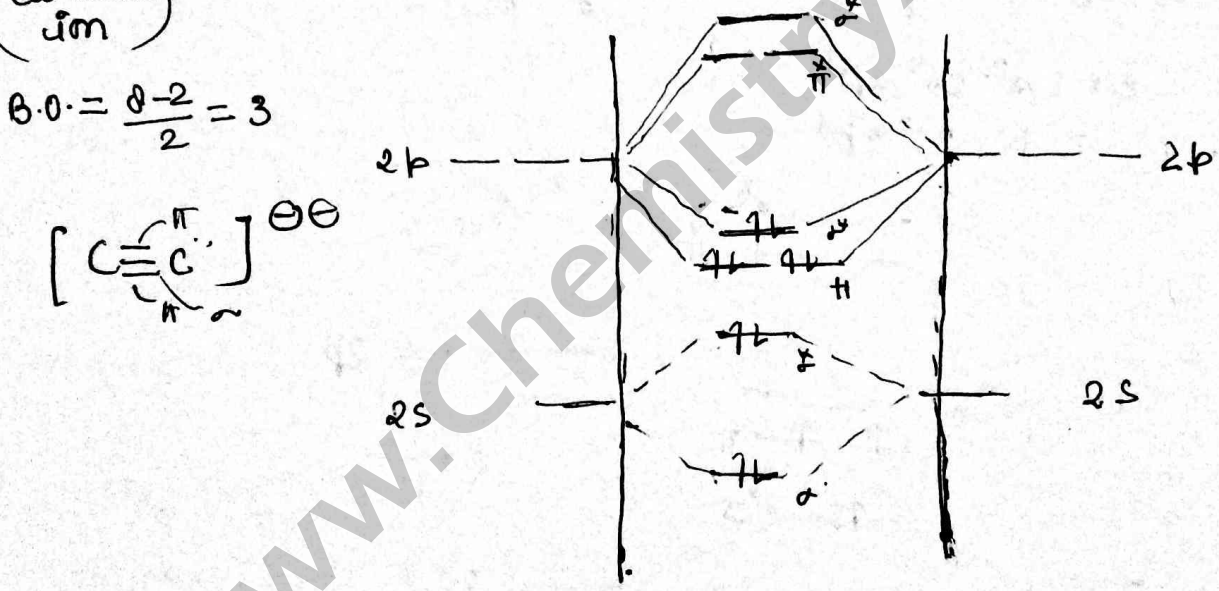
$[C \equiv C]$ (H, π)

* $C_2^{\ominus\ominus}$ ${}_6C = K\ 2s^2 2p^2$ CaC_2

(Ethaphore) use in (fruit ripening)

↓

(carbide ion)



$[C \equiv C]^{\ominus\ominus}$ (π, π, σ)

$CaC_2 \xrightarrow{H_2O} Ca(OH)_2 + HC \equiv CH$

$CaC_2 + N_2 \longrightarrow CaCN_2 + C$

↓

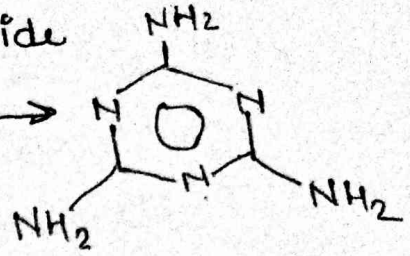
Nitrolicum

(Best fertilizer)

$CaCN_2 \xrightarrow{H_2SO_4} CaSO_4 + H_2CN_2$ or H_2N-CN

$H_2N-CN \xrightarrow{\Delta} (H_2NCN)_2$ (Dicyanamide) $\xrightarrow{\text{Red hot}}$ (Melamine)

Cyanamide



(In melamine after mixing formaldehyde/ it is biodegradable).

(It is use in making fibre plate)

* Configuration of C_2 :-

$\sigma_{1s}^2 \sigma^*_{1s}^2 \sigma^*_{2s}^2 \sigma^*_{2s}^2 \pi^2_{2px} \pi^2_{2py}$

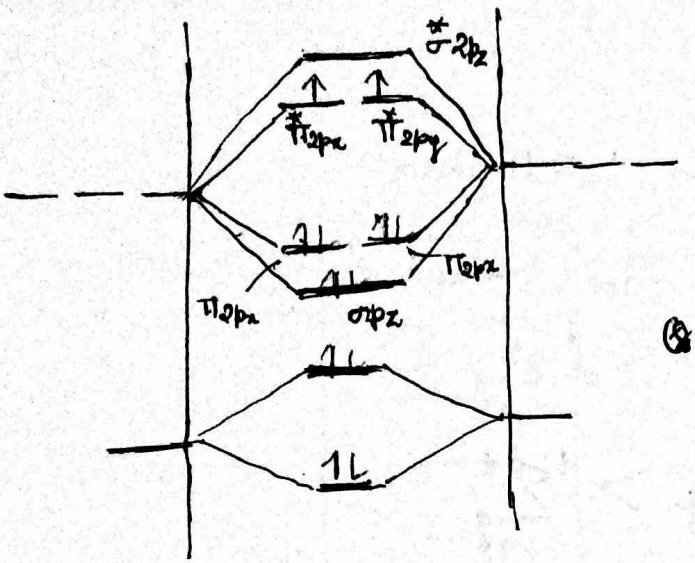
$\sigma_{1g}^2 \sigma_{1u}^2 \sigma_{2g}^2 \sigma_{2u}^2 \pi_u^4$ } (Symmetrify theory)

C_2, C_2^+, C_2^{++}, C_2^-, C_2^{--} (Arrangle ~~bond~~ .BO, BDE, BL, I

$\bar{\nu}_c = c \cdot T\text{-}S$)

* O_2

$2O = K\ 8s^2\ 2p^4$



$BO = \frac{8-4}{2} = \frac{4}{2} = 2$

$O = O$

Paramagnetic (diradical)

Ques - Find no. of possible Microstate of O_2 ?

$$M_S = \frac{4!}{2!(4-2)} = \frac{^{2}4 \times 3!}{2! \times 2!} = 6$$

Ques Find the no. of existing Microstate of O_2 ?

↑ ↑

$l = +1 \quad -1$

$L = +1-1 = 0\ (\Sigma$

$S = \frac{1}{2}+\frac{1}{2} = 1$

$M = 2S+1 = 3$

$^3\Sigma_g^-$

↑ ↓

$S = \frac{1}{2}-\frac{1}{2} = 0$

$M = 1$

$L = +1-1 = 0$

$^1\Sigma_g^+$

1L —

$S = 0$

$m = 1$

$L = +1+1 = 2\ (\Delta)$

$^1\Delta_g$

↓ ↓

$S = 1$

$L = +1-1 = 0\ (\Sigma)$

$M = 3$

$^3\Sigma_g^-$

↓ ↑

$S = 0$

$M = 1$

$L = 0\ (\Sigma)$

$^1\Sigma_g^+$

— 1L

$S = 0$

$M = 1$

$L = +1+1 = 2\ (\Delta$

$^1\Delta_g$

Hund's Rule –

For stability (lowest energy)

- For lowe energy –

① Spin Multiplicity higher

② If M is same then L = Higher

⇒ Energy $^3\Sigma_g^- < {}^1\Delta_g < {}^1\Sigma_g^+$

⇒ Stability $^3\Sigma_g^- > {}^1\Delta_g > {}^1\Sigma_g^+$

↓ Ground state

↓ Ist Excited state

↓ IInd Excited state

Ques

① B_2.

O_2^+ — Oxygen monocation

O_2^- — Super oxide

O_2^{--} — Peroxide

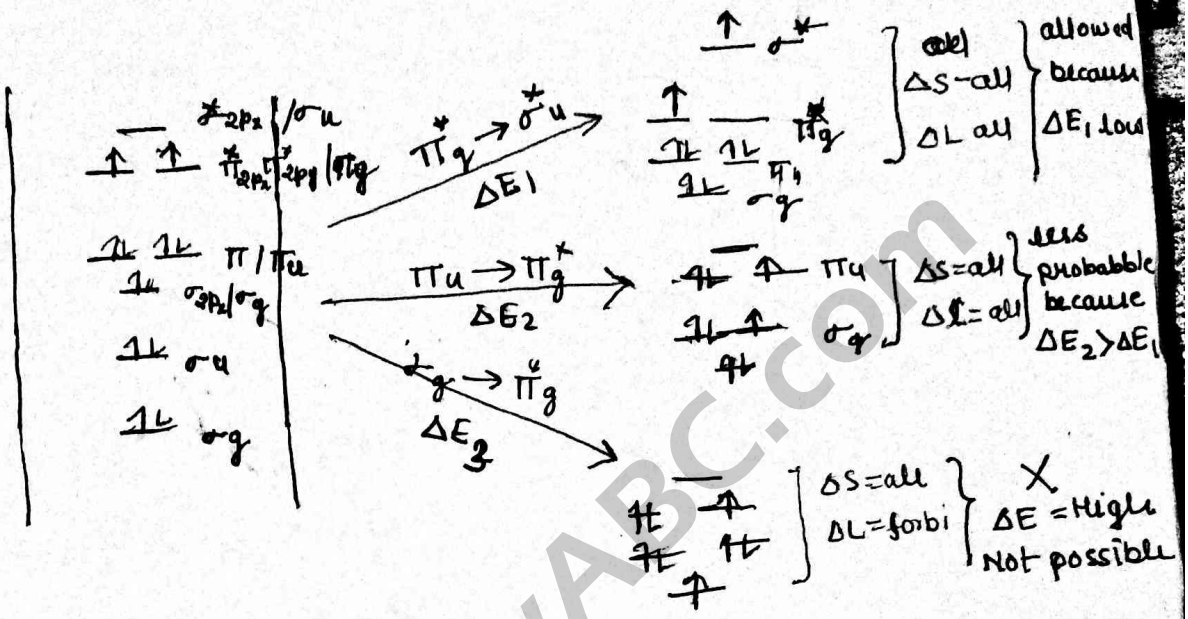
O_2^{++}

O_2

$NaO_2 \rightarrow Na^+ + O_2^-$

$KO_3 \rightarrow K^+ + O_3^-$

$Al^{\oplus}O_2^{\ominus} \rightarrow Al^{+++} + O_2^{----}$



⇒ O_2 ΔE_1 is low., Hence, O_2 need less Energy for transition

⇒ More 'λ' (wavelength) for transistion

⇒ i.e., O_2 absorb at Red en.

⇒ ∴ Colour of O_2 will be at ~~red~~ Blue end.

O_2 (gas) paramagnetic (light blue) → $[O_2]$ (liquid) (Blue color) → $[O_2]_2$ (solid) or O_4 Dimerise (diamagnetic) (Dark Blue)

O---O
‖ ‖
O--O

Pairing of unpaired electron.

H_3 H_3^+ H_3^- H_2

⇅	—	—	
↑	—	↑↓	—
↑↓	↑↓	↑↓	↑↓

B.O. = $\frac{2-0}{2}=1$ $\frac{2-0}{2}=1$ $\frac{2-0}{2}=1$ $\frac{2-0}{2}=1$

T.S order ⇒ $H_3^{\oplus} > H_3 > H_3^{\ominus}$

BDE ⇒ $H_3^{\oplus} > H_3 > H_3^{\ominus}$

BL ⇒ $H_3^{\oplus} < H_3 < H_3^{\ominus}$

IE ⇒ $H_3^{\oplus} > H_3 > H_3^{\ominus}$

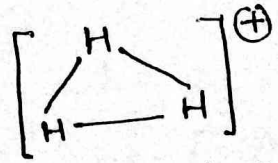
H_3^+

$[H-H-H]^{\oplus}$

3C-2e bond

Linear

$\theta = 180$

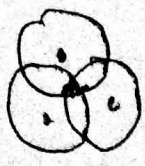


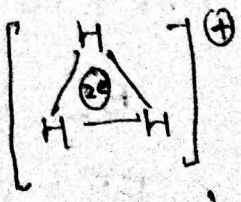
3C-2e bond

close

$\theta = 60'$

* At room temperature
  Mix of linear + cyclic (major)
  (minor)





Aromatic
2e system
follow Huckel rule.

* Temperature increases.
  Linear ↓ increases

N_2 IN: $1s^2 2s^2 2p^3$

HOMO — All are bonding

N_2 & CO — BDE = ~900 KJ/mol

Among diatomic species Highest BDE

N_2 ⇒ All bonded e's are in BMO

i.e., lower energy

∴ Less reactive

∴ N_2 is ⇒ Inert gas,

Non-polar Polar

$N \equiv N < C \equiv O^+$

Stability ↑es

Reactivity ↑es

$N_2^{\ominus\ominus}$	$N_2^{\oplus}$	N_2	$N_2^{\oplus}$	$N_2^{\oplus\oplus}$
$BO = \frac{6-2}{2} = 2$	$\frac{6-1}{2} = 2.5$	$\frac{6-0}{2} = 3$	$\frac{5-0}{2} = 2.5$	$\frac{4-0}{2} = 2$
Paramagnetic	Paramagnetic	Diamagnetic	Paramagnetic	Paramagnetic

BDE & TS ⇒ $N_2 > N_2^+ > N_2^- > N_2^{++} > N_2^{--}$

BL ⇒ $N_2 < N_2^+ < N_2^- < N_2^{++} < N_2^{--}$

I.E ⇒ $N_2^{++} > N_2^+ > N_2 > N_2^- > N_2^{--}$

Reducing agent (electron donar) ⇒ $N_2^{\ominus\ominus} > N_2^{\ominus}$

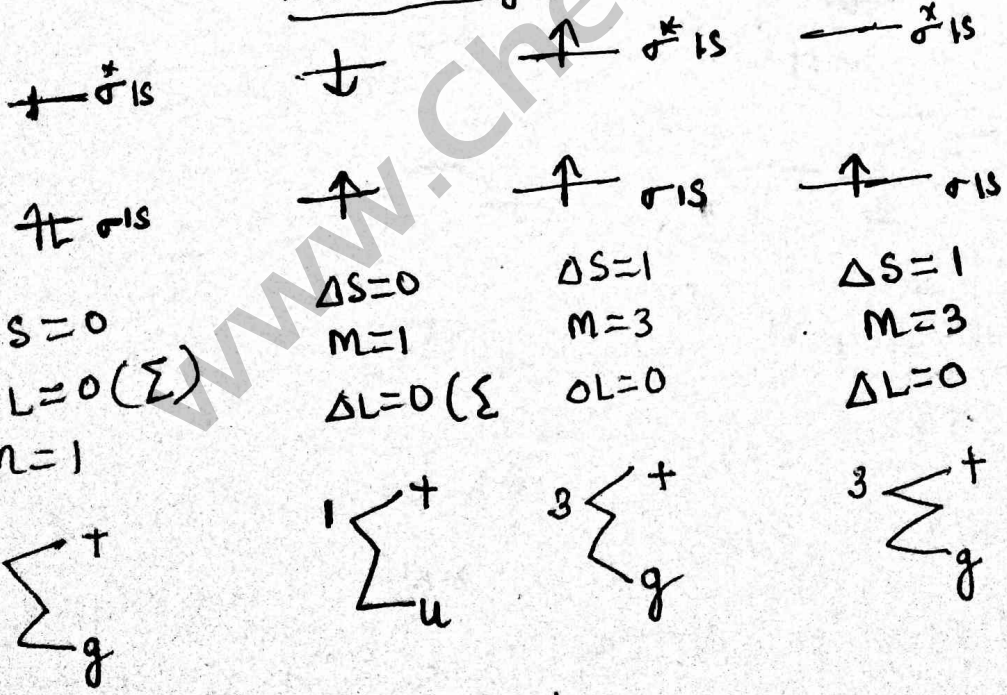
Oxiding agent (electron gain) ⇒ $N_2^{\oplus\oplus} > N_2^{\oplus}$

$\bar{\nu}_{N-N}$ ⇒ $N_2 > N_2^+ > N_2 > N_2^{++} > N_2^{--}$

$H_2 \xrightarrow{h\nu} H_2^*$

G.S. E.S

Probability for E.S —



He_2^+ He^+

$He_2^{\oplus}$

σ_{2s} ↑↓

σ^*_{1s} ↑↓

σ_{1s} ↑↓

$B.O = \frac{3-2}{2} = \frac{1}{2}$

$He^{\oplus}$

σ_{2s} —

σ^*_{1s} ↑↓

σ_{1s} ↑↓

$B.O = \frac{2-1}{2} = \frac{1}{2}$

CO, NO, BN, CN (0)

HF, LiH (+)

(−)

solid ionic

vapour / covalent

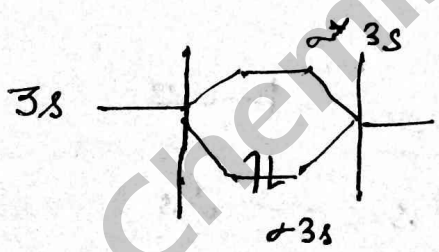
Thermal stability ⇒ $He_2^{\oplus}$ > $He_2^{\ominus}$

(higher stability e⁻ is in lesser energy orbital)

⇒ Na_2 (Na — Na)

exist covalent in (vapour state)

Na = [Ne] 3s¹



$B.O = \frac{2-0}{2} = 1$

⇒ P

* HETRO ATOM :—

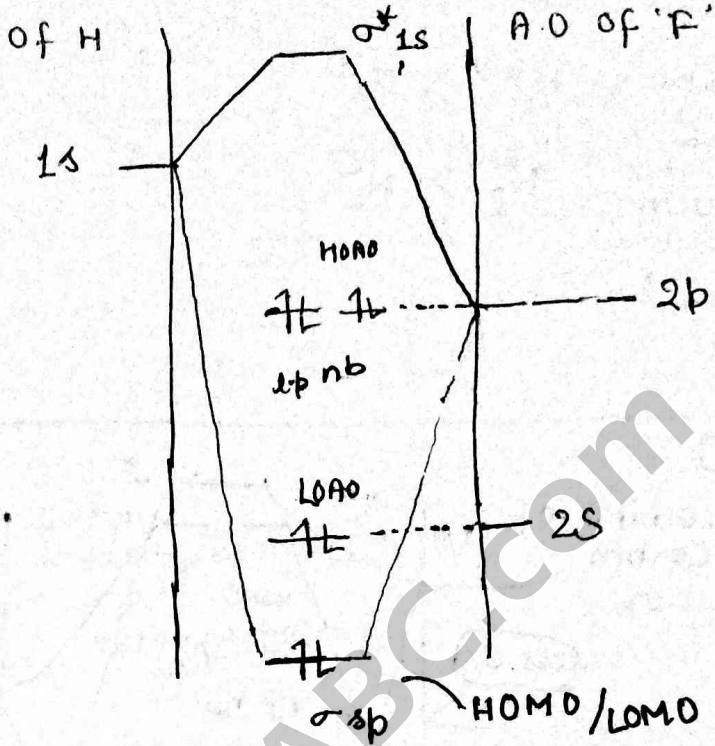
* HF

H = $1s^1$

F = $1s^1\ 2s^2\ 2p^5$

$BO = \frac{2-0}{2} = 1$

H—F:



* More E.N. atom ~~has~~
  - ↙ BMO — Attract towards
  - ↓ Orbital have low energy

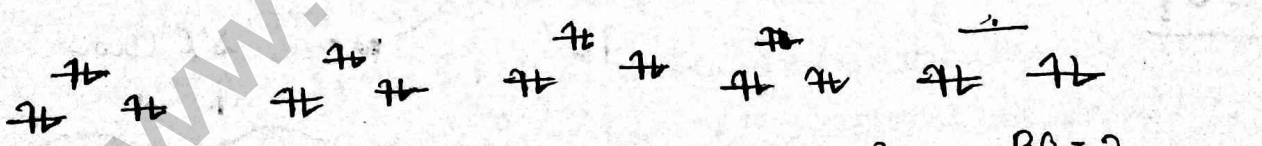
Ques. HOMO of HF ?

⇒ σsp BMD

Ques HOAO of HF

⇒ 2p

$N_2^{\ominus\ominus} \xleftarrow{+e} N_2^{\ominus} \xleftarrow{+e} N_2 \xrightarrow{-e} N_2^{+} \xrightarrow{-e} N_2^{++}$



BO = 2 | BO = 2.5 | BO = 3 | BO = 2.5 | BO = 2

Paramagnetic Para | Dia. | Para | Diamagnetic

$\vec{\mu} \Rightarrow N_2^{\ominus\ominus} > N_2^{\ominus} = N_2^{\oplus} > N_2 = N_2^{\oplus\oplus}$

$BO \Rightarrow N_2 > N_2^{\oplus} \neq N_2^{\ominus} > N_2^{\oplus\oplus} = N_2^{\ominus\ominus}$

$BDE \Rightarrow N_2 > N_2^{\oplus} > N_2^{\ominus} > N_2^{\oplus\oplus} > N_2^{\ominus\ominus}$

$BL \Rightarrow N_2 < N_2^{\oplus} < N_2^{\ominus} < N_2^{\oplus\oplus} < N_2^{\ominus\ominus}$

$\nu_{N-N} \Rightarrow N_2 > N_2^{\oplus} > N_2^{\oplus\oplus} > N_2^{\ominus\ominus}$

I.E $\Rightarrow N_2^{\oplus\oplus} > N_2^{\oplus} > N_2 > N_2^{\ominus} > N_2^{\ominus\ominus}$

Oxidation agent (e gain) $\Rightarrow N_2^{\oplus\oplus} > N_2^{\oplus}$

Reducing agent (e loss) $N_2^{\ominus\ominus} > N_2^{\ominus}$

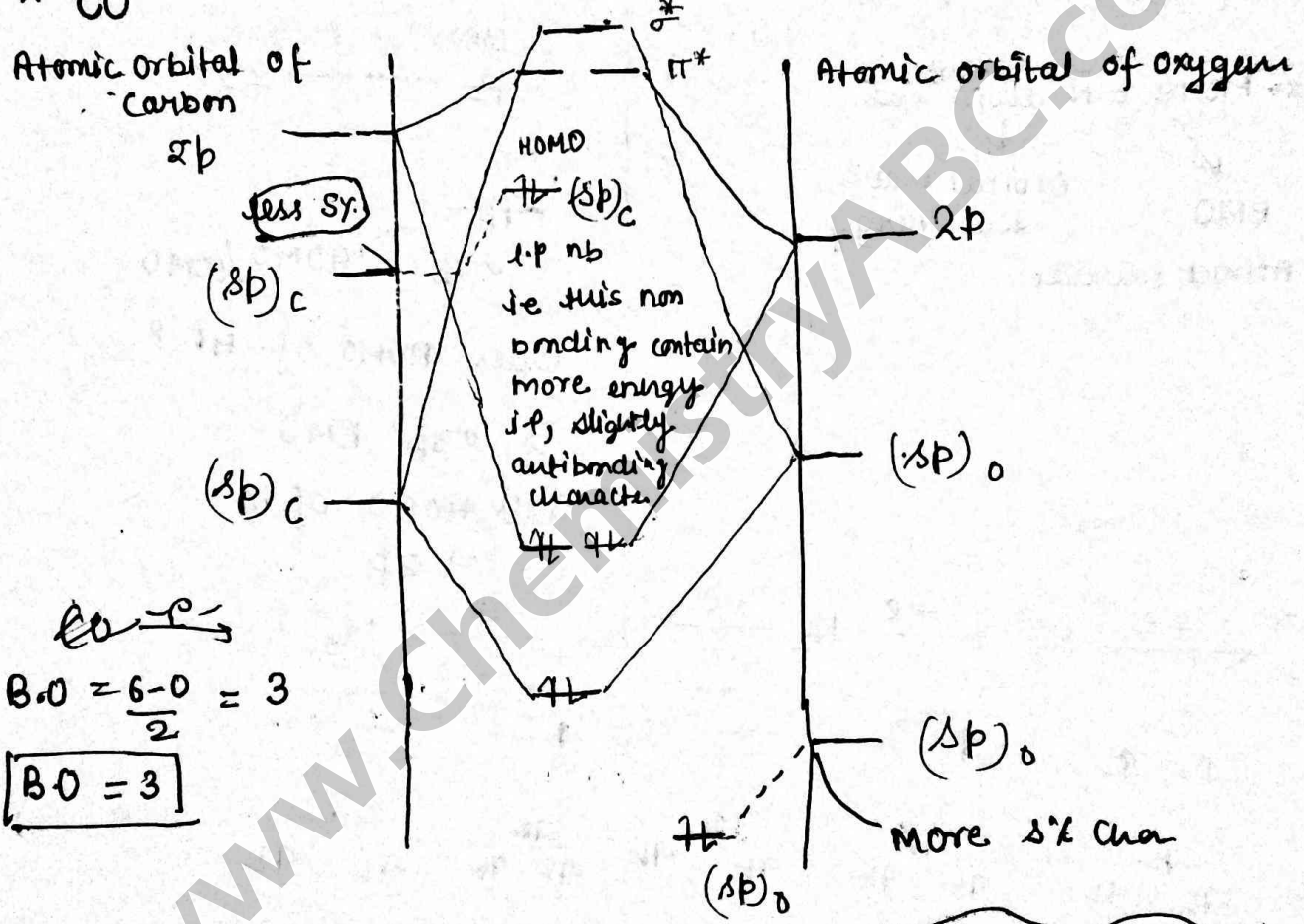
E

Available → waste-use

Unavailable → S

	N_2	CO
Total e's	14	14 } isoelectronic
T. Atom	2	2 } isoatomic
Struc	N≡N	C≡O } isostructural

* CO



CO

B.O = $\frac{6-0}{2} = 3$

B.O = 3

* In CO⁺ no. of e's decreases ∴ interelectronic i.p repulsion ↓es ∴ BL ↓es.

* In case CO the MOT failed because

CO^+, CO

BO = 2.5, 3

$BO \propto \frac{1}{BL} \Rightarrow BL = CO^+ > CO$ (Expected)

But experimentaly CO^+ (BL) < CO (BL). thus MOT of CO is explained by Coulson called (Coulson Modification)

AO → MO
VBT → HO → MOT

C = $k 2s^2 2p^2$

C = (sp) (2p unhybrid)

O =

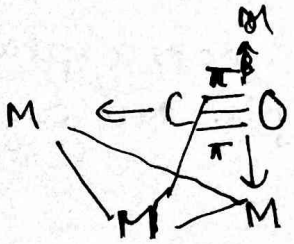
(sp) (2p)

M ← C ≡ O:

%s ↓es → stability is more
↓ → ↓
energy ↑es → energy of (sp)o is very less

* CO is good ligand because its HOMO is in higher energy state therefore CO easily donate lone pair.

*



* CO generally monodentate ; sometime its behave bidentate and tridentate (to donating their π-bond to metal). If CO bidentate or tridentate then Metal to Metal bond also exist b/c C≡O bond is small.

* Molecular orbital energy can be determined by using UVPES (UV Photo electron spectroscopy)

Molecular Orbital Diagram of 'CO'

CO $\quad$ $CO^{\oplus}$

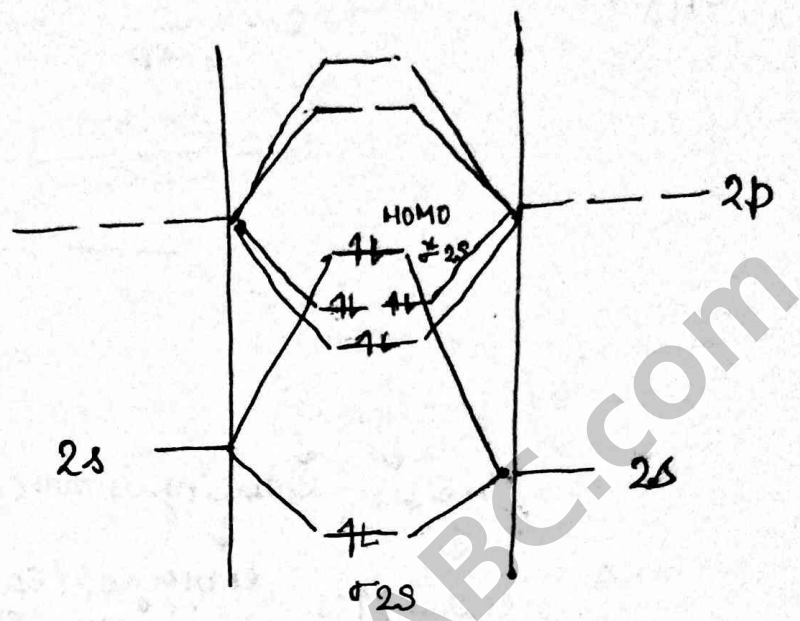
BO $= \frac{8-2}{2}$, BO $= \frac{8-1}{2}$

$= 3 \quad = 3.5$

$\longrightarrow$

BO ↑es

BL ↓es



Notes - The MO diagram of NO is similar to that of 'CO' even Coulsm and Mordvin are same

However simple MO diagram of 'NO' can explain all the properties therefore simple MO digram of NO are generally used.

NO

7 + 8 = 15

$NO^{\ominus} \xleftarrow{+e} NO \xrightarrow{-e} NO^{\oplus}$

$\frac{8-4}{2}=2 \quad \frac{8-3}{2} \quad \frac{8-2}{2}$

$=2 \quad = 2.5 \quad = 3$

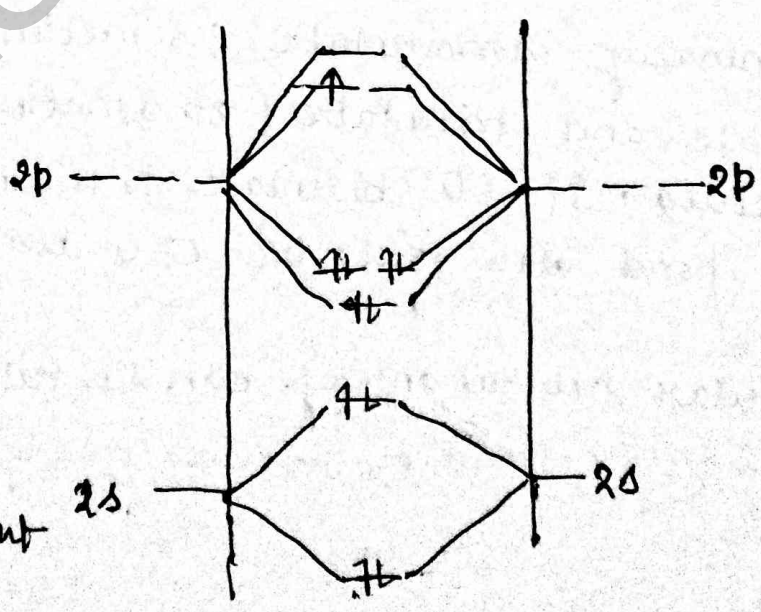
$\longrightarrow$

BO increases

BL decreases

(NO) → Reducing agent ~~Red orgent~~

free radical



N_2O
NO } → Neutral

N_2O_3
NO_2 } → acidic
N_2O_5

* (NO) is highly reactive (cause cell division) → (cancer)

* But NO formed in cell which used in cell signaling → Feeling of sensation

H.W

C_nCN, $CN^{\ominus}$, $CN^{\oplus}$, BN, $BN^{\oplus}$, $BN^{\ominus}$

PHYSICAL BONDING :-

- Vander Waal Force ~ 5 KJ/mol
- H-bond i4— ~45 KJ/mol

Hydrogen bonding :-

By Lattimer & Rodebush

$X^{\delta-} \leftarrow H^{\delta+} \cdots :D$

X → Electronegative atom

D → (e's density)

(7) O—H-- O (I)

O—H---$\delta^{\ominus}$ (II)

O—H---F$^{\ominus}$ (III)

(III) > (II) > (I)

(8) F—H---N (I)

$\dot{F}$—H---O (II)

O—H---F (III)

O:—H---F$^{\ominus}$ (IV)

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

9. $O \leftarrow H \cdots O^{\oplus}$ < $O-H^{\delta+}-N^{\ominus}$

(10) $O \leftarrow H^{\delta+} \cdots \delta^{\ominus}$ < $O-H-\cdots N^{\oplus}$

Strength of H-bond

(1) $O^{\delta-} \leftarrow H^{\delta+} \cdots O$ < O—H---N

(2) $O^{\delta-} \leftarrow H^{\delta+} \cdots N$ > N—H---O

(3) O—H---S > S—H---O

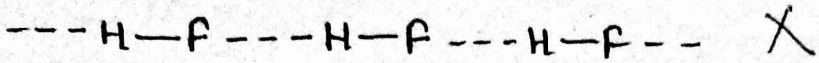
(4) $O \leftarrow H^{\delta+} \cdots O^{\ominus}$ > O—H---O

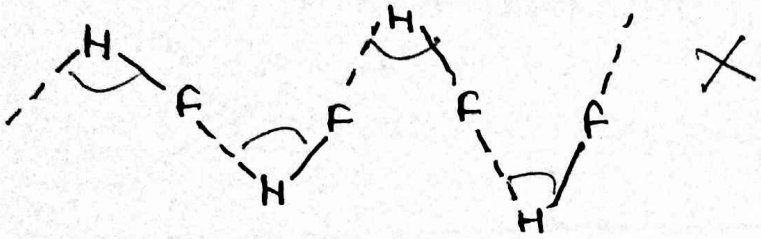
(5) $O \leftarrow H^{\delta+} \cdots N^{\ominus}$ > N—H---$O^{\ominus}$

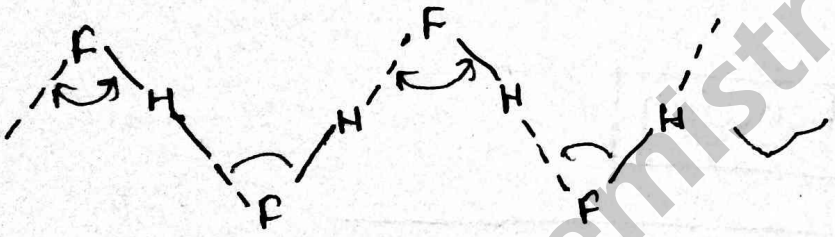
(6) $O \leftarrow H^{\delta+} \cdots \delta^{\ominus}$ > $S \leftarrow H^{\delta+} \cdots O^{\ominus}$

(7)

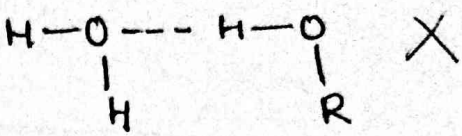
Types of H-bonding

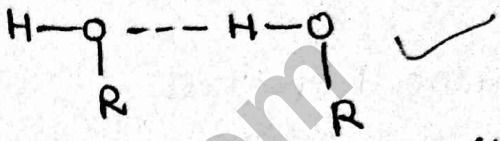


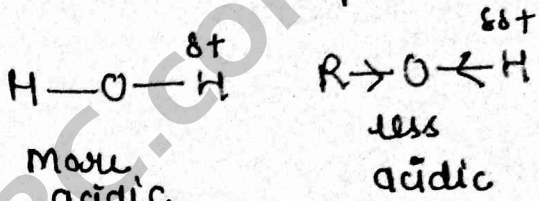


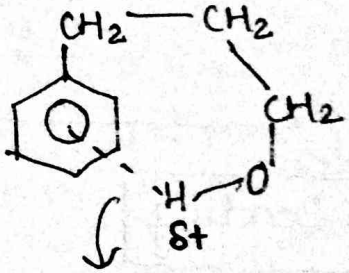


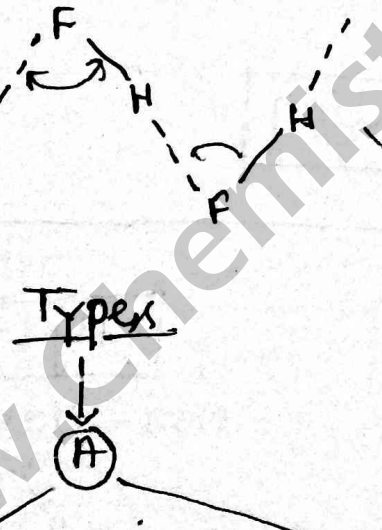
Representation of H-bonding











Types

(A)

① σ-Hydrogen bonding

- Inter
- Intra

② π-H-bonding (π bond act as donar)

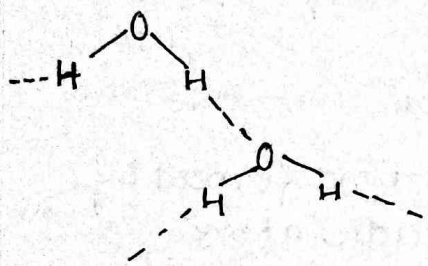
- Inter
- Intra

9/09/2018

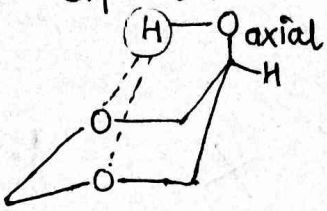
Types

H-bonding

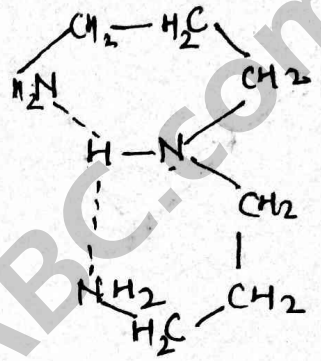
Mono furcated H. bonding



Bifurcated



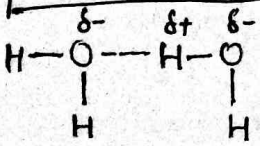
Trifurcated



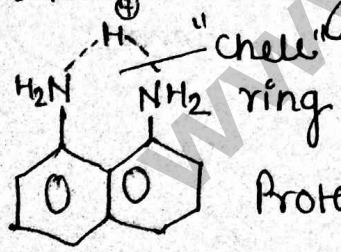
etc

Hydrogen bonding

Brioton Bonding



classical H. bonding



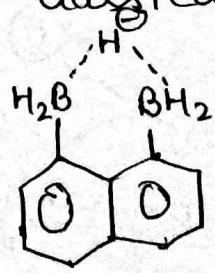
Proton sponge

Mono acid base

stable due to H. bonding & chelation instead of steric hinderence

Hydride bonding

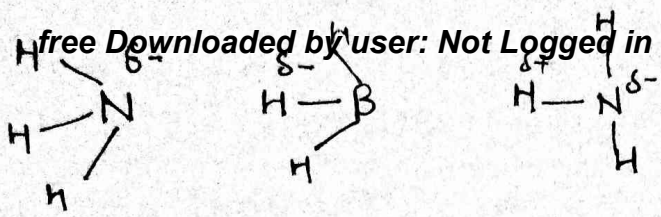
Non-classical H-bonding

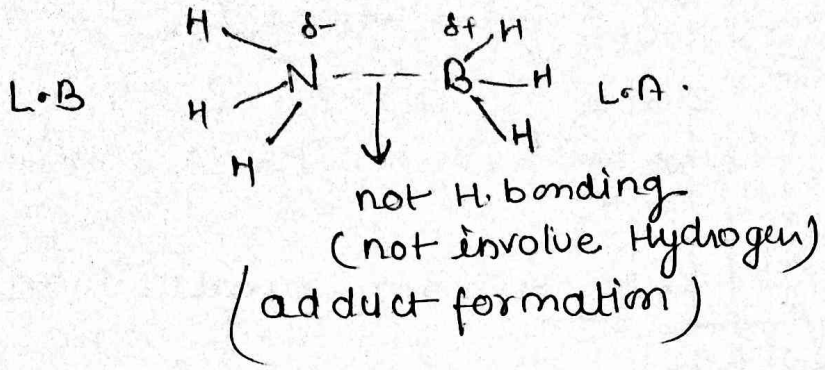


Mono basic acid

(Hydride sponge)

stable due to H. bonding & chelation instead of steric hinderence





Type of Hydrogen bonding

Symmetrical

Quasi H. bond

$[X \overset{a}{—} H \overset{b}{\cdots} X]^{n\pm}$

$a = b$

⇒ Bond dissociation energy is same for a & b

⇒ bond length same

$[F—H\cdots F \leftrightarrow F\cdots H—F]^{\ominus}$

very strong bond

∴ F-NMR ⇒ 1 singal

H-NMR ⇒ 1 singal

↓

triplet

∴ $HF_2^{\ominus}$ is highly stable.

Unsymmetrical

$[X \overset{a}{—} H \overset{b}{\cdots} X]$

$a \neq b$

$a < b$

BDE ↓ High

Bond dissociation energy is low.

$KF + HF \rightleftharpoons KHF_2 \equiv K^+ HF_2^-$

$KCl + HCl \rightleftharpoons KHCl_2$

$KBr + HBr \rightleftharpoons KHBr_2$] usually doesn't exist at Room temp^r

$KI + HI \rightleftharpoons KHI_2$

Strength of H-bonding decreases

$\therefore$ Thermal stability decreases

$HCl_2^\ominus$ similar to $HF_2^\ominus$ but H-bond - weaker than $HF_2^\ominus$

$HF_2^\ominus \Rightarrow [F \cdots H \cdots F]^\ominus$ (B.O = 1, B.O = 1)

$\{3C - 4e\}$ bond.

δ^- F — H δ^+ ··· $F^\ominus$

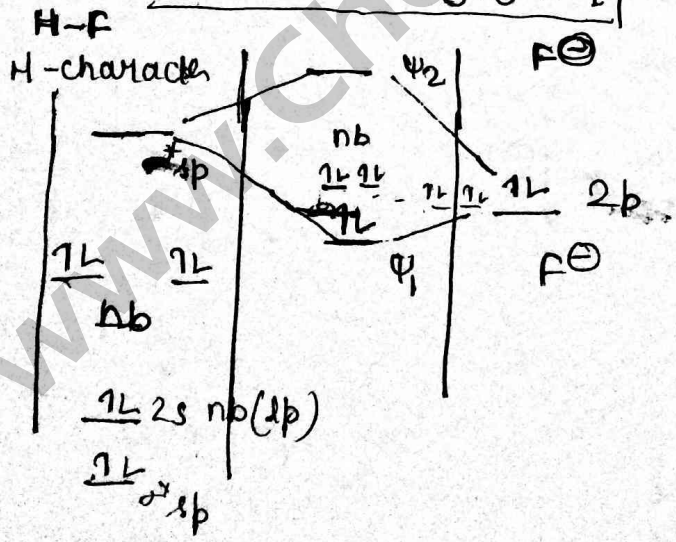
$2e^\ominus$, $2e^\ominus$ = 4e

$2e^\ominus \rightarrow$ Bond order

$4e^\ominus \rightarrow$ 2-Bond order

Bond order of $HF_2^\ominus = 1+1 = 2$ (total)

individual B.O = 1



"Lennard – Jone potential Diagram"

or

6 – 12 Diagram

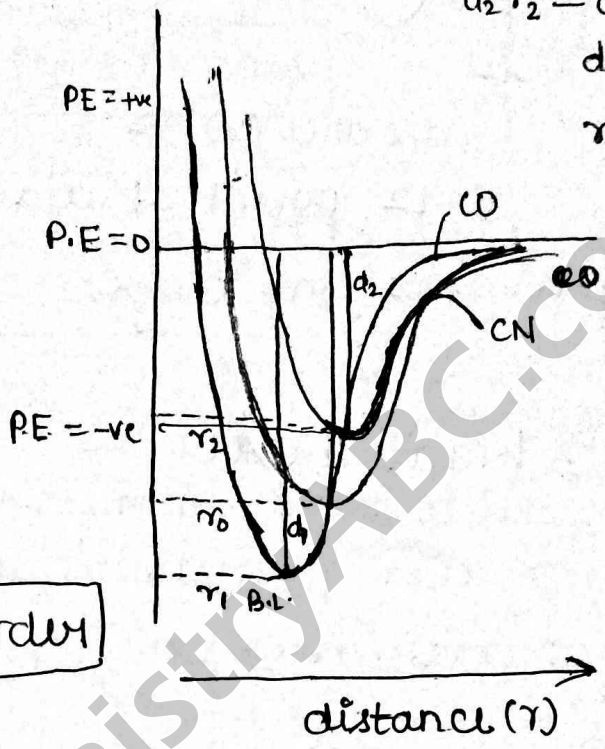
B.O
$d_1 r_1$ – CO 3.0
$d_2 r_2$ – CN 2.5
$d_1 > d_2$
$r_1 < r_2$

As attraction increases as Bond order ↑es.

∴ PE ↓es

∴ Depth ↑es

∴ Bond length ↓es



stability ∝ dipth

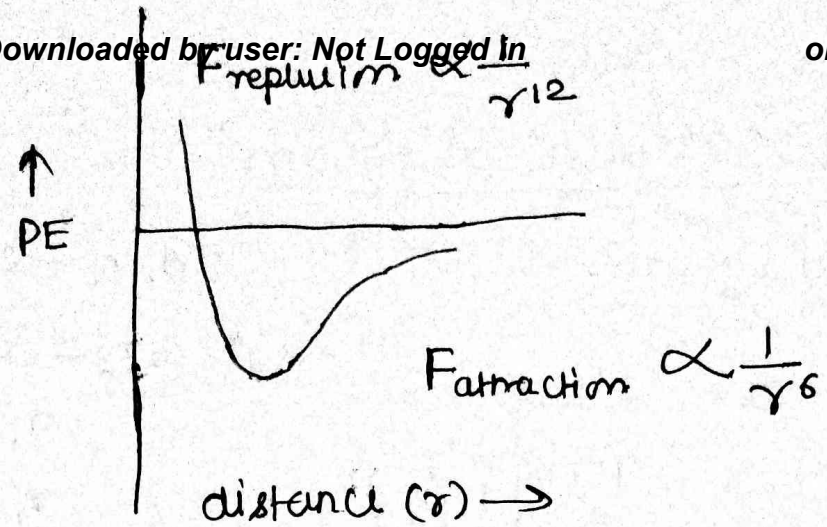
dipth ∝ Bond order

Bond	Energy	Force	Nature
1. ion – ion	r^{-1}	r^{-2}	Long range forces
2. ion – Dipole	r^{-2}	r^{-3}	
3. Ion – Induced dipole	r^{-4}	r^{-5} or r^{-6}	
4. Dipole – Dipole / Keesom force	r^{-6}	r^{-7}	Short range forces
5. Dipole – Induced / Debye force	r^{-6}	r^{-7}	
6. Dipole – Instantaneous / London dipole / Dispersion force	r^{-6}	r^{-7}	
7. Repulsion	r^{-12}	r^{-13}	

$W = F \times x \Rightarrow F \propto r^{-2}$

$W = F \times r \quad E \propto r^{-2} \times r$

$E \propto r^{-1}$



6-12 potential diagram

Strong force ⇒ long range.

* Vander Waal forces :-

When particle neither seems attraction nor seems repulsion then particle is ideal.

Ideal gas condition ⇒ Lower Pressure, High temp^r

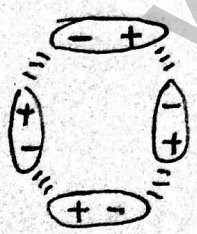
Dispersion or London.

Keeson

Dipole-Dipole interaction

In Polar –

HCl, HBr, H_2O etc



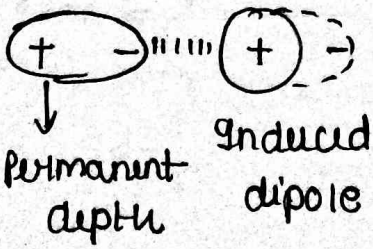
$\delta+$ $\delta-$
H—Cl dipole

Debye

Dipole-Induced dipole interaction

In (Polar + Non polar)

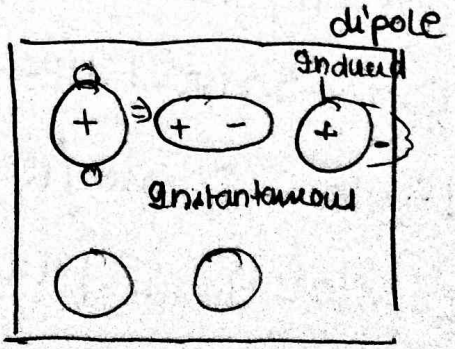
HCl H_2



London

Instantenous dipole — Induced dipole

In Non-polar



Factors :-

Vander Waal force $\propto$ surface area

$\propto \frac{1}{\text{Branching}}$

VWF $\propto$ Molar mass

Boiling point, melting point $\propto$ VWF

Liquification ability $\propto$ VWF

H_2 & He are difficult to liquify.

He
Ne
Ar
Kr
Xe

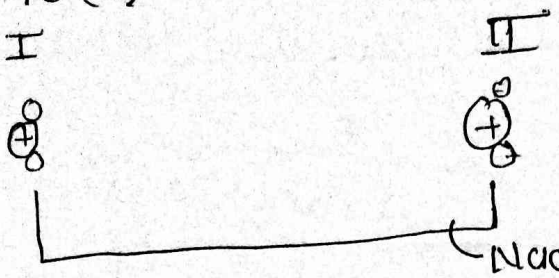
* size increases (↑el)
* surface area (↑el)
* VWF (London force) ↑el
* liquification ability ↑es

$$He(g) \xrightarrow[P-High]{\text{Temp}^{r}\text{ low}} He(l)$$

liq He Boiling point = 3.2K

$$He(l)_{I} \xrightarrow{2.2\,K} He(l)_{II}$$

* He-II (liquid) flow opposite to other liquid like water etc.
* He-liquid is very important for future. as it use in vechicles or in electricity produce. at continuous flow in glass for infinite time



due to two different nuclear spin state (energy state) He-I & He-II shows different properties.

He-II is called wave mechanical and have special property —

⇒ Viscosity almost zero

⇒ Resistance almost zero, hence superconductor

⇒ Free flowing

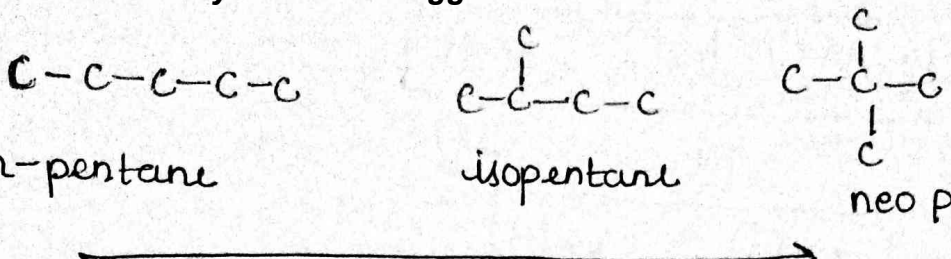
and this temp^r is @ 2.2 K is called λ-temp^r or transition temp^r.

liquid N_2 = −78°C
liquid NH_3 = −34°C

Mercury is soluble in liquid N_2.

10/9/2018

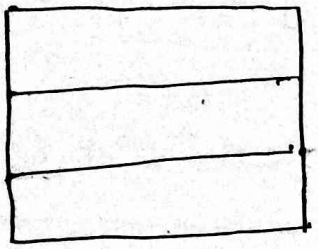
Note The boiling depends upon force of attraction However melting points depend upon force of attraction as well as close packing.



n-pentane isopentane neo pentane

→ ∵ Branching increases
∴ surface area decreases (↓es)
∴ VWF ↓es
∴ Boiling point ↓es
∴ Melting point ↓es

1. For carboxylic acid & Alkane:



(5) → less closed packing
(4) → More closed packing

$C_5 \quad C_6 \quad C_7 \quad C_8 \quad C_9 \quad C_{10}$ →

no. of c-atom ↑es, Molar mass ↑es ∴ VWF ↑es.

$C_5 < C_6 > C_7 < C_8 > C_9 < C_{10}$

Mass ↑es Mass ↑es but closed packing ↓es.
Melting pt ↑es.

< > < > < >

Oscillation or Alternation Effect of m.pt. ; bb pt

Melting point of even > melting point of nearer odd

∴ Over all

$C_5 < C_7 < C_6 < C_9 < C_8 < C_{11} < C_{10}$

Boiling point ↑es

Usually Hydrogen bond > VWF

rarely H-bonding < VWF

HF

HCl
HBr
HI

Size ↑es., Mass ↑es
VWF ↑es
b.pt. ↑es.

No H-bonding only VWF

HF > HI > HBr > HCl

boiling point ↓es.

* H_2O — Strong H-bonding

H_2S
H_2Se
H_2Te

size, mass ↑es
VWF ↑
b.pt ↑es

only VWF

$H_2O \geq H_2Te > H_2Se > H_2S$

Boiling point ↓es.

H-bonding — NH_3 — H-bonding weak

PH_3
AsH_3

H-bonding > VWF of NH_3 of PH_3 & AsH_3

SbH_3
BiH_3

H-bonding < VWF of SbH_3 & BiH_3 of NH_3

very large surface area

$BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$

boiling point ↓es

$(HF)_s$ $(HF)_l$ $(HF)_g$ → Extent of H-bonding ↓es

Water & HF show H-bonding in all state (liquid, gas solid)

$(H_2O)_s$ $(H_2O)_l$ $(H_2O)_g$ → Extent of H-bonding ↓es

In solid. H-bonding maximum

NH_3 — strong H-bonding.

VWF ↓es

PH_3
AsH_3
SbH_3
BiH_3

VWF < H-bond

$NH_3 > BiH_3 > SbH_3 > AsH_3 > PH_3$

Melting point ↓es.

In $H-C\equiv C-H$

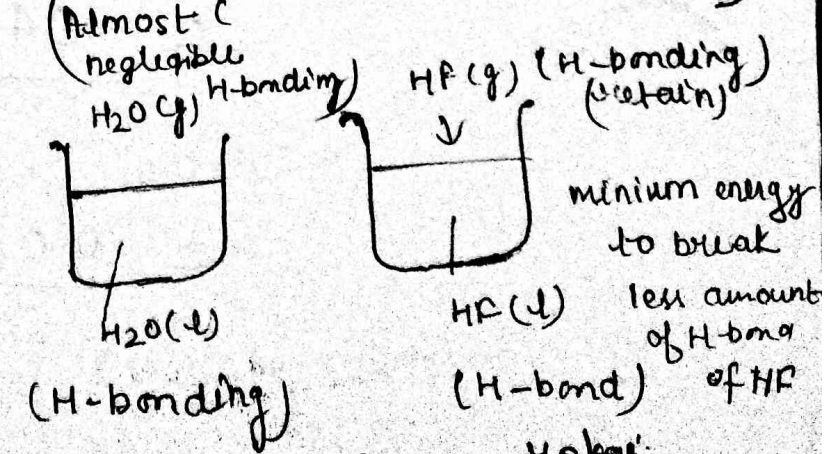
$H-C\equiv C-H$ (g) H-bonding ✗ $\equiv C \sim 3.5$ (EN)

$H-C\equiv C-H$ (l) H-bonding $\equiv C \sim 2.9 \sim 3$ (EN)

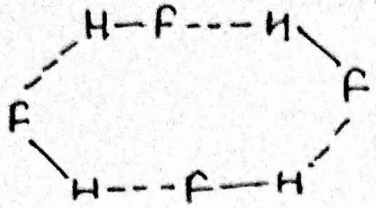
$H-C\equiv C-H$ (s) H-bonding (because in particle close to each other) $-\overset{|}{C}- \sim 2.5$ (EN)

strength of H-bond $HF > H_2O$

boiling point $HF > H_2O$



HF shows one dimensional H-bonding in its liquid form. But in its gas state it shows cyclisation by H-bonding



$(HF)_4$

$\Updownarrow$

$(HF)_n$ In gaseous form it is in tetramer

Qu gas HF

↓

$T = 27°C$ $\quad PV = nRT$

$P = 1\ atm$ $\quad P = \frac{nRT}{V}$

$d = 0.04\ g/L$

$P = \frac{d \cdot w}{\text{molecular wt} \times V} RT = \frac{d}{\text{Mol. wt}} \times RT$

d = density = gm/L

Molecular wt. $= \frac{dRT}{P}$

$= \frac{0.04\ g/L \times 300\ K \times 0.082\ atm\ L/K}{L \times 1\ atm}$

$= \frac{0.04 \times 2.4}{}$

$=$

$T = 27°C$ $P = 1$ atm $d = 45.8$ g/l

Molecular wt = 45.8×2.46

$= 112.66$ g

i.e., HF exis in $(HF)_n$

$$n = \frac{172.660}{20}$$

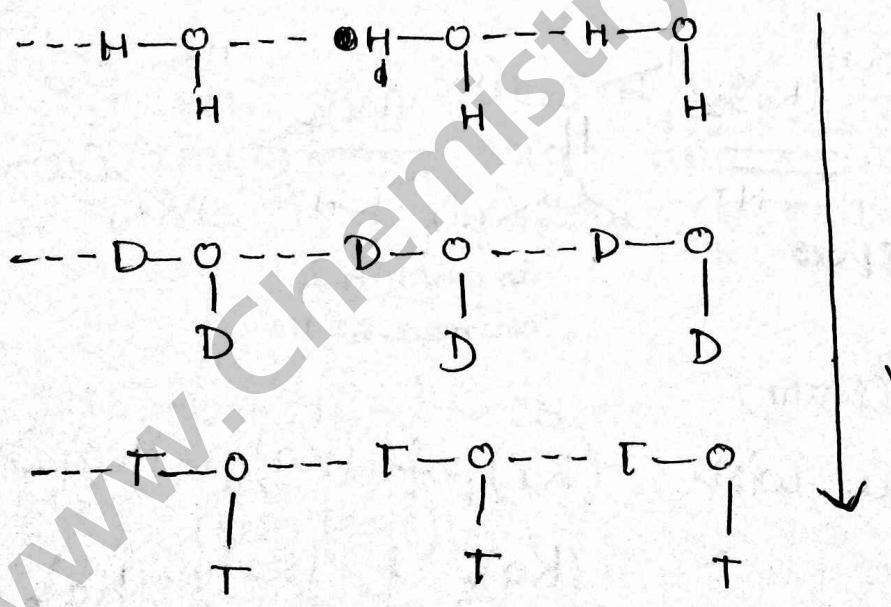
$n = 5.56$

$n \simeq 6$

Imp

Note !—

Heavier isotopes forms stronger bonds



Strength of H-bonding ↑es
∴ boiling pt. ↑es
& Viscosity ↑es

Normal water : Heavy water

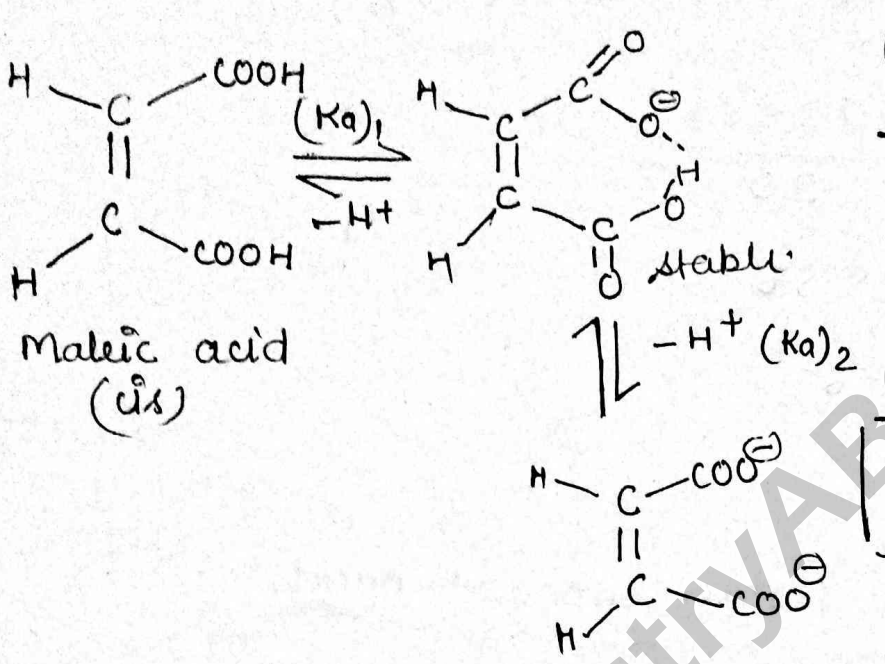
6000 l : 1 l

Regular electrolysis of 6000 l normal water we get 1 l Heavy water.

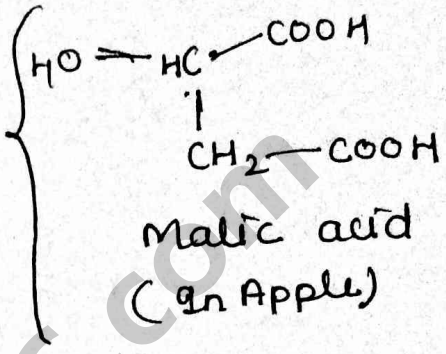
Acidic strength :-

Poly basic acid $K_1 > K_2 > K_3$ ----

But in HF it is opposite

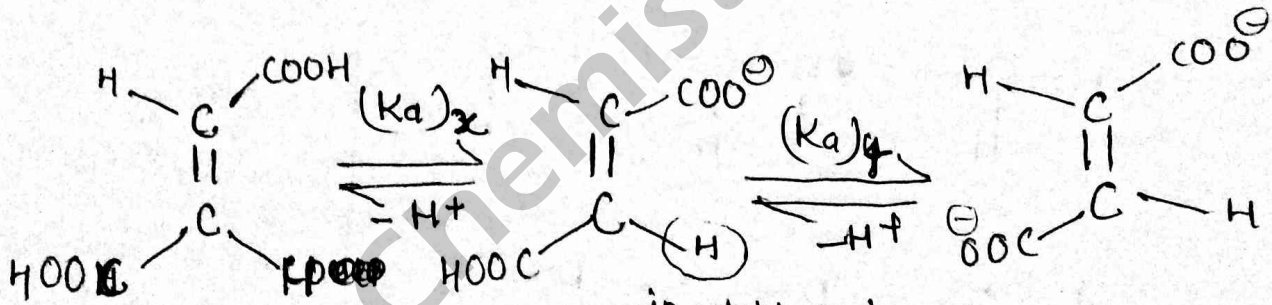


Maleic acid (cis)



Malic acid (in Apple)

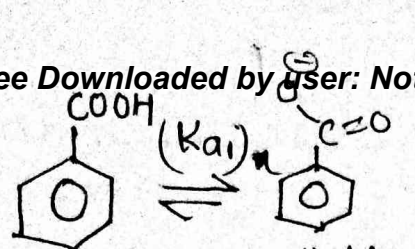
$(Ka_1)_1 > (Ka)_2$



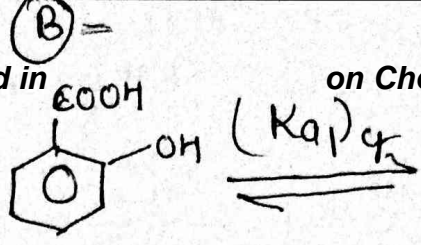
Fumaric acid (trans)

compare with $(Ka)_1$ & $(Ka)_x$ $(Ka)_1 > (Ka)_x$

$(Ka)_2$ & $(Ka)_y$ $(Ka)_2 < (Ka)_y$

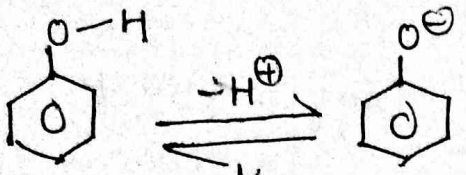


(A) = Benzoic acid



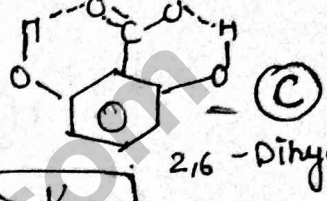
Salicylic Acid — stable

$(Ka_1)_y > (Ka_1)_n$



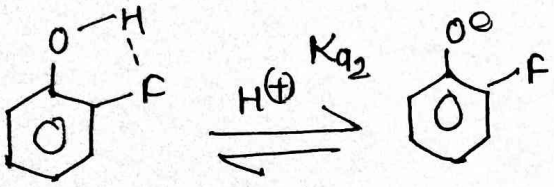
In which charge produce due to resonance

more stable conjugated base (In which -ve charge neutralised by resonance)



2,6 - Dihydroxy Benzoic acid

$Ka_1 > Ka_2$

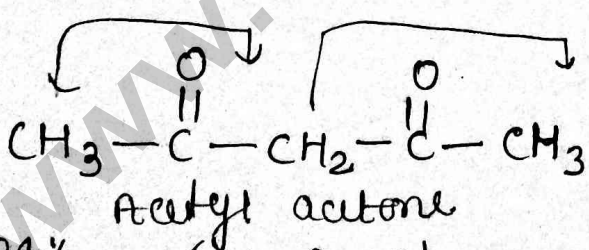


Acidic strength in (A), (B) & (C)

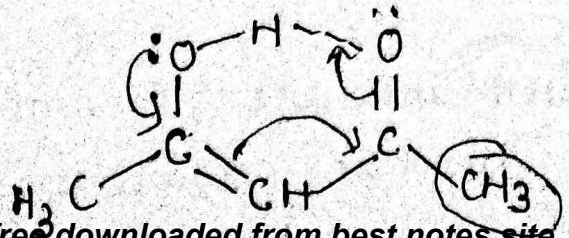
(C) > (B) > (A)

Acidic strength order

Acidic strength decrease Hydrogen bonding take place in conjugated acid and acidic strength increase when take place in conjugated base

* 

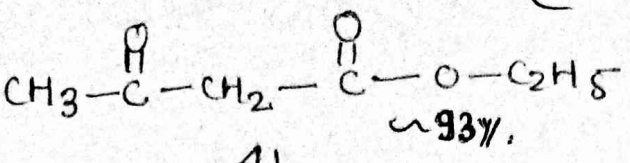
Acetyl acetone (Keto form) ~ 24%



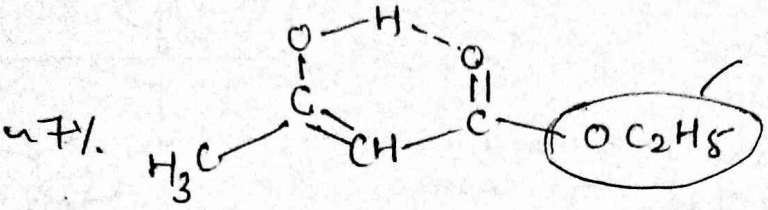
Enol

AAE or EAA

Aceto acetic ester — Ethyl aceto acetate (Less acidic than acetyl acetone)

* 

~93%.



~7%.

Bigger group less chance of Resonance

∴ Less stable enol as compare to acetyl acetone.

⇒ Bulkyness more than CH_3

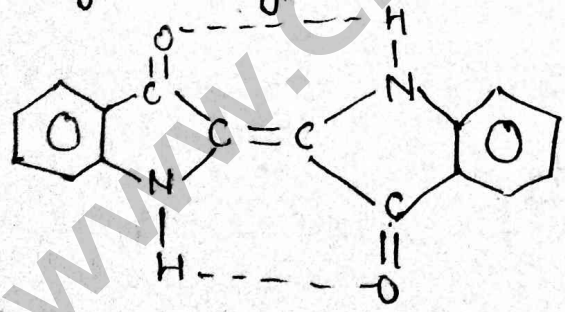
→ Less planarity

→ less resonance.

In polar solvent Keto more

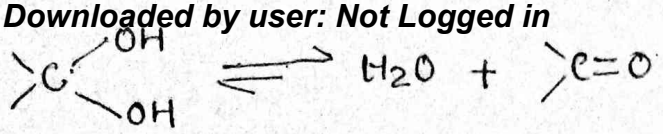
In Non-polar solven enol more

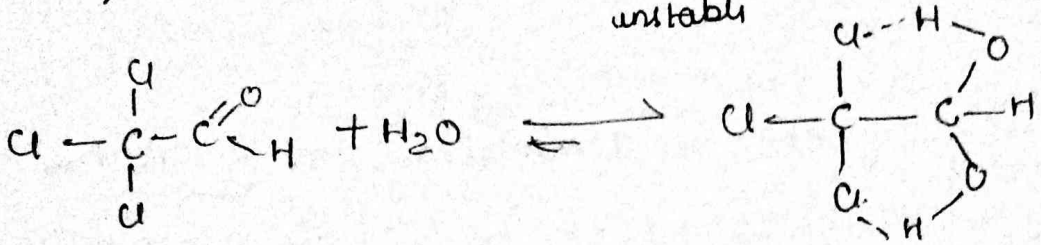
* Indigotin Dye

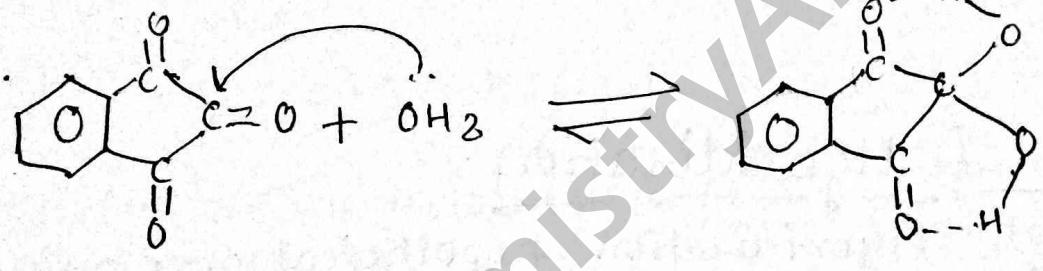


Trans (more stable)
due to H-bonding

When it is blue it is water insoluble, to make it soluble when reducing, it becomes colourless. As the O_2 present in the air it turns back with colourless indigotin.







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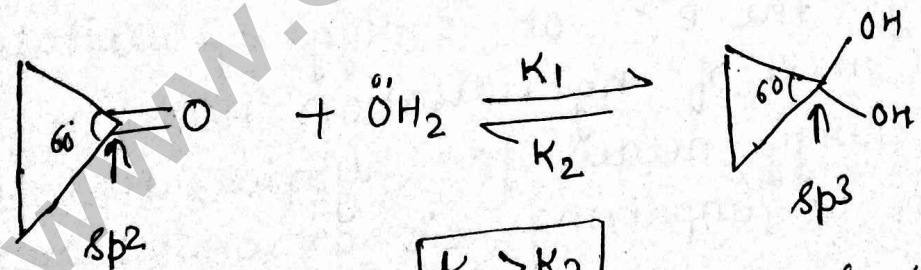


$K_1 > K_2$

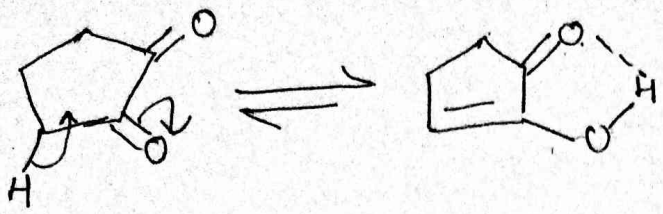
angle strain $= \frac{120 - 60}{2} = 30°$

angle strain $= \frac{109°20' - 60}{2}$

$= 24°44'$

angle strain ↓ er

∴ stability ↑ er



Enolisation of only one C=O due to stability gain by H-bonding thr

* H-bonding factor is dominating on Resonance
  Real. Hypothetical

Cost of Hybridisation.

Although Hybridisation hypothetical phenomenon However it can be mathmetically explain in terms of cost of Hybridisation. If the energy needed for hybridisation is more than energy of unpairing the e^{-s} or energy of orbitals then no need of hybridisation. However if the energy needed for hybridisation is less than unpairing e's or orbital energies then it may take place.

Energy of orbital of C

$E_s \Rightarrow 2s \Rightarrow -1870\ KJ\ mol^{-1}$

$E_p \Rightarrow 2p \Rightarrow -1020\ KJ\ mol^{-1}$

$$E_{(sp)} = \frac{-(1870 + 1020)}{2} = -1453\ KJ/mole$$

3756
2906
850

C = $2s^2 2p^2 \xrightarrow{sp} (sp)^1 (sp)^1 2p_y^1 2p_z^1$

Cost of Hybridisation = $\Delta H = H_P - H_R$

$= [2 \times E_{sp} + 2E_{2p}] - [2E_s + 2E_p]$

$= [2 \times E(-1453) + 2 \times (-1020)] - [2 \times (-1070) + 2 \times (-1020)]$

$= (-2906 - 2056) - [3756 - 2056]$

$= -2906 + 3756$

$= +850$ KJ/mol

⇒ Hybridisation is endothermic process hence it it is hypothetical.

CH_3, NH_3

{ Released Energy of bond formation > cost of Hybridisation ⇒ ∴ ΔH = -ive Hybridisation ✓

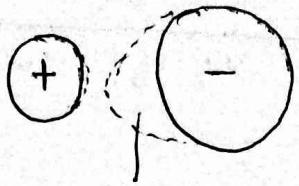
Released Energy of bond formation < Cost of Hybridisation ⇒ Hybrid" ✗

for drago drago

Polarisation:-

In ionic compound:-

let an ionic compound, usually anion is bigger than cation



distortion of ion

shape of anion by cation ⇒ Polarisation

→ Polarising Power (P.P) — attracting Power of cation

Polarisibility / P_z — e^- releasing power of anion

Type of Polarisation

↓ cation Polarisation

↓ anion Polarisation

P.P. ∝ ionic Potential (ϕ)

$$\phi = \frac{\text{charge}}{\text{radius}} \quad ; \quad \text{P.P.} \propto \frac{\text{charge of cation}}{\text{radius of cation}}$$

Factors Affecting Polarisation —

$Pol^n \propto$ P.P.

$Pol^n \propto P_z$

P.P — ① $\propto$ charge of cation (High)

② $\propto \frac{1}{\text{radius of cation (small)}}$

③ depend upon e^- - configuration

P.P — ④ charge of e^- configuration (High charge of cation & anion)

⑤ size of anion (large)

All 6 points are Fajan's Rule and they favours polarisation.

Impact of polarisation :—

As the polarisation increase covalent character in ionic compound increases.

Covalent character $\propto$ Polarisation

Li^+ → Na^+ → K^+ → Rb^+ → Cs^+ ↓

size of cation ↑es.

∴ Polarising Power ↓es

F^- → Cl^- → Br^- → I^- ↓

size of anion ↑es.

∴ P_Z (Polarisibility) ↓es.

X^- O^{--} N^{---} →

charge increase

∴ P_Z ↑es.

Na^+ Mg^{++} Al^{+++}

→

charge increases ↑es
size decreases (↓es)
∴ P.P. ↑es.

Isoelectronic

SiO_4^{4-} PO_4^{3-} SO_4^{--} ClO_4^-

→

4+24+4 = 32 | 5+24+3 = 32 | 6+24+2 = 32 | 7+24+1 = 32

charge ↓ ∴ P_Z ↓

$BeCl_2$ $HgCl_2$ — Isoelectronic.

NaCl KCl — Isoelectronic

Isoelectronics are those either have same total number electrons or same valence electron.

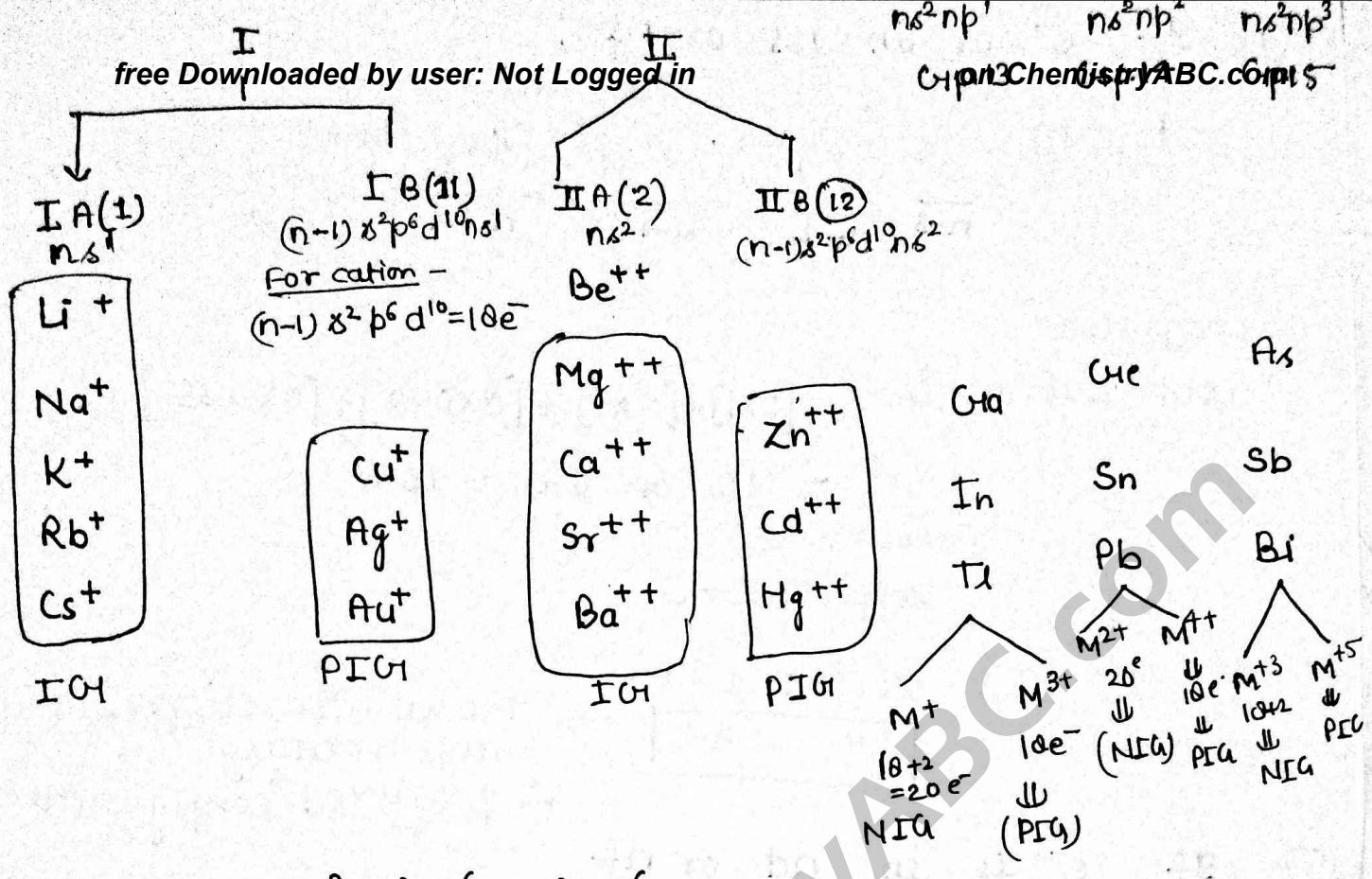
* Electronic configuration of cation

→ Nobel configuration or inert configuration (IC) ⇒ last shell 8e⁻ ⇒ complete octet

→ Pseudo Nobel conf^n (PIC) or (Pseudo inert conf^n) ⇒ last shell ⇒ 18 e⁻s

→ Non Nobel conf^n (NIC) or Non-inert conf^n ⇒ Valence e⁻s = 18+2 = 20

He
Ne
Ar
— only 3 inert gas (No compound is found at room temp^r)
Kr
Xe
Rn



$Cu = 29 = 1s^2 2s^2 2p^6\ 3s^2\ 3p^6$

P.P. $\propto$ Zeff. of cation

Slater's Rules for 'S' (screening constant)

① Write Aufbau configuration

② Arrange like

$1s\ (2s\ 2p)\ (3s\ 3p)\ (3d)\ (4s\ 4p)\ (4d)\ (4f)$

⊕)))) ← last shell

$Z_{eff} = Z - S$

S → Screening constant

③ Look – e^- – orbital

(ns np) (nd) (nf)

④ If e^- is in nd or np :

$$K = 19 = \underset{n-3}{1s^2}\ \underset{n-2}{(2s^2 2p^6)}\ \underset{n-1}{(3s^2 3p^6)}\ \underset{n}{(4s^1)}$$

~~configu~~

contribution in S = [2×1] + [8×1] + [8×0.85] + [0×0.35]

= 10 + 6.8 = 16.8

$$Z_{eff} = Z - S$$

$$Z_{eff} = 19 - 16.8$$

$$\boxed{Z_{eff} = 2.2}$$ → More attraction
less energy
∴ puffered configuration

⑤ If e^- is in nd or nf

$$K = 19 \Rightarrow \underset{n-3}{(1s^2)}\ \underset{n-2}{(2s\,2p)^8}\ \underset{n-1}{(3s^2 3p^6)}\ \underset{n}{(3d)^1}$$

S = [2×1] + [8×1] + [8×1] + [0×0.35]

= 18

$$Z_{eff} = Z - S$$

$Z_{eff} = 19 - 18 = 1$ ∵ lower value
∴ less attraction
∴ more energy.
∴ Non-preferred conf^n

Q. Find the Z_{eff} of 22nd e^- of Fe

$Fe = 26 = (1s^2)(2s^2 2p^6)(3s^2 3p^6)(4s^2)(3d^6)$

$(n-3)(n-2)(n-1)(n=1)\ n$

S = (2×1) [8×1] + [8×1] + [2×1] + [6×0.35]

= 2 + 8 + 8 + 2 + 6 × 0.35

* Jab tak Kaha ho to Chemistry ABC.com on Zeff Nikalte hain.

$= 19.75$

$Zeff = 26 - 19.75$

$Zeff = 6.25$

$Zeff = 6.25$

$11^{th}\ e^-$

Fe(26) $1s^2\ (2s^2\ 2p^6)\ 3s^2\ 3p^6\ 4s^2\ 3d^6$.

$\underbrace{(1s^2)}_{n-2}\ \underbrace{(2s^2\ 2p^6)}_{n-1}\ \underbrace{(3s^2\ 3p^6)}_{n}$

$S = [2 \times 1] + [8 \times 0.85] + [7 \times 0.35]$

$= 2 + 6.80 + 2.45$

$=$

$Zeff = 26 -$

* If the ~~last~~ ~~one~~ first shell is last shell

* $H = 1s^1$

$Zeff = Z$

* $He = 1s^2$

$S = [1 \times 0.3]$

$= 0.3$

$Zeff = 2 - 0.3$

$= 1.7$

$Li = \underbrace{1s^2}_{n-1}\ \underbrace{2s^1}_{n}$

$S = [2.0 \times 0.5) + 0 \times 0.35)$

$S = 1.7$

$Zeff = 3 -$

If Zeff to be determine at: <u>period</u> wise,
use all electron.

Beyond this e's

$$K = \underbrace{(1s^2)}_{n-3}\ \underbrace{(2s^2 2p^6)}_{n-2}\ \underbrace{(3s^2 3p^6)}_{n-1}\ \underbrace{(4s)^2}_{n}$$

$$S = [2\times1] + [8\times1] + [8\times0.85] + [2\times0.35]$$

$$S = 2 + 8 + 6.8 + 0.6$$

Li $\xrightarrow{0.65}$ Be (Zeff 1.95) B

Na (Zeff = 2.2) $\xrightarrow{0.65}$ Mg (2.85) Al

K (S = 16.8, Zeff = 2.2) $\longrightarrow$ Ca (2.85) $\xrightarrow{Sc-Zn\ d^{10}}$ Ga

Rb (Zeff = 2.2) $\longrightarrow$ Sr (2.85) $\xleftrightarrow{d^{10}}$ In

Cs (Zeff = 2.2) $\longrightarrow$ Ba 2.85 $\xleftrightarrow{d^{10}+f^{14}}$ Tl

Ga(31) $1s^2, 2s^2 2p^6 3s^2 4s^2 3p^6 3d^{10} 4p^1$

$$\underbrace{(s^2)}_{n-4}\ \underbrace{(2s\,2p)^8}_{n-3}\ \underbrace{(3s\,3p)^8}_{n-2}\ \underbrace{(3d)^{10}}_{n-1}\ \underbrace{(4s)^2(4p^1)}_{n}$$

$$(2\times1) + (1\times8) + [1\times8] + (8\times0.85) + (2\times0.35)$$

$$= 2 + 8 + 8 + 10 + 1.7 + 0.$$

$Z_{eff} = 30$

$Cu = (1s^2)\ (2s^2 2p^6)\ (3s^2 3p^6)\ (3d^{10})\ (4s^1 4p^0)$

$n-3 \quad n-1 \quad n-1 \quad n$

$S = [10 \times 1] + [10 \times 0.85] + 0.35 \times 1$

$S = 26$

$Z_{eff} = 31 - 26$

$= 5$

$Z_{eff} \Rightarrow M_{(g)}^{2+} > M$

$Z \Rightarrow M^{n+} = M$

Hw

✓ * Na^+, Cu^+, Cr^{a+}

$Be\ (4) = (1s^2)(2s^2)$

$n-1 \quad n$

$= (2 \times 0.85)(1 \times 0.35)$

$= 1.70 + 0.35$

$= 2.05$

$Z_{eff} = 4 - 2.05$

$Z_{eff} = 1.95$

Note

*

$$\text{Size} \propto \frac{1}{Z_{eff}}$$

Period → ∵ Z_{eff} ↑ ∴ size ↓

Group

Z_{eff} not valid in Group.

NCr PICr

Zeff ↑es.

if size similar

* gp. of same orbital no. of lobes increase that's why

ns^2np^6

(NCr) ⊖Proton, sp ⟵ 8e⁻s. ⟶ 8e

No. d electrons ∴ Normal attraction

$(n-1)s^2p^6d^{10}$

(PICr) ⊖+10e ⟵ spd 8e⁻ ⟶

$(n-1)s^2p^6d^{10}ns^2$

(NICr) ⊖e⁺ 10e ⟵ 8e. ⟶

d^{10} ⇒ diffused ∴ no. e⁻–e⁻ repulsion power. But due. d^{10} ⇒ protons will be more in nucleus. ∴ More Zeff

Note gf difference in sizes more than 'bigger atom have lower Zeff whatever conf^n i.e. NCr, PICr, NICr should be considered for similar sized atom.

*

Na^+ Cu^+

2,8 2,8,18

NCr PICr

Zeff ↑es

∴ P.P ↑es

∴ Polarisation ↑es

Ca^{++} Zn^{++}

2,8,8 2,8,18

NCr PICr

Zeff ↑es

∴ P.P ↑es

∴ Pol^n ↑es

* Application of polarisation

r Thermal stability :–

Main two factor

→ ① Pol^n ⇒

→ ② Lattice energy

① Polarisation ⇒ When anion is polyatomic or Bulky or bigger.

SO_4^{--}, SO_4^{-}, CO_3^{--}, HCO_3^{-}, $S_2O_8^{--}$, $Cr_2O_7^{--}$

O_3^{-} → (ozonide), O_2^{-} O_2^{--}, MnO_4^{-}

NO_3^{-}, NO_2^{-} etc

② Lattice energy :- When anion is either monoatomic

H^-, X^-, N^{---}, O^{--}

or small sized ⇒ OH^- (some times)

* **Thermal stability ∝ Lattice energy**

T.S ∝ $\frac{1}{\text{Polarisation}}$

(M_2CO_3)

① Li_2CO_3
Na_2CO_3
K_2CO_3
Rb_2CO_3
CS_2CO_3

size of cation ↑
∴ P.P. ↓
∴ Polarisation ↓
∴ T.S. ↑

Anion ⇒ Polyatomic
∴ factor = Polarisation.

anion ⇒ Polyatomic
⇑ factor ⇒ Polarisation

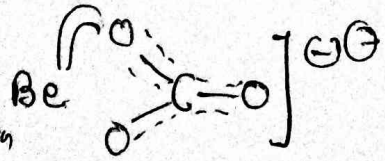
$MnCO_3$
$BeCO_3$
$MgCO_3$
$CaCO_3$
$SrCO_3$
$BaCO_3$

∴ size of cation ↑
∴ P.P. ↓
∴ Polarisation ↓
∴ T.S. ↑

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$MCO_3 \xrightarrow{\Delta} MO + CO_2$

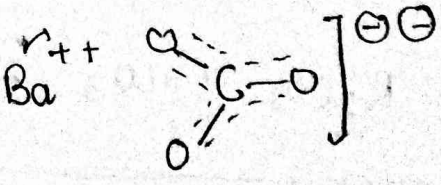
More P.P. more Pol^n



Decomposition temp^r T_1 → low

$BeO + CO_2$

less P.P. less Pol^n



T_2 → High $T_1 < T_2$

$BaO + CO_2$

T.S ∝ Decomposition temp^r

$MO \xrightarrow{\Delta} M + \frac{1}{2}O_2$ *

BeO ↓ size of cation ↑ ∴ Lattice energy ↓ ∴ T·S ↓

BeO

Anion ⇒ mono atom

∴ factor ⇒ L·E

$CaCO_3 \xrightarrow{\Delta}$ ↓

$CaO + CO_2\uparrow$ (gas)

*

I	II
M_2CO_3	MCO_3
e.g. K_2CO_3	$CaCO_3$

→

∴ charge on cation ↑es

& size of cation ↓es.

∴ Polarisation ↑es

∴ T·S ↓es.

* Na_2CO_3 thermally most stable that's why it not use for carboxylic acid test it doesnot decompose while $NaHCO_3$ easily decompose.

$CaCO_3$ $ZnCO_3$

Ca^{++} Zn^{++}

→

more T·S. PICH

More Zeff

∴ More P.P.

∴ More Pol^n

∴ lower T·S

K_2CO_3 $CaCO_3$ $ZnCO_3$ (PaICH)

→

Thermal stability decreases

HCO_3^- ⇒ Polyatomic ∴ factor Polarisation

∴ T.S & Poln

$LiHCO_3$	$Be(HCO_3)_2$	
$NaHCO_3$	$Mg(HCO_3)_2$	
$KHCO_3$	$Ca(HCO_3)_2$	
$RbHCO_3$	$Sr(HCO_3)_2$	
$CsHCO_3$	$Ba(HCO_3)_2$	exist only in soln not in solid state

Exist in solid state

∴ size of cation ↑

∴ Poln ↓ es

∴ T.S ↑ es

size of cation ↓ es.

Charge of cation ↑ es.

∴ Poln ↑ es

∴ T.S ↑ es.

$$NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O$$

$$NaOH \uparrow H_2O + CO_2$$

* How many — Metal bicarbonate exist in solid state.
⇒ 4 ($NaHCO_3$, $KHCO_3$, $RbHCO_3$, $CsHCO_3$)

Another solid is NH_4HCO_3 (Non-metal)

* carbonates are more stable than bicarbonates.

MNO_3	$M(NO_3)_2$
$LiNO_3$	$Be(NO_3)_2$
↓	|
$CsNO_3$	$Ba(NO_3)_2$

size of cation ↑ es

∴ Poln ↓

∴ T.S. ↑ es.

$$MNO_3 \xrightarrow[\text{High ten}]{\Delta} MNO_2 + O_2$$

(Nitrate) — Nitrite

$$NaNO_3 \xrightarrow{400^\circ C} NaNO_2 + O_2$$

$$\xrightarrow{800^\circ C} Na_2O + NO_2 + O_2$$

Anion ⇒ Monoatomic ion of above

T.S ∝ L.E

Li_3N
Na_3N
K_3N
Rb_3N
Cs_3N

∴ Size of cation ↑es

∴ L.E ↓

∴ T.S ↓es

Na_3N Mg_3N_2

charge ↑s , size ↓

∴ L.E ↑s

∴ T.S ↑es

Lattice energy $\propto \frac{q_1 q_2}{r} \propto \frac{\text{charge}}{\text{size}}$

$M^I + N_2 \longrightarrow M_3N$, −(Lattice energy) (exo)

(N≡N)

↓

BDE = very high needed endo

① L.E (exo) > BDE (endo) ⇒ ΔH = enthalpy change −ve (spontaneous)

② < ⇒ +ive (non-spontaneous)

$Li + N_2 \longrightarrow Li_3N$ → L.E > BDE

$Na + N_2 \longrightarrow Na_3N$

$K + N_2 \longrightarrow K_3N$

$Rb + N_2 \longrightarrow Rb_3N$

$Cs + N_2 \longrightarrow Cs_3N$

L.E ↓

L.E < BDE

∴ only Li can react with N_2 directly not rest metal of I^s gp.

* But 2nd element have high L.E
∴ they react with N_2 directly.

* However Be_3N_2 show very high polarisation effect therefore it is unstable

NaF
NaCl
NaBr
NaI
↓ size of anion ↑
∴ Pol^n ↑
∴ C.V.C ↑

LiCl
NaCl
KCl
RbCl
CsCl
↓ size of cation ↑
∴ Pol^n ↓
∴ C.V.C ↓

Zeff ↓ Pol^n ↓

$TlCl$	$TlCl_3$
↓	↓
Tl^+	Tl^{3+}
↓	↓
$2e^-$	$18e^-$
(NIG)	(PIG)

Note :- Hg^{++} ⇒ Having d^{10}, f^{14}
Pseudo Nobel conf^n (PIG)
∴ Zeff = very high
∴ Pol^n = very high
∴ Covalent character (CV) = very high

Hence almost more than 95% compounds of Hg are covalent.

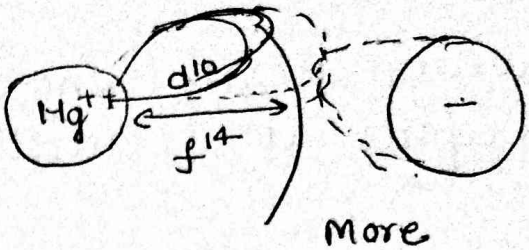
$Hg_2(NO_3)_2$, $Hg(NO_3)_2$ → only ionic compounds of Hg

Cation Polarising Power

d-Block

Zn
Cd
Hg ↓

size ↑ₑ
d-orbital exposed
∴ Both cation & anionic Polⁿ ↑, more Proton
Z_{eff} = more ∴ more $P_{o.P.}$ = High.



More anion Polⁿ.

$ZnCl_2$
$CdCl_2$
$HgCl_2$ ↓

size of cation ↑ₑ
size of 'd' ↑.
exposed of d ↑ₑ
∴ Both cationic & anionic Polⁿ ↑ₑ

∴ Overall Polⁿ ↑.