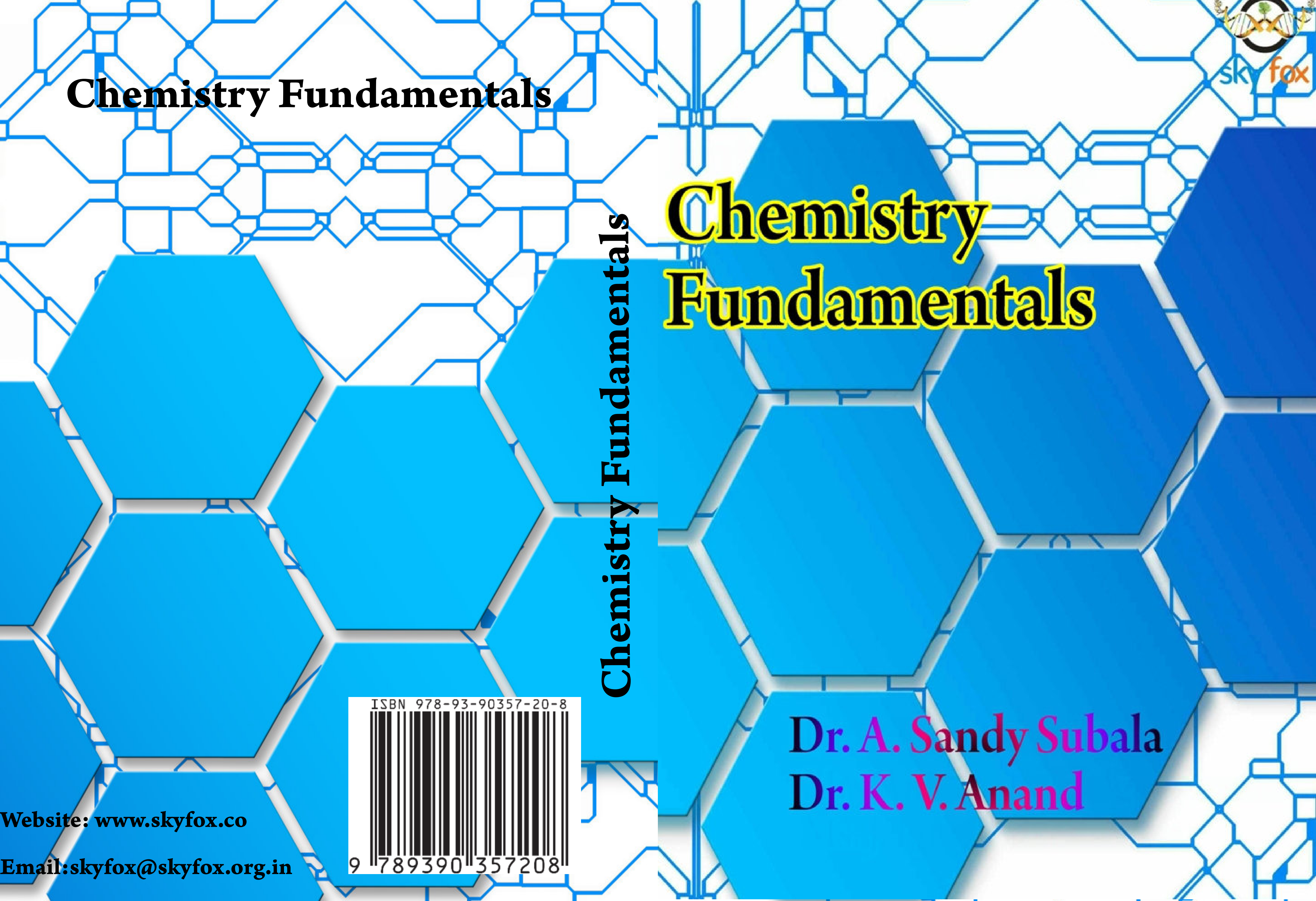

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From the desk of
Dr. T. X. A. ANANTH, BBA, MSW, MBA, MPhil, PhD,
President – University Council
Dear Learner,

Welcome to DMI – St. Eugene University!

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I am happy at the efforts taken by the University in publishing this book not only in printed format, but also in PDF format in the Internet.
With warm regards

Dr. T. X. A. ANANTH
President – University Council

Significant figures - SI units - Dimensions - Writing number in scientific notation - Conversion of scientific notation to decimal notation - Factor label method - Calculations using densities and specific gravities - Calculation of formula weight - Understanding Avogadro’s number - Mole concept - mole fraction of the solvent and solute - Conversion of grams into moles and moles into grams - Calculation of empirical formula from quantitative analysis and percentage composition - Calculation of molecular formula from empirical formula - Stoichiometric equations - Balancing chemical equation in its molecular form - Oxidation reduction - Oxidation number - Balancing Redox equation using oxidation number - Calculations based on equations. - Mass/Mass relationship - Methods of expressing concentration of solution - Calculations on principle of volumetric analysis - Determination of equivalent mass of an element - Determination of equivalent mass by oxide, chloride and hydrogen displacement method - Calculation of equivalent mass of an element and compounds - Determination of molar mass of a volatile solute Laws of Chemical combinations.

Brief introduction of history of atoms - Chronology of atomic structure development - Dalton’s Atomic Theory - Thomson’s Model of Atom - Rutherford’s Scattering Experiment - Rutherford’s Nuclear Model of Atom - Defect of Rutherford’s Model - Bohr's Model of atom - Postulates of Bohr’s Model of Atom - Bohr’s Model of Hydrogen Atom - Hydrogen Energy levels - Hydrogen Spectrum - Rydberg’s formula – Limitations of Bohr’s Model - Sommerfeld’s Extension of Bohr’s Model - Overview of progress in Atomic Models - Dual properties of electrons - difference between a wave and a particle - Experiments to prove particle and wave property of Electrons - Verification of Wave character - Davisson and Germer’s Experiment - Thomson’s Experiment - Verification of particle character - De Broglie relation -Significance of De Broglie waves - Heisenberg’s Uncertainty

Valence Shell Electron Pair Repulsion (VSEPR) model - Effect of bonding and nonbonding electrons on the structure of molecules - Valance Bond theory - Orbital overlap concept - Types of bonds Strength of sigma and pi bonds – overlapping of atomic orbitals - Theory of Hybridisation - Promotion (Excitation) of electrons - Hybridisation (mixing of orbitals) - Concept of Resonance - Salient features of hybridisation - Types of hybridization - Geometry of molecules - Molecular Orbital (MO) theory - LCAO method - Criteria for orbital overlap - Symmetry - Energy - Combination of atomic orbitals and their schematic illustration -Conditions for the Combination of Atomic Orbitals - Types of Molecular Orbitals - Qualitative MO energy level diagram of homo and hetero diatomic molecules – H_2, He, Li, Be_2, CO, NO and HCl - Bond order - Stability of molecules - Co-ordinate-covalent bonding or Dative bonding - Intermolecular forces - Hydrogen bonding - Strength of H-bonding - Types of H-bonds - Importance of H-bonding.

(Classification and Isomerism)Catenation - Classification of organic compounds - Functional groups - Nomenclature - Isomerism – Reagents and Reaction intermediates -Types of organic reactions - Fission of bonds - Carbonium ion Carbanion - Free radicals.

Geometrical isomerism - Conformations of cyclic compounds – Optical isomerism - Optical activity - Chirality - Compounds containing chiral centers - D-L and R-S notation - Isomerism in benzene

Chapter I - Chemical Calculations

Significant figures - SI units - Dimensions - Writing number in scientific notation - Conversion of scientific notation to decimal notation - Factor label method - Calculations using densities and specific gravities - Calculation of formula weight - Understanding Avogadro's number - Mole concept - mole fraction of the solvent and solute - Conversion of grams into moles and moles into grams - Calculation of empirical formula from quantitative analysis and percentage composition - Calculation of molecular formula from empirical formula - Laws of chemical combination and Dalton's atomic theory - Laws of multiple proportion and law of reciprocal proportion - Postulates of Dalton's atomic theory and limitations - Stoichiometric equations - Balancing chemical equation in its molecular form - Oxidation reduction - Oxidation number - Balancing Redox equation using oxidation number - Calculations based on equations. - Mass/Mass relationship - Methods of expressing concentration of solution - Calculations on principle of volumetric analysis - Determination of equivalent mass of an element - Determination of equivalent mass by oxide, chloride and hydrogen displacement method - Calculation of equivalent mass of an element and compounds - Determination of molar mass of a volatile solute using Avogadro's hypothesis.

1.01 Significant figures

Many a times in the study of chemistry, one has to deal with experimental data as well as theoretical calculations. There are meaningful ways to handle the numbers conveniently and present the data realistically with certainty to the extent possible. These ideas are discussed below in detail.

Every experimental measurement has some amount of uncertainty associated with it. However, one would always like the results to be precise and accurate. Precision and accuracy are often referred to while we talk about the measurement.

Precision refers to the closeness ofvariousmeasurements for the same quantity. However, accuracy is the agreement of a particular valueto the true value of the result. For example, ifthe true value for a result is 2.00 g and astudent ‘A’ takes two measurements andreports the results as 1.95 g and 1.93 g. Thesevalues are precise as they are close to eachother but are not accurate. Another studentrepeats the experiment and obtains 1.94 g and2.05 g as the results for two measurements.These observations are neither precise noraccurate. Third student repeat the measurements and reports 2.01g and 1.99gas the result for both measurement. These values are both precise andaccurate. This can be more clearly understoodfrom the data given in Table.

Measurements/g			
	1	2	Average (g)
Student A	1.95	1.93	1.940
Student B	1.94	2.05	1.995
Student C	2.01	1.99	2.000

The uncertainty in the experimental or the calculated values is indicated by mentioning the number of significant figures. Significant figuresare meaningful digits which are known with certainty. The uncertainty is indicated by writing the certain digits and the last uncertaindigit. Thus, if we write a result as 11.2 mL, wesay the 11 is certain and 2 is uncertain andthe uncertainty would be +1 in the last digit.Unless otherwise stated, an uncertainty of +1in the last digit is always understood.There are certain rules for determining thenumber of significant figures. These are statedbelow:

(1) All non-zero digits are significant. Forexample in 285 cm, there are threesignificant figures and in 0.25 mL, thereare two significant figures.

(2) Zero’s preceede to first non-zero digit arenot significant. Such zero indicates theposition of decimal point.Thus, 0.03 has one significant figure and0.0052 has two significant figures.

(3) Zeros between two non-zero digits are significant. Thus, 2.005 has four significantfigures.

(4) Zeros at the end or right of a number aresignificant provided they are on the rightside of the decimal point. For example,0.200 g has three significant figures.But, if otherwise, the terminal zeros are notsignificant if there is no decimal point. Forexample, 100 has only one significantfigure, but 100. has three significantfigures and 100.0 has four significantfigures. Such numbers are betterrepresented in scientific notation. We canexpress the number 100 as 1×10^2 for onesignificant figure, 1.0×10^2 for twosignificant figures and 1.00×10^2 for threesignificant figures.

(5) Counting numbers of objects, for example,2 balls or 20 eggs, have infinite significantfigures as these are exact numbers and canbe represented by writing infinite numberof zeros after placing a decimal i.e.,2 = 2.000000 or 20 = 20.000000

In numbers written in scientific notation,all digits are significant e.g., 4.01×10^2 has threesignificant figures, and 8.256×10^{-3} has foursignificant figures.

Addition and Subtraction of SignificantFigures

The result cannot have more digits to the rightof the decimal point than either of the originalnumbers.

$$12.11 + 18.0 + 1.012 = 31.122$$

Here, 18.0 have only one digit after the decimalpoint and the result should be reported onlyup to one digit after the decimal point whichis 31.1.

Multiplication and Division of SignificantFigures

In these operations, the result must be reportedwith no more significant figures as are there inthe measurement with the few significantfigures.

$$2.5\times1.25 = 3.125$$

Since 2.5 has two significant figures, theresult should not have more than twosignificant figures, thus, it is 3.1.While limiting the result to the requirednumber of significant figures as done in theabove mathematical operation, one has to keepin mind the following points for rounding offthe numbers.

1. If the rightmost digit to be removed is morethan 5, the preceding number is increased by one. For example,1.386, if we have to remove 6, we have to round itto 1.39.
2. If the rightmost digit to be removed is lessthan 5, the preceding number is not changed.For example, 4.334 if 4 is to be removed,then the result is rounded upto 4.33.
3. If the rightmost digit to be removed is 5,then the preceding number is not changedif it is an even number but it is increasedby one if it is an odd number. For example,if 6.35 is to be rounded by removing 5, wehave to increase 3 to 4 giving 6.4 as theresult. However, if 6.25 is to be roundedoff it is rounded off to 6.2.

1.02 SI units

The International System of Units (French *Le Systeme International d'Unitès* abbreviated as SI Units*)* was established by the 11th General Conference on Weights and Measures (CGPM from *Conference Generale des Poids et Measures*). The CGPM is an inter-governmental treaty organization created bya diplomatic treaty known as Metre Conventionwhich was signed in Paris in 1875.The SI system has seven *base units* andthey are listed in the table below. These units pertainto the seven fundamental scientific quantities.

Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	Kilogram	kg
Time	t	second	s
Electric Current	I	ampere	A

Thermodynamic temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I_v	candela	cd

The other physical quantities such as speed, volume, density etc. can be derived from these quantities. The SI system allows the use of prefixes toindicate the multiples or submultiples of a unit.These prefixes are listed in Table. Let us now quickly go through some of thequantities which you will be often using in thisbook.

Multiple	Prefix	Symbol
10^{-24}	yocto	y
10^{-21}	zepto	z
10^{-18}	atto	a
10^{-15}	femto	f
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}	hector	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P
10^{18}	exa	E
10^{21}	zeta	Z
^{24}	yotta	Y

1.03 Dimensional Analysis (Factor label method)

Often while calculating, there is a need to convert units from one system to other. The method used to accomplish this is called factor label method or unit factor method or dimensional analysis. This is illustrated below.

Example

A piece of metal is 3 inch (represented by in) long. What is its length in cm?

We know that 1 in = 2.54 cm. From this equivalence, we can write,

$$\frac{1in}{2.54cm} = 1 = \frac{2.54cm}{1in}$$

Thus 1 inch / 2.54cm equals 1 and 2.54cm / 1 inch also equals 1. Both of these are called unit factors. If some numbers is multiplied by these unit factors (i.e., 1), it will not be affected otherwise.Say, the 3 in given above is multiplied by the unit factor. So,

$$3 \text{ in} = 3 \text{ in} \times \frac{2.54cm}{1in} = 3 \times 2.54 \text{ cm} = 7.62 \text{ cm}$$

Now the unit factor by which multiplication is to be done is that unit factor (2.54cm / 1 inch in the above case) which gives the desired units i.e., the numerator should have that part which is required in the desired result.

It should also be noted in the above example that units can be handled just like other numerical part. It can be cancelled, divided, multiplied, squared etc. Let us study one more example for it.

Solved Examples

1. A jug contains 2L of milk. Calculate the volume of the milk in m^3.

Solution

Since 1L = 1000 cm^3,

$$\frac{1\ m}{100\ cm} = 1 = \frac{100\ cm}{1}$$

To get m^3 from the above unit factors, the first unit factor is taken and it is cubed.

$$\left(\frac{1\,m}{100\,cm}\right)^3 = \frac{1m^3}{10^6 cm^3} = (1)^3 = 1$$

Now 2L = 2 x 1000 cm^3, the above is multiplied by the unit factor,

$$2 \times 1000\ cm^3 \times \frac{1m^3}{10^6 cm^3} = \frac{2m^3}{10^3} = 2 \times 10^{-3} m^3$$

2. How many seconds are there in 2 days?

Solution

1 day = 24 hours

$$\frac{1\ day}{24\ h} = 1 = \frac{24\ h}{1\ day}$$

To calculate the seconds, we need to calculate how many minutes are there in a day.

$$\frac{1\ hr}{60\ min} = 1 = \frac{60\ min}{1\ hr}$$

So converting 2 days into seconds, we need to multiply the unit factors as follows:

$$2\ days = \frac{24\ hr}{1\ day} \times \frac{60\ min}{1\ hr} \times \frac{60\ sec}{1\ min}$$

$$2\ days = 24 \times 60 \times 60\ s$$

$$2\ days = 172800\ s$$

1.04 Writing number in scientific notation

As chemistry is the study of atoms and molecules which have extremely low massesand are present in extremely large numbers,a chemist has to deal with numbers as largeas 602, 200,000,000,000,000,000,000 for themolecules of 2 g of hydrogen gas or as smallas 0.00000000000000000000000166 gmass of a H atom. Similarly other constantssuch as Planck’s constant, speed of light,charges on particles etc., involve numbers ofthe above magnitude.

It may look funny for a moment to write orcount numbers involving so many zeros but itoffers a real challenge to do simplemathematical operations of addition,subtraction, multiplication or division withsuch numbers. You can write any twonumbers of the above type and try any one ofthe operations you like to accept the challengeand then you will really appreciate the difficultyin handling such numbers.This problem is solved by using scientificnotation for such numbers, *i.e.,* exponentialnotation in which any number can berepresented in the form $N \times 10^n$ where n is anexponent having positive or negative valuesand N is a number (called digit term) whichvaries between 1.000... and 9.999....Thus, we can write 232.508 as2.32508×10^2 in scientific notation. Note thatwhile writing it, the decimal had to be movedto the *left* by two places and same is theexponent (2) of 10 in the scientific notation.Similarly, 0.00016 can be written as1.6×10^{-4}. Here the decimal has to be movedfour places to the *right* and (– 4) is the exponentin the scientific notation.Now, for performing mathematicaloperations on numbers expressed in scientific notations, the following points are to be keptin mind.

Multiplication and Division

Multiplication

These two operations follow the same ruleswhich are there for exponential numbers, i.e.

$$\begin{aligned}(5.6 \text{ x } 10^5) \text{ x } (6.9 \text{ x } 10^3) &= (5.6 \text{ x } 6.9)\ (10^{5+3}) \\ &= (5.6 \text{ x } 6.9) \text{ x } 10^{13} \\ &= 38.64 \text{ x } 10^{13} \\ &= 3.864 \text{ x } 10^{14}\end{aligned}$$

Similarly,

$$\begin{aligned}(9.8 \text{ x } 10^{-2}) \text{ x } (2.5 \text{ x } 10^{-6}) &= (9.8 \text{ x } 2.5)\ (10^{-2\,+[-6]}) \\ &= (9.8 \text{ x } 2.5) \text{ x } 10^{-2\,-6} \\ &= 24.50 \text{ x } 10^{-8}\end{aligned}$$

$= 2.450 \times 10^{-7}$

Division

$$\frac{2.7 \times 10^{-3}}{5.5 \times 10^{4}} = (2.7 \div 5.5)(10^{-3-4}) = 0.4909 \times 10^{-7}$$
$$= 4.909 \times 10^{-8}$$

Addition and subtraction

For these two operations, first the numbers are written in such a way that they have same exponent. After that, the coefficient are added or subtracted as the case may be. Thus, for adding,

6.65×10^4 and 8.95×10^3, exponent is made same for both the numbers as $6.65 \times 10^4 + 0.895 \times 10^4$.

Then, these numbers can be added as follows,

$(6.65 + 0.895) \times 10^4 = 7.545 \times 10^4$.

Similarly, the subtraction of two numbers can be done as shown below:

$2.5 \times 10^{-2} - 4.8 \times 10^{-3} = (2.5 \times 10^{-2}) - (0.48 \times 10^{-2})$
$= (2.5 - 0.48) \times 10^{-2} = 2.02 \times 10^{-2}$

1.05Calculation of formula weight

Formula Weight (FW) or Formula Mass

The formula weight of a substance is the sum of the atomicweights ofall atoms in a formula unit of the compound, whether molecular or not.Sodium chloride, NaCl, has aformula weight of 58.44 u (22.99 ufrom Na + 35.45 u from Cl). NaCl is ionic, so strictly speaking theexpression "molecular weight of NaCl" has no meaning. On the other hand,the molecular weight and the formula weight calculated from the molecular formula of a substance are identical.

Solved Problem

Calculate the formula weight of each of the following to three significant figures, using a table of atomic weight (AW): (a) chloroform $CHCl_3$ (b) Iron (III) sulfate $Fe_2(SO_4)_3$.

Solution

a. Chloroform ($CHCl_3$)
1 x AW of C = 12.0 u
1 x AW of H = 1.0 u
3 x AW of Cl = 3 x 35.45 = 106.4 u
Formula weight of $CHCl_3$ = 119.4 u
The answer rounded to three significant figures is 119 u.

b. Iron (III)Sulfate
2 x Atomic weight of Fe = 2 x 55.8 = 111.6 u
3 x Atomic weight of S = 3 x 32.1 = 96.3 u
3 x 4 Atomic weight of O = 12x16 = 192.0 u

Formula weight of $Fe_2(SO_4)_3$ = 399.9 u
The answer rounded to three significant figures is 4.00 x 10^2u.

1.06Understanding Avogadro's number

The number of atoms in a 12-g sample of carbon - 12 is calledAvogadro's number (to which we give the symbol N_A).
Recent measurements of this number give the value 6.0221367 x 10^{23},which is 6.023 x 10^{23}.A mole of a substance contains Avogadro's number of molecules. Adozen eggs equals 12 eggs, a gross of pencils equals 144 pencils and a moleof ethanol equals 6.023 x 10^{23} ethanol molecules.

Significance

The molecular mass of SO_2 is 64 g mol^{-1}. 64 g of SO_2 contains6.023 x 10^{23} molecules of SO_2. 2.24 x $10^{-2}m^3$ of SO_2 at S.T.P. contains 6.023 x

10^{23} molecules of SO_2.Similarly the molecular mass of CO_2 is 44 g / mol. 44g of CO_2 contains6.023 x 10^{23} molecules of CO_2. 2.24 x $10^{-2}m^3$ of CO_2 at S.T.P contains6.023 x 10^{23} molecules of CO_2.

1.07 Mole concept

While carrying out reaction we are often interested in knowing the number of atoms and molecules. Sometimes, we have to take the atoms or molecules of different reactants in a definite ratio.

Eg. Consider the following reaction

$$2H_2 + O_2 \rightarrow 2H_2O$$

In this reaction one molecule of oxygen reacts with two molecules ofhydrogen. So it would be desirable to take the molecules of H_2 and oxygenin the ratio 2:1, so that the reactants are completely consumed during thereaction. But atoms and molecules are so small in size that is not possible tocount them individually.

In order to overcome these difficulties, the concept of mole wasintroduced. According to this concept number of particles of the substanceis related to the mass of the substance.

Definition

The mole may be defined as the amount of the substance that containsas many specified elementary particles as the number of atoms in 12g ofcarbon - 12 isotope.(i.e.,) one mole of an atom consists of Avogadro number of particles.

One mole = 6.023 x 10^{23} particles

One mole of oxygen molecule = 6.023 x $10^{23}O_2$molecules

One mole of oxygen atom = 6.023 x 10^{23} oxygen atoms

One mole of ethanol = 6.02x 10^{23}ethanol molecules

In using the term mole for ionic substances, we mean the number offormula units of the substance. For example, a mole of sodium carbonate,Na_2CO_3 is a quantity containing 6.023 x 10^{23}, Na_2CO_3 units.

But eachformula unit of Na_2CO_3 contains 2 x 6.023 x 10^{23} Na^+ ions and one CO_3^{2-}ions and 1 x 6.023 x $10^{23}$$CO_3^{2-}$ ions.

When using the term mole, it is important to specify the formula of theunit to avoid any misunderstanding.

Eg. A mole of oxygen atom (with the formula O) contains 6.023 x 10^{23}oxygen atoms. A mole of oxygen molecule (formula O_2) contains6.023 x 10^{23} O_2 molecules (i.e.) 2 x 6.023 x 10^{23} oxygen.

Molar mass

The molar mass of a substance is the mass of one mole of thesubstance. The mass and moles can be related by means of the formula.

Molar mass = $\frac{Mass}{Mole}$

Eg. Carbon has a molar mass of exactly 12g/mol.

Solved Problems

1. What is the mass in grams of a chlorine atom, Cl?

2. What is the mass in grams of a hydrogen chloride, HCl?

Solution

1. The atomic weight of Cl is 35.5 u, so the molar mass of Cl is 35.5 g/mol. Dividing 35.5 g (per mole) by 6.023 x 10^{23} gives the mass of one atom.

$$\text{Mass of Cl atom} = \frac{35.5\ g}{6.023\ \times 10^{23}} = 5.90\ \times\ 10^{-23}g$$

2. The molecular weight of HCl equal to the atomic weight of H, plus the atomic weight of Cl, (ie) (1.01 + 35.5) u = 36.5 u. Therefore, 1 mol of HCl contains 36.5 g HCl.

$$\text{Mass of a HCl molecules} = \frac{36.5\ \text{g}}{6.023\ \times 10^{23}}$$
$$= 6.06\ \times\ 10^{-23}\text{g}$$

1.08 Mole calculations

i. How much does a given number of moles of a substance weight?

ii. How many moles of a given formula unit does a given mass ofsubstance contains.

Both of them can be known by using dimensional analysis.

To illustrate, consider the conversion of grams of ethanol, C_2H_5OH, tomoles of ethanol. The molar mass of ethanol is 46.1 g/mol. So, we write1 mol C_2H_5OH = 46.1 g of C_2H_5OH. Thus, the factor converting grams of ethanol to moles of ethanol is1mol C_2H_5OH/46.1g C_2H_5OH. To covert moles of ethanol to grams of ethanol, we simply convert the conversion factor (46.1 g C_2H_5OH/1 molC_2H_5OH).

Again, suppose if we are going to prepare acetic acid from 10.0g ofethanol, C_2H_5OH. How many moles of C_2H_5OH is this? we convert 10.0g. $C_2H_5OH$to moles C_2H_5OH by multiplying by the appropriate conversionfactor.

$$10.0 \text{ g } \mathrm{C_2H_5OH} \times \frac{1 \text{ mol } \mathrm{C_2H_5OH}}{46.1 \text{ g } \mathrm{C_2H_5OH}} = 0.217 \text{ mol } \mathrm{C_2H_5OH}$$

1.09 Conversion of grams into moles and moles into grams

Solved Problems

1. ZnI_2, can be prepared by the direct combination of elements. How a chemist determines from the amounts of elements that 0.0654 mol ZnI_2 can be formed?

Solution

The molar mass of ZnI_2 is 319 g/mol. (The formula weight is 319 u,which is obtained by summing the atomic weight in the formula) Thus,

$$0.0654\, mol\, ZnI_2 \times \frac{319\, g\, ZnI_2}{1\, mol\, ZnI_2} = 20.9\, g\, ZnI_2$$

In the preparation of lead (II) chromate $PbCrO_4$, 45.6 g of lead (II) chromate is obtained as a precipitate. How many moles of $PbCrO_4$ is this?

The molar mass of $PbCrO_4$ is 323 g/mol (i.e.) 1 mol $PbCrO_4$ = 323 g$PbCrO_4$. Therefore,

$$\frac{45.6\ g\ PbCrO_4\ \ \times 1\ mol\ PbCrO_4}{323\ g\ PbCrO_4} = 0.141\ g\ PbCrO_4$$

Calculation of the Number of Molecules in a Given Mass

Solved Problem: How many molecules are there in a 3.46 g sample of hydrogen chloride,HCl?

Note: The number of molecules in a sample is related to moles ofcompound (1 mol HCl = 6.023×10^{23} HCl molecules). Therefore if you first convert grams HCl to moles, then you can convert moles to number ofmolecules).

$$3.46\ g\ HCl\ \times \frac{1\ mol\ HCl}{36.5\ g\ HCl} \times \frac{6.023\ \times\ 10^{23}\ HCl\ molecules}{1\ mol\ HCl}$$

$$= 5.71\ \times 10^{22}\ HCl\ molecules$$

1.10Calculation of empirical formula from quantitative analysis and percentage composition

Empirical Formula

"An empirical formula (or) simplest formula for a compound is theformula of a substance written with the smallest integer subscripts".For most ionic substances, the empirical formula is the formula of thecompound. This is often not the case for molecular substances. Forexample, the formula of sodium peroxide, an ionic compound of Na^+ andO_2^{2-}, is Na_2O_2. Its empirical formula is NaO. Thus empirical formula tellsyou the ratio of numbers of atoms in the compound.

Steps for writing the Empirical formula

The percentage of the elements in the compound is determined by suitable methods and from the data collected, the empirical formula is determined by the following steps.

1. Divide the percentage of each element by its atomic mass. This will give the relative number of moles of various elements present in the compound.
2. Divide the quotients obtained in the above step by the smallest of them so as to get a simple ratio of moles of various elements.
3. Multiply the figures, so obtained by a suitable integer of necessary in order to obtain whole number ratio.
4. Finally write down the symbols of the various elements side by side and put the above numbers as the subscripts to the lower right hand of each symbol. This will represent the empirical formula of the compound.

Solved Problem

A compound has the following composition Mg = 9.76%,S = 13.01%, O = 26.01, H_2O = 51.22, what is its empirical formula?

[Mg = 24, S = 32, O = 16, H = 1]

Solution

Element	%	Relative No.of moles	Simple ratio moles	Simplest whole No.ratio
Magnesium	9.76	$\frac{9.76}{24} = 0.406$	$\frac{0.406}{0.406} = 1$	1
Sulphur	13.01	$\frac{13.01}{32} = 0.406$	$\frac{0.406}{0.406} = 1$	1
Oxygen	26.01	$\frac{26.01}{16} = 1.625$	$\frac{1.625}{0.406} = 4$	4
Water	51.22	$\frac{51.22}{18} = 2.846$	$\frac{2.846}{0.406} = 7$	7

Hence the empirical formula is $MgSO_4.7H_2O$.

Problems for practice

1. A substance on analysis, gave the following percentage composition, Na = 43.4%, C = 11.3%, 0 = 43.3% calculate its empirical formula [Na = 23, C = 12, O = 16].
Ans: Na_2CO_3.
2. What is the simplest formula of the compound which has the following percentage composition: Carbon 80%, hydrogen 20%.
Ans: CH_3
3. A compound on analysis gave the following percentage composition: C - 54.54%, H = 9.09%, 0 = 36.36%.
Ans: C_2H_4O

1.11 Calculation of molecular formula from empirical formula

The molecular formula of a compound is a multiple of its empiricalformula.

Example

The molecular formula of acetylene, C_2H_2 is equivalent to $(CH)_2$, andthe molecular formula of benzene, C6H6 is equivalent to $(CH)_6$. Therefore,the molecular weight is some multiple of the empirical formula weight,which is obtained by summing the atomic weights from the empiricalformula. For any molecular compound,

Molecular Weight = n x empirical formula weight

Where `n' is the whole number of empirical formula units in the molecule.The molecular formula can be obtained by multiplying the subscripts of theempirical formula by `n' which can be calculated by the following equation,

$$n = \frac{Molecular\ weight}{Emprical\ formula\ weight}$$

Steps for writing the molecular formula

1. Calculate the empirical formula.
2. Find out the empirical formula mass by adding the atomic mass of all the atoms present in the empirical formula of the compound.

3. Divide the molecular mass (determined experimentally by some suitable method) by the empirical formula mass and find out the value of n which is a whole number.

4. Multiply the empirical formula of the compound with n, so as to find out the molecular formula of the compound.

Solved Problem

A compound on analysis gave the following percentagecomposition C = 54.54%,H = 9.09%, O = 36.36 %. The vapor density of thecompound was found to be 44. Find out the molecular formula of thecompound.

Solution

Calculation of empirical formula

Element	%	Relative No.of moles	Simple ratio moles	Simplest whole No.ratio
C	54.54	$\frac{54.54}{12} = 4.53$	$\frac{4.53}{2.27} = 2$	2
H	9.09	$\frac{9.09}{1} = 0.09$	$\frac{9.09}{2.27} = 4$	4
O	36.36	$\frac{36.36}{16} = 2.27$	$\frac{2.27}{2.27} = 1$	1

Empirical formula is C_2H_4O.

Calculation of Molecular formula

Empirical formula mass = 12 x 2 + 1 x 4 + 16 x 1 = 44

Molecular mass = 2 x Vapor density

= 2 x 44 = 88

$$n = \frac{Molecular\ weight}{Emprical\ formula\ weight} = \frac{88}{44} = 2$$

Molecular formula = Emprical formula weight x n [Since n = 2],

= C_2H_4O x 2

= $C_4H_8O_2$

2. A compound on analysis gave the following percentage composition: Na=14.31% S = 9.97%, H = 6.22%, O = 69.5%, calculate the molecular formula of the compound on the assumption that all the hydrogen in the compound is present in combination with oxygen as water of crystallization. Molecular mass of the compound is 322 [Na = 23, S = 32,H = 1, 0 = 16].

Solution: Calculation of empirical formula

Element	%	Relative No.of moles	Simple ratio moles	Simplest whole No.ratio
Na	14.31	$\frac{14.31}{23} = 0.62$	$\frac{0.62}{0.31} = 2$	2
S	9.97	$\frac{9.97}{32} = 0.31$	$\frac{0.31}{0.31} = 1$	1
H	6.22	$\frac{6.22}{1} = 6.22$	$\frac{6.22}{0.31} = 20$	20
O	69.5	$\frac{69.5}{16} = 4.34$	$\frac{4.34}{0.31} = 14$	14

The empirical formula is $Na_2SH_{20}O_{14}$

Calculation of Molecular formula

Empirical formula mass = (23 x 2) + 32 + (20 x 1) + (16 x 14)

$$n = \frac{Molecular\ weight}{Emprical\ formula\ weight} = \frac{322}{322} = 1$$

Hence molecular formula is $Na_2SH_{20}O_{14}$.
Since all hydrogens are present as H_2O in the compound, it means 20 hydrogen atoms must have combined. It means 20 hydrogen atoms must have combined with 10 atoms of oxygen to form 10 molecules of water of crystallization. The remaining (14 – 10 = 4) atoms of oxygen should be present with the rest of the compound.
Hence, molecular formula = $Na_2SO_4.10H_2O$.

1.12 Stoichiometric equations

Stoichiometry

Stoichiometry is the calculation of the quantities of reactants and products involved in the chemical reaction. It is the study of the relationship between the number of mole of the reactants and products of a chemical reaction. A stoichiometric equation is a short scientific representation of a chemical reaction.

Rules for writing stoichiometric equations

a. In order to write the stoichiometric equation correctly, we must know the reacting substances, all the products formed and their chemical formula.

b. The formulae of the reactant must be written on the left side of arrow with a positive sign between them.

c. The formulae of the products formed are written on the right side of the arrow mark. If there is more than one product, a positive sign is placed between them. The equation thus obtained is called skeleton equation. For example, the Chemical reaction between Barium chloride and sodium sulphate producing $BaSO_4$ and NaCl is represented by the equation as:

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + NaCl$$

d. This skeleton equation itself is a balanced one. But in many cases the skeleton equation is not a balanced one. For example, the decomposition of Lead Nitrate giving Lead oxide, NO_2 and oxygen. The skeletal equation for this reaction is:

$$Pb(NO_3)_2 \rightarrow PbO + NO_2 + O_2$$

e. In the skeleton equation, the numbers and kinds of particles present on both sides of the arrow are not equal.

f. During balancing the equation, the formulae of substances should not be altered, but the number of molecules with it only be suitably changed.

g. Important conditions such as temperature, pressure, catalyst etc., may be noted above (or) below the arrow of the equation.

h. An upward arrow (↑) is placed on the right side of the formula of a gaseous product and a downward arrow (↓) on the right side of the formulae of a precipitated product.

i. All the reactants and products should be written as molecules including the elements like hydrogen, oxygen, nitrogen, fluorine chlorine, bromine and iodine as H_2, O_2, N_2, F_2, Cl_2, Br_2 and I_2.

1.13 Balancing chemical equation in its molecular form

A chemical equation is called balanced equation only when thenumbers and kinds of molecules present on both sides are equal. Theseveral steps involved in balancing chemical equation are discussed below.

Example 1

Hydrogen combines with bromine giving HBr

$$H_2 + Br_2 \rightarrow HBr$$

This is the skeletal equation. The number of atoms of hydrogen on the left side is two but on the right side it is one. So the number of molecules of HBr is to be multiplied by two. Then the equation becomes:

$$H_2 + Br_2 \rightarrow HBr$$

This is the balanced (or) stoichiometric equation.

Example 2

Potassium permanganate reacts with HCl to give KCl and other products. The skeletal equation is:

$$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$$

If an element is present only one substance in the left hand side of the equation and if the same element is present only one of the substances in the right side, it may be taken up first while balancing the equation.

According to the above rule, the balancing of the equation may be started with respect to K, Mn, O (or) H but not with Cl. There are:

		L.H.S.	R.H.S
K	=	1	1
Mn	=	1	1
O	=	4	1

So the equation becomes:

$$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$$

Now there are eight hydrogen atoms on the right side of the equation, we must write 8 HCl.

$$KMnO_4 + 8HCl \rightarrow KCl + MnCl_2 + 4H_2O + Cl_2$$

Of the eight chlorine atoms on the left, one is disposed of in KCl and two in $MnCl_2$ leaving five free chlorine atoms. Therefore, the above equation becomes:

$$KMnO_4 + 8HCl \rightarrow KCl + MnCl_2 + 4H_2O + 5/2Cl_2$$

Equations are written with whole number coefficient and so the equation is multiplied throughout by 2 to become:

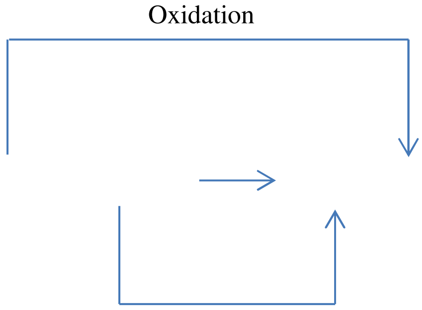
$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 2Cl_2$$

1.14Redox reactions [Reduction - Oxidation]

In our daily life we come across process like fading of the color of theclothes, burning of the combustible substances such as cooking gas, wood,coal, rusting of iron articles, etc. All such processes fall in the category ofspecific type of chemical reactions called reduction - oxidation (or) redoxreactions. A large number of industrial processes like, electroplating, extraction of metals like aluminium and sodium, manufactures of causticsoda, etc., are also based upon the redox reactions. Redox reactions alsoform the basis of electrochemical and electrolytic cells. According to theclassical concept, oxidation and reduction may be defined as, Oxidation is a process of addition of oxygen (or) removal of hydrogenReduction is a process of removal of oxygen (or) addition of hydrogen.

Example

Reaction of Cl_2 and H_2S



In the above reaction, hydrogen is being removed from hydrogensulphide (H_2S) and is being added to chlorine (Cl_2). Thus, H_2S is oxidizedand Cl_2 is reduced.

Electronic concept of oxidation and Reduction

According to electronic concept, oxidation is a process in which anatom taking part in chemical reaction loses one or more electrons. The lossof electrons results in the increase of positive charge (or) decrease ofnegative of the species. For example,

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \text{ [Increase of positive charge]}$$

$$Cu \rightarrow Cu^{2+} + 2e^{-} \text{[Increase of positive charge]}$$

The species which undergo the loss of electrons during the reactions arecalled reducing agents or reductants. Fe^{2+} and Cu are reducing agents in theabove example.

Reduction

Reduction is a process in which an atom (or) a group of atoms takingpart in chemical reaction gains one (or) more electrons. The gain ofelectrons result in the decrease of positive charge (or) increase of negativecharge of the species. For example,

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \text{ [Decrease of positive charges]}$$

$Zn^{2+} + 2e^{-} \rightarrow$ Zn[Decrease of positive charges]

The species which undergo gain of electrons during the reactions are called oxidizing agents (or) oxidants. In the above reaction, Fe^{3+} and $Zn^{2+}$are oxidizing agents.

1.15 Oxidation number

Oxidation number of the element is defined as the residual chargewhich its atom has (or) appears to have when all other atoms from the molecule are removed as ions.Atoms can have positive, zero or negative values of oxidation numbersdepending upon their state of combination.

General Rules for assigning Oxidation Number to an atom

The following rules are employed for determining oxidation number ofthe atoms.

1. The oxidation number of the element in the free (or) elementarystate is always Zero.

   Oxidation number of Helium in He = 0

   Oxidation number of chlorine in Cl_2 = 0

2. The oxidation number of the element in monoatomic ion is equal tothe charge on the ion.
3. The oxidation number of fluorine is always - 1 in all its compounds.
4. Hydrogen is assigned oxidation number +1 in all its compoundsexcept in metal hydrides. In metal hydrides like NaH, MgH_2, CaH_2, LiH,etc., the oxidation number of hydrogen is -1.
5. Oxygen is assigned oxidation number -2 in most of its compounds,however in peroxides like H_2O_2, BaO_2, Na_2O_2, etc., its oxidation number is -1. Similarly the exception also occurs in compounds of Fluorine andoxygen like OF_2 and O_2F_2 in which the oxidation number of oxygen is +2and +1 respectively.
6. The oxidation numbers of all the atoms in neutral molecule is Zero.In case of polyatomic ion the sum of oxidation numbers of all its atoms isequal to the charge on the ion.
7. In binary compounds of metal and non-metal the metal atom haspositive oxidation number while the non-metal atom has negative oxidation number. Example:

Oxidation number of K in KI is +1 but oxidation number of I is - 1.

8. In binary compounds of non-metals, the more electronegative atomhas negative oxidation number, but less electronegative atom has positiveoxidation number. Example: Oxidation number of Cl in ClF_3 is positive(+3) while that in ICl is negative (-1).

Problem

Calculate the oxidation number of underlined elements in the followingspecies.

$\underline{C}O_2$, $\underline{Cr}_2O_7^{2-}$

Solution

1. C in CO_2. Let oxidation number of C be x. Oxidation number of eachO atom = -2.

   Sum of oxidation number of all atoms = x + 2(-2) x - 4. As it is neutral molecule, the sum must be equal to zero.

x - 4 = 0 (or) x = + 4

2. Cr in $Cr_2O_7^{2-}$. Let oxidation number of Cr = x. Oxidation number ofeach oxygen atom =-2. Sum of oxidation number of all atoms2x + 7(-2) = 2x – 14.

   Sum of oxidation number must be equal to the charge on the ion.Thus, 2x - 14 = -2

2x = +12

x = 12/2

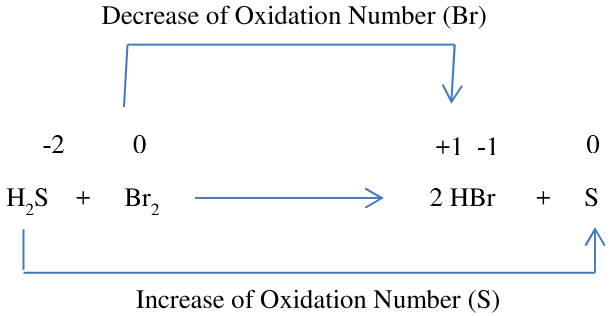
x = 6

Oxidation and reduction in terms of oxidation number

Oxidation: Chemical process in which oxidation number of the element increases.

Reduction: Chemical process in which oxidation number of the element decreases.

Eg.Reaction between H_2S and Br_2 to give HBr and Sulphur.



In the above reaction, the oxidation number of bromine decreases from0 to -1, thus it is reduced. The oxidation number of S increases from -2 to 0.Hence H_2S is oxidized.

Under the concept of oxidation number, oxidizing and reducing agent can be defined as follows.

a. Oxidizing agent is a substance which undergoes decrease in the oxidation number of one of its elements.

b. Reducing agent is a substance which undergoes increase in the oxidation number of one of its elements.

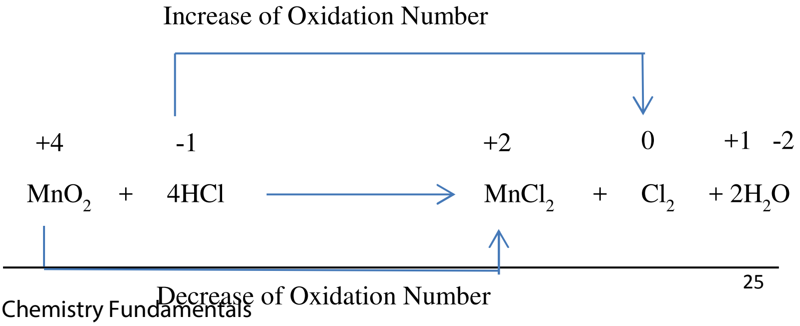
In the above reaction H_2S is reducing agent while $Br_2$is oxidizing agent.

Solved Problem

Identify the oxidizing agent, reducing agent, substanceoxidized andsubstance reduced in the following reactions.

a. $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

Solution



Balancing Redox equation using oxidation number

As it is clear, manganese decreased its oxidation number from +4 to +2. Hence, MnO_2 gets reduced and it is an oxidizing agent. Chlorine atom in HCl increases its oxidation number from -1 to 0. Thus, HCl gets oxidized and it is reducing agent.

Balancing Redox reaction by Oxidation Number Method

The various steps involved in the balancing of redox equations according to this method are:

1. Write skeleton equation and indicate oxidation number of each element and thus identify the elements undergoing change in oxidation number.
2. Determine the increase and decrease of oxidation number per atom. Multiply the increase (or) decrease of oxidation number of atoms undergoing the change.
3. Equalize the increase in oxidation number and decrease in oxidation number on the reactant side by multiplying the respective formulae with suitable integers.
4. Balance the equation with respect to all atoms other than O and H atoms.
5. Balance oxygen by adding equal number of water molecules to the side falling short of oxygen atoms.
6. H atoms are balanced depending upon the medium in same way as followed in ion electron method.

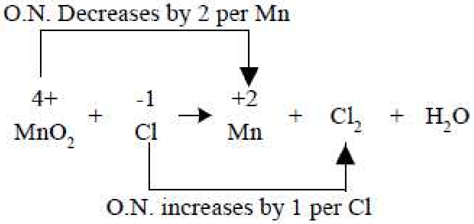
Let us balance the following equations by oxidation number method.

$$MnO^2 + Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O\text{, in acidic medium}$$

Step 1

$$MnO_2 + Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$$

Step 2



Step 3

Equalise the increase / decrease in O.N by multiply MnO_2 by 1 and Cl^{-1} by 2.

$$MnO_2 + 2\ Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$$

Step 4

Balance other atoms except H and O. Here they are all balanced.

Step 5

Balance O atoms by adding H_2O molecules to the side falling short of oxygen atoms.

$$MnO_2 + 2Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O + H_2O$$

Step 6

Balance H atoms by adding H^+ ions to the side falling short of H atoms

$$MnO_2 + 2Cl^- + 4H^+ \rightarrow Mn^{2+} + Cl_2 + 2H_2O$$

1.16Calculations based on equations

Stoichiometric problems are solved readily with reference to the equation describing the chemical change. From a stoichiometric chemical equation, we know how many molecules of reactant react and how many molecules of products are formed. When the molecular mass of the substances are inserted, the equation indicates how many parts by mass of reactants react to produce how many parts by mass of products. The parts by mass are usually in kg.

So it is possible to calculate desired mass of the product for a known mass of the reactant or vice versa.

Mass/Mass relationship

Example 1

Calculate the mass of CO_2 that would be obtained by completely dissolving 10 kg of pure $CaCO_3$ in HCl.**[Hint:** 100 kg of $CaCO_3$ produces 44 x 10^{-3} kg of CO_2**]**

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

100 kg of $CaCO_3$ produces 44 x 10^{-3} kg of CO_2

Therefore, 10 kg of $\mathrm{CaCO_3}$, produces,

$$= \frac{44 \times 10^{-3} kg\ of\ CO_2}{100 \times 10^{-3}} \times 10 = 4.4\ kg\ of\ CO_2$$

Example 2

Calculate the mass of oxygen obtained by complete decomposition of 10 kg of pure potassium chlorate (Atomic mass K = 39, O = 16 and Cl = 35.5).

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

Molecular mass of $KClO_3$ = 39 + 35.5 + 48 = 122.5

Molecular mass of O_2 = 16 + 16 = 32

According to the stoichiometric equation written above (2 X 122.5) x 10^{-3} kg of $KClO_3$ on heating gives (3 x 32) x 10^{-3} kg of oxygen.

$$10\mathrm{kg\ of\ KClO_3} = \frac{3 \times 32 \times 10^{-3}}{2 \times 122.5 \times 10^{-3}} = 3.92\ \mathrm{kg\ of\ O_2}$$

Example 3

Calculate the mass of lime that can be prepared by heating 200 kg of limestone that is 90 % pure $CaCO_3$. **[Hint:** 100 kg of $CaCO_3$produces 56 kg of CaO**]**

Solution

$$CaCO_3 \rightarrow CaO + CO_2$$

$$200\ \mathrm{kg\ of\ pure\ CaCO_3} = 200 \times \frac{90}{100} = 180\ \mathrm{kg\ of\ pure\ CaCO_3}$$

As we know that, 100 x 10^{-3} kg of $CaCO_3$produces 56 kg x 10^{-3} of CaO.

$$180 \text{ kg of pure } \mathrm{CaCO_3} \text{ gives on heating} = \frac{56\ \times 10^{-3}\ \times 180}{100\ \times 10^{-3}}$$
$$= 100.8 \text{ kg CaO}$$

Methods of expressing concentration of solution

The concentration of a solution refers to the amount of solute present in the given quantity of solution or solvent. Several ways by which the concentration of solutions could be described are: (1) Strength (2) Mass percentage (3) Volume percentage (4) Mass by volume percentage (5)Parts per million (6) Mole fraction (7) Molarity (8) Molalityand (9) Normality.

1. Strength

The Strength of a solution is defined as the amount of the solute in grams, present in one litre of the solution. It is expressed in g / L.

$$\text{Strength} = \frac{\text{Mass of solute in grams}}{\text{Volume of Solution in litres}}$$

If X gram of solute is present in V cm3 of a given solution then,

$$\text{Strength} = \frac{\text{X} \times 1000}{\text{V}}$$

2. Mass percentage (*w/w*): The mass percentage of a component of a solution is defined as:

$$\text{Mass \% of a component} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100$$

For example, if a solution is described by 10% glucose in water by mass, it means that 10 g of glucose is dissolved in 90 g of water resulting in a 100 g solution. Concentration described by mass percentage is commonly used in industrial chemical applications. For example, commercial bleaching solution contains 3.62 mass percentage of sodium hypochlorite in water.

3. Volume percentage (*v/v*): The volume percentage is defined as:

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of the solution}} \times 100$$

For example, 10% ethanol solution in water means that 10 mL of ethanol is dissolved in water such that the total volume of the solution is 100 mL. Solutions containing liquids are commonly expressed in this unit. For example, a 35% (*v/v*) solution of ethylene glycol, an antifreeze, is used in cars for cooling the engine. At this concentration the antifreeze lowers the freezing point of water to 255.4K (–17.6°C).

4. Mass by volume percentage: Another unit which is commonly used in medicine and pharmacy is mass by volume percentage. It is the mass of solute dissolved in 100 mL of the solution.

5. Parts per million: When a solute is present in tracequantities, it is convenient to express concentration in parts per million (ppm)and is defined as:

$$\text{Parts per million} = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

As in the case of percentage, concentration in parts per million can also be expressed as mass to mass, volume to volume and mass to volume. A litre of sea water (which weighs 1030 g) contains about 6×10^{-3} g of dissolved oxygen (O_2). Such a small concentration is also expressed as 5.8 g per 106 g (5.8 ppm) of sea water. The concentration of pollutants in water or atmosphere is often expressed in terms of $\mu g\ mL^{-1}$ or ppm.

6. Mole fraction

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the component}}$$

Commonly used symbol for mole fraction is *x* and subscript used on the right hand side of *x* denotes the component. For example, in a binary mixture, the number of moles of the components A and B are denoted as n_A and n_A respectively.

$$x_A = \frac{n_A}{n_A + n_B}$$

Then, for a solution containing 'i' number of components:

$$x_i = \frac{n_i}{n_1 + n_2 + \ldots\ldots\ldots + n_i} = \frac{n_i}{\sum n_i}$$

It can be shown that in a given solution sum of all the mole fraction is unity, i.e.,

$$x_1 + x_2 + \ldots\ldots\ldots.. + x_i = 1$$

7. Molarity: Molarity (*M*) is defined as the number of moles of solute dissolved in one litre (or one cubic decimeter) of solution.

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

8. Molality: Molality (*m*) is defined as the number of moles of the solute per kilogram (*kg*) of the solvent and is expressed as:

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

Difference between Molarity and Molality

Molarity is defined as the number of moles of solute per liter of solution. This means that if you have a 1 M solution of some compound, evaporating one liter will cause one mole of the solute to precipitate.

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Liters of solution}}$$

Molality is defined as the number of moles of solute per kilogram of solvent. To make a 1 m solution, you'd take one mole of a substance and add it to 1 L of solvent. As a result, the final volume of a 1 m solution will be somewhat more than 1 L.

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Kilograms of solvent}}$$

Molality is a mass-based unit

- Uses solvent mass (not solution)
- It is temperature independent (unlike molarity)

9. Normality

Normality of a solution is defined as the number of gram equivalents of the solute dissolved per liter of the given solution.

$$\text{Normality} = \frac{\text{Number of gram} - \text{equivalents of solute}}{\text{Volume of Solution in liter}}$$

If X grams of the solute is present in V cm^3 of a given solution, then

$$\text{Normality} = \frac{\text{X}}{\text{Equivalent mass}} \times \frac{1000 \text{ mL}}{\text{V}}$$

Normality is represented by the symbol N. Normality can also be calculated from strength as follows.

$$\text{Normality} = \frac{\text{Strength in grams per liter}}{\text{Eq. mass of the solute}}$$

For example, a 0.1 N (or decinormal) solution of H_2SO_4 (Eq. mass = 49) means that 4.9 g of $H_2SO_4$is present in one liter (1000 cm^3) of the solution.

1.17Calculations on principle of volumetric analysis

Volumetric Analysis

An important method for determining the amount of a particular substance is based on measuring the volume of reactant solution. Suppose substance A in solution reacts with substance B. If you know the volume and concentration of a solution of B that just reacts with substance A in a sample, you can determine the amount of A.

Titration is a procedure for determining the amount of substance A by adding a carefully measured volume of a solution of A with known concentration of B untill the reaction of A and B is just completed. Volumetric analysis is a method of analysis based on titrations.

Law

"Equal volumes of equinormal solutions exactly neutralize the other solution having same concentration and volume".

$V_1N_1 = V_2N_2$

V_1, V_2 - Volume of solutions.

N_1, N_2 - Strength of solutions.

Solved problem

Calculating the volume of reactant solution needed

1. What volume of 6M HCl and 2M HCl should be mixed to get one litre of 3M HCl?

Solution

Suppose the volume of 6M HCl required to obtain 1L of 3M HCl = XL.

Volume of 2M HCl required = (1-x)L

Applying the molarity equation

$M_1V_1 + M_2V_2 = M_3V_3$

6MHCl + 2MHCl = 3MHCl

$6x+2(1-x) = 3x1$

$6x+2-2x = 3$

$4x = 1$

$x = 0.25L$

Hence, Volume of 6M HCl required = 0.25L

Volume of 2M HCl required = 0.75L

2. How much volume of 10M HCl should be diluted with water to prepare 2.00L of 5M HCl?

Solution

$N_1V_1 = N_2V_2$

10N HCl = 5N HCl

$10xV_1 = 5 x 2.00$

$$\text{Therefore, } V_1 = \frac{5 \times 2.00}{10} = 1.00 \text{ L}$$

1.18 Determination of equivalent mass of an element

Equivalent masses can be determined by the following methods:

1. Hydrogen displacement method
2. Oxide method
3. Chloride method
4. Metal displacement method

Hydrogen displacement method

This method is used to determine the equivalent mass of those metals such as magnesium, zinc and aluminium which react with dilute acids and readily displace hydrogen.

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$

From the mass of the metal and the volume of hydrogen displaced, the equivalent mass of the metal can be calculated.

Problem 1

0.548 g of the metal reacts with dilute acid and liberates 0.0198 g ofhydrogen at S.T.P. Calculate the equivalent mass of the metal.

Solution

0.548 g of the metal displaces 0.0198 g of hydrogen,

The mass of the metal which will displace is given as,

$$1.008 \text{ g of hydrogen} = \frac{1.008 \times 0.548}{0.0198} \text{ g of metal}$$

Therefore, the equivalent mass of the metal = 27.90 g equiv^{-1}.

Oxide Method

This method is employed to determine the equivalent mass of those elements which readily form their oxides eg. magnesium, copper etc. Oxide of an element can be formed by direct method or by indirect method.Magnesium forms its oxide directly on heating,

$$2Mg + O_2 \rightarrow 2MgO$$

In the case of copper, its oxide is obtained in an indirect manner i.e. copper is dissolved in concentrated nitric acid and the copper (II) nitrate formed after evaporation is strongly heated to give copper (II) oxide.

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4\ NO_2 + O_2$$

Calculations

Mass of the element taken = w_1 g

Mass of the oxide of the element = w_2 g

Mass of oxygen = $(w_2 - w_1)$ g

$(w_2 - w_1)$ g of oxygen has combined with w_1 g of the metal.

$$\text{Therefore, 8 g of oxygen will combine} = \frac{w_1}{w_2 - w_1} \times 8$$

This value represents the equivalent mass of the metal.

Problem

0.635 g of a metal gives on oxidation 0.795g g of its oxide. Calculate the equivalent mass of the metal.

Mass of the metal oxide = 0.795g

Mass of the metal = 0.635g

Mass of oxygen = 0.795 – 0.635 = 0.16g

0.16 g of oxygen has combined with 0.635 g of a metal

$$\text{Therefore, 8 g of oxygen will combine} = \frac{8 \times 0.635}{0.16} = 31.75$$

Equivalent mass of the metal = 31.75g equiv^{-1}.

Chloride Method

The equivalent mass of those elements which readily form their chlorides can be determined by chloride method. For example, a known mass of pure silver is dissolved completely in dilute nitric acid. The resulting silver nitrate solution is treated with pure hydrochloric acid when silver chloride is precipitated. It is then filtered, dried and weighed. Thus from the masses of the metal and its chloride, the equivalent mass of themetal can be determined as follows:

Calculations

Mass of the metal = w_1 g

Mass of the metal chloride = w_2 g

Mass of chlorine = $(w_2 - w_1)$ g

$(w_2 - w_1)$ g of chlorine has combined with w_1g of the metal

$$Therefore, 35.46\ \ g\ of\ oxygen\ will\ combine = \frac{35.46\ \times w_1}{w_2 - \ w_1}$$

This value gives the equivalent mass of the metal.

Uses of volumetric laws

If the volume of the acid is represented as V_1, the normality of the acid as N_1, volume of base as V_2 the normality of the base as N_2, then from the law of volumetric analysis it follows that:

$$V_1 \times N_1 = V_2 \times N_2$$

All volumetric estimations are based on the above relationship. If any three quantities are known, the fourth one can readily be calculated using the above expression.

1.19 Equivalent mass of acid, base, salt, oxidising agent and reducing agent

1. Equivalent mass of an acid

Acids contain one or more replaceable hydrogen ions. The number of replaceable hydrogen ions present in a molecule of the acid is referred to its basicity.

Equivalent mass of an acid is the number of parts by mass of the acid which contains 1.008 parts by mass of replaceable hydrogen ions.

$$\text{Equivalent mass of an acid} = \frac{\text{Molar mass of an acid}}{\text{No. of replaceable hydrogen ions}}$$

Or

$$\text{Equivalent mass of an acid} = \frac{\text{Molar mass of an acid}}{\text{Basicity of the acid}}$$

For example, the basicity of H_2SO_4 acid is 2.

Therefore, the equivalent mass of H_2SO_4 is given as,

$$\text{Equivalent mass of } H_2SO_4 = \frac{\text{Molar mass of } H_2SO_4}{\text{Basicity of the acid}} = \frac{98}{2} = 49$$

2. Equivalent mass of the base

Equivalent mass of a base is the number of parts by mass of the basewhich contains one replaceable hydroxyl ion or which completely neutralizes one gram equivalent of an acid. The number of hydroxyl ionspresent in one mole of a base is known as the acidity of the base. Sodiumhydroxide, potassium hydroxide, ammonium hydroxide are examples ofmonoacidic bases.Calcium hydroxide is a diacidic base. In general,

$$\text{Equivalent mass of a base} = \frac{\text{Molar mass of a base}}{\text{No. of replaceable hydroxyl ions}}$$

Or

$$\text{Equivalent mass of a base} = \frac{\text{Molar mass of a base}}{\text{Acidity of a base}}$$

For example, acidity of KOH is 1, therefore the molar mass of KOH is:

$$\text{Equivalent mass of KOH} = \frac{\text{Molar mass of KOH}}{\text{Acidity of a base}} = \frac{56}{1} = 56$$

3. Equivalent mass of a salt

Equivalent mass of a salt is a number of parts by mass of the salt that isproduced by the neutralization of one equivalent of an acid by a base.In the case of salt like potassium chloride, the salt formed by the neutralisation of one equivalent of an acid by a base.

$$KOH + HCl \rightarrow KCl + H_2O$$

Therefore, the equivalent mass of the salt is equal to its molar mass.

4. Equivalent mass of an oxidizing agent

The equivalent mass of an oxidizingagent is the number of parts by mass which can furnish 8 parts by mass of oxygen for oxidation either directly or indirectly.

For example, potassium permanganate is an oxidizing agent. In acid medium potassium permanganate reacts as follows

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

80 parts by mass of oxygen are made available from 316 parts by massof $KMnO_4$.

8 parts by mass of oxygen will be furnished by:

$$\frac{316\ \times 8}{80} = 3.16$$

Equivalent mass of $KMnO_4$ = 31.6g equiv^{-1}

5. Equivalent mass of a reducing agent

The equivalent mass of a reducing agent is the number of parts by massof the reducing agent which is completely oxidized by 8 parts by mass of oxygen or with one equivalent of any oxidizing agent.

(i) Ferrous sulphate reacts with an oxidizing agent in acid medium according to the equation.

$$2FeSO_4 + H_2SO_4 + (O) \rightarrow Fe_2(SO_4)_3 + H_2O$$

16 parts by mass of oxygen oxidized 304 parts by mass of ferroussulphate

8 parts by mass of oxygen will oxidize 304/16 x 8 parts by mass of ferrous sulphate.

The equivalent mass of ferrous sulphate (anhydrous) is 152.

The equivalent mass of crystalline ferrous sulphate, $FeSO_4.7H_2O$ is 152 + 126 = 278

126 is the mass corresponding to 7 moles of water.

(ii) In acid medium, oxalic acid is oxidized according to the equation

$$(COOH)_2 + (O) \rightarrow 2CO_2 + H_2O$$

16 Parts by mass of oxygen oxidized 90 parts by mass of anhydrousoxalic acid.

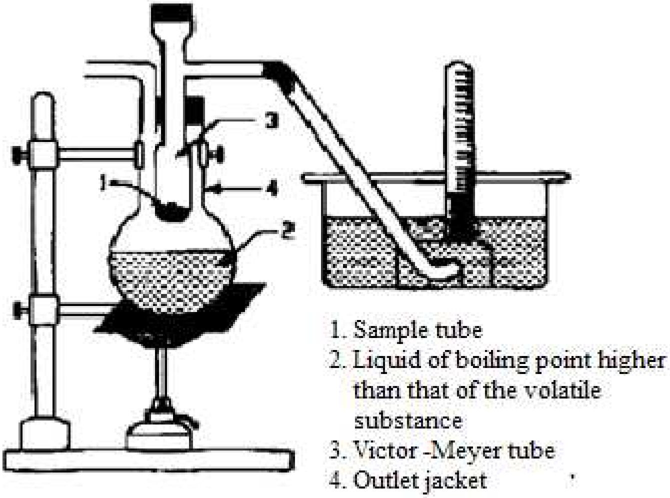
8 parts by mass of oxygen will oxidize 90/16 x 8 = 45 parts by mass ofanhydrous oxalic acid.

Therefore, Equivalent mass of anhydrous oxalic acid = 45 g equiv^{-1}

But equivalent mass of crystalline oxalic acid, $(COOH)_2.2H_2O$=126/2 = 63 g equiv^{-1}.

1.20 Determination of Molecular Mass Victor-Meyer's Method

Principle



In this method a known mass of a volatile liquid or solid is converted into its vapor by heating in a Victor-Meyer's tube. The vapor displaces its own volume of air. The volume of air displaced by the vapor is measured at the experimental temperature and pressure. The volume of the vapor at standard temperature and pressure (S.T.P.) is then calculated. From this the mass of 2.24 x 10-2m3 of the vapor at S.T.P. is calculated. This value represents the molecular mass of the substance.

The apparatus consists of an inner Victor-Meyer tube, the lower end ofwhich is in the form of a bulb. The upper end of the tube has a side tubewhich leads to a trough of water. The Victor-Meyer tube is surrounded byan outer jacket. In the outer jacket is placed a liquid which boils at atemperature at least 30 K higher than the boiling point of the volatilesubstance under study. A small quantity of glass wool or asbestos fibercovers the bottom of the Victor-Meyer tube to prevent breakage when thebottle containing the substance is dropped in.

Procedure

`The liquid in the outer jacket is allowed to boil and when no more air escapes from the side tube, a graduated tube filled with water is invertedover the side tube dipping in a trough full of water. A small quantity of thesubstance is exactly weighed in a small stoppered bottle and quicklydropped in the heated Victor-Meyer tube and corked immediately.

The bottle falls on the asbestos pad and its content suddenly changes into vapor, blow out the stopper and displace an equal volume of air whichcollects in the graduated tube. The volume of air in the graduated tube ismeasured by taking it out by closing its mouth with the thumb and dippingit in a jar full of water. When the water levels outside and inside the tubeare the same, the volume of air displaced is noted. The atmosphericpressure and laboratory temperature are noted.

Calculations

Mass of the volatile substance = wg

Volume of air displaced = Volume of vapor = V_1 m^3

Laboratory temperature = $_{T1}$ K

Let the atmospheric pressure be P

Pressure of dry vapor = Atmospheric pressure - aqueous tension at T_1 K

Let the aqueous tension be p Nm^{-2} at that temperature.

Pressure of dry vapor = P1 = [P-p]

Standard temperature = T_0 = 273 K

Standard pressure = $P_0 = 1.013 \times 10^5$ Nm^{-2}

Let the volume of the vapor at standard temperature and pressure be V_0 m^3

From the gas equation, it follows

$$\frac{P_0\,V_0}{T_0} = \frac{P_1\,V_1}{T_1}$$

$$V_0 = \frac{P_1 V_1}{T_1} \times \frac{T_0}{P_0}$$

The mass of V_0 m^3 of vapor at S.T.P. is w g.The mass of 2.24×10^{-2} m^3 of the vapor at S.T.P. is,

$$\frac{2.24 \times 10^{-2} \times W}{V_0}$$

The value thus calculated gives the molecular mass.

Molecular mass = 2 x vapor density

$$Vapor\ Density = \frac{Molecular\ mass}{2}$$

Problem

In the determination of molecular mass by Victor-Meyer's Method0.790 g of a volatile liquid displaced $1.696 \times 10^{-4} m^3$ of moist air at 303 Kand at 1×10^5 Nm^{-2}pressure. Aqueous tension at 303 K is $4.242 \times 10^3 Nm^{-2}$. Calculate the molecular mass and vapor density of the compound.

Mass of the organic compound = 0.79 g

Volume of Vapor = V_1=1.696x $10^{-4} m^3$

Volume of air displaced = Volume of vapor

P_1 = (atmospheric pressure - aqueous tension)

= $(11 \times 10^5) - (4.242 \times 10^3) = 0.958 \times 10^5$ Nm^{-2}

T_1 = 303 K

Lab Values Values at S.T.P

$V_1 = 1.696 \times 10^{-4}$ Nm^{-2} V_0= ?

$P_1 = 0.958 \times 10^{-5}$ $Nm^{-2}$$P_0 = 1.013 \times 10^5$ Nm^{-2}

T_1 = 303 K T_0 = 273 K

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

$$V_0 = \frac{P_1 V_1}{T_1} \times \frac{T_0}{P_0} = \frac{P_1 V_1 T_0}{T_1 P_0}$$

$$V_0 = \frac{0.958 \times 10^5 \times 1.696 \times 10^{-4} \times 273}{1.13 \times 10^5 \times 303}$$

The mass of $1.445 \times 10^{-4} m^3$ of vapor at S.T.P = 0.79 g.

The mass of $2.24 \times 10^{-2} m^3$ of vapor at S.T.P is

$$= \frac{2.24 \times 10^{-2} \times 0.79}{1.445 \times 10^{-4}}$$

The molecular mass of the substance = 122.46

$$Vapor\ Density\ of\ the\ compound = \frac{Molecular\ mass}{2} = \frac{122.46}{2}$$

$$= 61.23$$

1.21 Laws of Chemical Combinations

The combination of elements to form compounds is governed by the following five basic laws.

A. Law of Conservation of Mass

It states that *matter can neither be created nor destroyed.* This law was put forth by Antoine Lavoisier in 1789. He performed careful experimental studies for combustion reactions for reaching basis for several later developments in chemistry. In fact, this was the result of exact measurement of masses of reactants and products, and carefully planned experiments performed by Lavoisier.

B. Law of Definite Proportions

This law was given by a French Chemist, Joseph Proust. He stated that *a given compound always contains exactly the same proportion of elements by weight.*

Proust worked with two samples of cupric carbonate – one which was of natural origin and the other was synthetic one. He found that the composition of elements present in it was same for both the samples as shown below.

Sample	% of copper	% of oxygen	% of carbon
Natural sample	51.35	9.74	38.91
Synthetic sample	51.35	9.74	38.91

Thus, irrespective of the source, a given compound always contains same elements in the same proportion. The validity of this law has been confirmed by various experiments. It is sometimes also referred to as Law of definite composition.

C. Law of Multiple proportions

This law was proposed by Dalton in 1803. According to this law, *if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.*

For example, hydrogen combines with oxygen to form two compounds, namely, water and hydrogen peroxide.

Hydrogen + Oxygen → Water
2g 16g 18g
Hydrogen + Oxygen → Hydrogen Peroxide
2g 32g 34g

Here, the masses of oxygen (i.e. 16 g and 32 g) which combine with a fixed mass of hydrogen (2 g) bear a simple ration, i.e. 16:32 or 1:2.

D. Gay Lussac's Law of Gaseous Volumes

This law was given by Gay Lussac in 1808. He observed that *when gases combine or are produced in a chemical reaction they do so in a simple ration by volume provided all gases are at same temperature and pressure.*

Thus, 100 mL of hydrogen combine with 50 mL of oxygen to give 100 mL of water vapor.

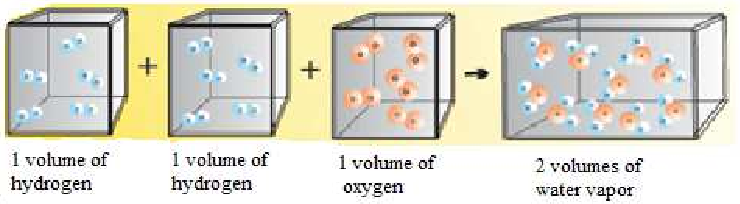
Hydrogen + Oxygen → Water
100 ml 50 ml 100 ml

Thus, the volumes of hydrogen and oxygen which combine together (i.e. 100 mL and 50 mL) bear a simple ratio of 2:1. Gay-Lussac's discovery of integer ratio in volume relationship is actually the law of definite proportions by volume. The law of definite proportions, stated earlier, was with respect to mass. The Gay-Lussac's law was explained properly by the work of Avogadro in 1811.

E. Avogadro Law

In 1811, Avogadro proposed that *equal volumes of gases at the same temperature and pressure should contain equal number of molecules.* Avogadro made a distinction between atoms and molecules which is quite understandable in the present times. If we consider again the reaction of hydrogen and oxygen to produce water, we see that two volumes of hydrogen combine with one volume of oxygen to give two volumes of water without leaving any unreacted oxygen.

Note that in the figure shown below each box contains equal number of molecules.



Two volumes of Hydrogen react with One volume of oxygen to give two volume of water vapor

In fact, Avogadro could explain the above result by considering the molecules to be polyatomic. If hydrogen and oxygen were considered as diatomic as recognized now, then the above results are easily understandable. However, Dalton and others believed at that time that atoms of the same kind cannot combine and molecules of oxygen or hydrogen containing two atoms did not exist. Avogadro’s proposal was published in the French Journal de Physique. In spite of being correct, it did not gain much support. After about 50 years, in 1860, first international conference on chemistry was held in Karlsruhe, Germany to resolve various ideas. At the meeting, Stanislao Cannizaro presented a sketch of a course of chemical philosophy which emphasized the importance of Avogadro’s work.

Chapter II Atomic Structure

Brief introduction of history of atoms - Chronology of atomic structure development - Dalton’s Atomic Theory - Thomson’s Model of Atom - Rutherford’s Scattering Experiment - Rutherford’s Nuclear Model of Atom - Defect of Rutherford’s Model - Bohr's Model of atom - Postulates of Bohr’s Model of Atom - Bohr’s Model of Hydrogen Atom - Hydrogen Energy levels - Hydrogen Spectrum - Rydberg’s formula – Limitations of Bohr’s Model - Sommerfield’s Extension of Bohr’s Model - Overview of progress in Atomic Models - Dual properties of electrons - difference between a wave and a particle - Experiments to prove particle and wave property of Electrons - Verification of Wave character - Davisson and Germer’s Experiment - Thomson’s Experiment - Verification of particle character - De Broglie relation -Significance of De Broglie waves - Heisenberg’s Uncertainty principle - explanation of uncertainty principle - Wave nature of electrons - Bohr’s quantum condition - Energy of an electron in an atom - significance of negative electronic energy - Schrödinger wave equation - significance of wave functions - Orbit, Orbital and its importance - Orbital and quantum numbers - Shapes of s, p and d orbitals - Pauli’s Exclusion principle - Hund’s rule - Aufbau principle - Electronic configuration.

2.01 Brief introduction of history of structure of atom

The introduction of the atomic theory by John Dalton in 1808 marksthe inception of a modern era in chemical thinking. According to thistheory, all matter is composed of very small particles called atoms. Theatoms were regarded to be structure-less, hard, impenetrable particleswhich cannot be subdivided. Dalton’s ideas of the structure of matterwere born out by a considerable amount of subsequent experimentalevidences towards the end of the nineteenth century. Early in thetwentieth century, it has been proved that an atom consists of smallerparticles such as electrons, protons and neutrons. The proton, a positivelycharged particle, is present in the central part of the atom called nucleus.The electron, a negatively charged particle, is present around the nucleus.The neutron, a neutral particle, is also present in the nucleus of the atom.Since the atom is electrically neutral, the number of positive charges onthe nucleus is exactly balanced by an equal number of orbital electrons.

Chronology of Atomic Structure Development

1. Dalton : Discovery of atom(1808)
2. Julius Plucker : First discoverer of cathode rays(1859)
3. Goldstein : Discovered anode rays and proton(1886)
4. Sir J.J.Thomson: Discovered electron anddetermined charge/mass(e/m)ratio for electron(1897)
5. Rutherford: Discovered nucleus and propsed atomic model (1891)
6. MaxPlanck :Proposed quantum theory of radiation (1901)
7. RobertMillikan: Determined charge of an electron(1909)
8. H.G.J.Mosely : Discovered atomic number(1913)
9. Niels Bohr : Proposed a new model of atom(1913)
10. Clark Maxwell: Electromagnetic wave theory(1921)
11. de-Broglie : Established wave nature of particles(1923)
12. Pauli : Discovery of neutrino(1927)
13. Werner Heisenberg : Uncertainty Principle(1927)
14. James Chadwick : Discovery of neutron(1932)
15. Anderson : Discovery of positron(1932)
16. Fermi : Discovered antineutrino(1934)
17. Hideki Yukawa : Discovered mesons(1935)
18. Segre : Discovered antiproton(1955)
19. Cork and Association : Discovered antineutron(1956)

2.03 Dalton's Atomic Theory

Although the origin of idea that matter is composed of small indivisible particles called *'a-tomio'* (meaning — *indivisible*), dates back to the time of Democritus, a Greek Philosopher (460 — 370 BC), it again started emerging as a result of several experimental studies which led to the Laws mentioned above.

In 1808, Dalton published 'A New System of Chemical Philosophy' in which he proposed the following:

1. Matter consists of indivisible atoms.
2. All the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.
3. Compounds are formed when atoms of different elements combine in a fixed ratio.
4. Chemical reactions involve re-organization of atoms. These are neither created nordestroyed in a chemical reaction.

Dalton's theory could explain the laws of chemical combination.

2.04 Thomson's Model of atom

In 1904 Sir J. J. Thomson proposed the first definite theory as to the internal structure of the atom. According to this theory the atom was assumed to consist of a sphere of uniform distribution of about 10^{-10} m positive charge with electrons embedded in it such that the number of electrons equal to the number of positive charges and the atom as a whole is electrically neutral.

This model of atom could account the electrical neutrality of atom, but it could not explain the results of gold foil scattering experiment carried out by Rutherford.

2.05 Rutherford's Scattering Experiment

Rutherford conducted a scattering experiment in 1911 to find out the arrangement of electrons and protons. He bombarded a thin gold foil with a stream of fast moving α particles emanating from radium.

Rutherford's Nuclear model of atom

This model resulted from conclusion drawn from experiments on thescattering of alpha particles from a radioactive source when the particleswere passed through thin sheets of metal foil. According to him:

(i) Mass of the space in the atom is empty as most of the α particles passed through the foil.

(ii) A few positively charged α particle's were deflected. The deflectionmust be due to enormous repulsive force showing that the positivecharge of the atom is not spread throughout the atom as Thomson hadthought. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α particles. This very small portion of the atom was called nucleusbyRutherford.

(iii) Calculations by Rutherford showed that the volume occupied by thenucleus is negligibly small as compared to the total volume of theatom. The diameter of the atom is about 10^{-10} m while that of nucleusis 10-15m. One can appreciate this difference in size by realizing that if a cricket ball represents a nucleus, then radius of the atom would beabout 5 km.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model:

(a) An atom consists of a tiny positively charged nucleus at its center.

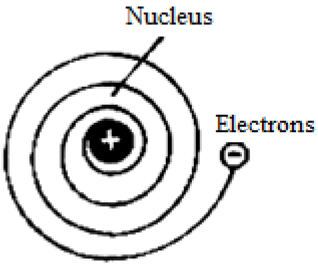
(b) The positive charge of the nucleus is due to protons. The mass of thenucleus, on the other hand, is due to protons and some neutralparticles each having mass nearly equal to the mass of proton. Thisneutral particle, called neutron, was discovered later on by Chadwickin 1932. Protons and neutrons present in the nucleus are collectivelyalso known as nucleons. The total number of nucleons is termed asmass number(A)of the atom.

(c) The nucleus is surrounded by electrons that move around the nucleuswith very high speed in circular paths called **orbits**. Thus,Rutherford's model of atom resembles the solar system in which thesun plays the role of the nucleus and the planets that of revolvingelectrons.

(d) The number of electrons in an atom is equal to the number of protonsin it. Thus, the total positive charge of the nucleus exactly balancesthe total negative charge in the atom making it electrically neutral.The number of protons in an atom is called its atomic number**(**Z**)**.

(e) Electrons and the nucleus are held together by electrostatic forces ofattraction.

Defects of Rutherford's model

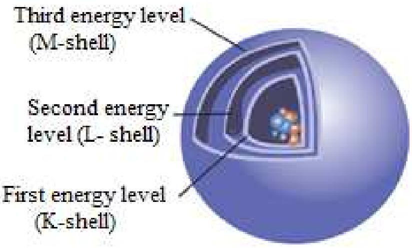


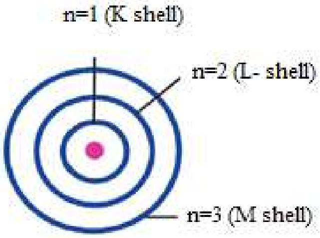
According to Rutherford's model, an atom consists of a positivenucleus with the electrons moving around it in circular orbits. However ithad been shown by J. C. Maxwell that whenever an electron is subjectedto acceleration, it emits radiation and loses energy. As a result of this, itsorbit should become smaller and smaller and finally it shoulddrop into the nucleus by following a spiral path (as shown in the figure). This means that atomwould collapse and thus Rutherford's model failed to explain stability ofatoms.

Another drawback of the Rutherford's model is that it says nothing about the electronic structure of the atoms i.e., how the electrons are distributed around the nucleus and what are the energies of these electrons. Therefore, this model failed to explain the existence of certain definite lines in the hydrogen spectrum.

2.06Bohr's Theory

The electron in an atom moves in a definite circular orbit with a fixed energy. These orbits are called stationary states because the energy of the electrons remains stationary as long as they keep on moving in the same orbit. Since each orbit is associated with a definite energy, they are also called energy levels. Starting from the nucleus these orbits are numbered as 1, 2, 3, 4, etc. or K, L, M, N, etc. The mathematical condition for stationary orbits is that the angular momentum of the moving electron is an integral multiple of $h/2\pi$, where h is the Planck's constant. Thus $mvr = n.h/2\pi$ .Where mvr denotes the angular momentum and n is called principal quantum number and is equal to 1, 2, 3.





Postulates of Bohr's model of an atom

To overcome the above defects of Rutherford's model, Niels Bohr in1913 gave a modification based on Quantum theory of radiation. The important postulates are:

(1) The electrons revolve round the nucleus only in certain selected circular paths called orbits. These orbits are associated with definiteenergies and are called energy shells or energy levels or quantum levels. These are numbered as 1, 2, 3, 4 ….. etc. (starting from thenucleus) are designated as K, L, M, N ….etc. (Fig. 3.2).

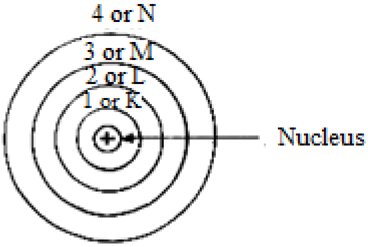
(2) As long as an electron remains in a particular orbit, it does not lose orgain energy. This means that energy of an electron in a particular pathremains constant. Therefore, these orbits are also called stationarystates.

(3) Only those orbits are permitted in which angular momentum of the electron is a whole number multiple of $h/2\pi$ where h is the Planck's constant. An electron moving in a circular orbit has an angularmomentum equal to mυr where m is the mass of the electron and υ,the angular momentum, mυr is the whole number multiple of $h/2\pi$ i.e.,

$$m\upsilon r = nh / 2\pi, \text{ i.e. where } n = 1, 2, 3 \ldots$$

In other words, angular velocity of electrons in an atom is quantized.

(5) If an electron jumps from one stationary state to another, it will absorb or emit radiation of a definite frequency giving a spectral line of that frequency which depends upon the initial and final levels. When an electron jumps back to the lower energy level, it radiates same amount of energy in the form of radiation.

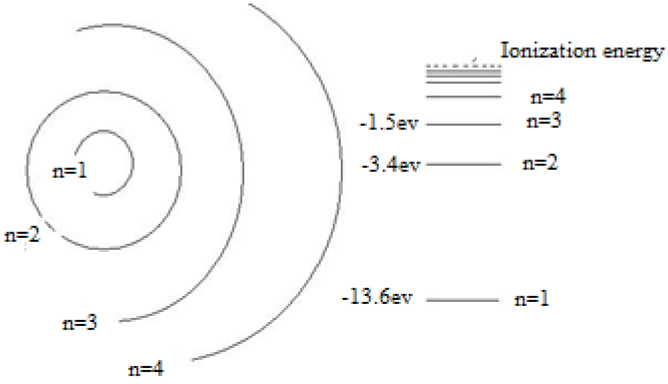


Bohr's model of Hydrogen atom

Niels Bohr introduced the atomic Hydrogen model in 1913. He described it as a positively charged nucleus, comprised of protons and neutrons, surrounded by a negatively charged electron cloud. In the model, electrons orbit the nucleus in atomic shells. The atom is held together by electrostatic forces between the positive nucleus and negative surroundings.

Hydrogen Energy Levels

The Bohr model is used to describe the structure of hydrogen energy levels. The image below represents shell structure, where each shell is associated with principle quantum number *n*. The energy levels presented correspond with each shell. The amount of energy in each level is reported in eV, and the maxiumum energy is the ionization energy of 13.598eV.



Some of the orbital shells of a Hydrogen atom.
The energy levels of the orbitals are shown to the right.

Hydrogen Spectrum

The movement of electrons between these energy levels produces a spectrum. The Balmer equation is used to describe the four different wavelengths of Hydrogen which are present in the visible light spectrum. These wavelengths are at 656, 486, 434, and 410nm. These correspond to the emission of photons as an electron in an excited state transitions down to energy level n=2. The Rydberg formula, below, generalizes the Balmer series for all energy level transitions. To get the Balmer lines, the Rydberg formula is used with an $n_f$of 2.

Rydberg Formula

The Rydberg formula explains the different energies of transition that occur between energy levels. When an electron moves from a higher energy level to a lower one, a photon is emitted. The Hydrogen atom can emit different wavelengths of light depending on the initial and final energy levels of the transition. It emits a photon with energy equal to the difference of square of the final (*nf*) and initial (*ni*) energy levels.

$$\text{Energy} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

The energy of a photon is equal to Planck's constant, h= 6.626 x 10^{-34} m^2kg/s, times the speed of light in a vacuum, divided by the wavelength of emission.

$$E = \frac{hc}{\lambda}$$

Combining the above two energy equations produces the Rydberg Formula.

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

The Rydberg Constant (R) = 10,973,731.6m^{-1} or 1.097×107m^{-1}.

Limitations of the Bohr Model

The Bohr Model was an important step in the development of atomic theory. However, it has several limitations.

- It is in violation of the Heisenberg uncertainty principle.The Bohr model considers electrons to have both a known radius and orbit, which is impossible according to Heisenberg.
- The Bohr Model is very limited in terms of size. Poor spectral predictions are obtained when larger atoms are in question.

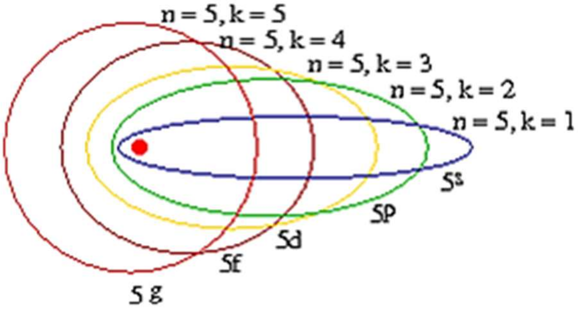
- It cannot predict the relative intensities of spectral lines.

- It does not explain the Zeeman Effect, when the spectral line is split into several components in the presence of a magnetic field.
- The Bohr Model does not account for the fact that accelerating electrons do not emit electromagnetic radiation.

2.07Sommerfield's extension of atomic structure

The Bohr's model is quite accurate but cannot explain the details of the optical spectra. The first one observed early was that the lines of the Balmer series consist of several components: the Ha line at 15233 cm^{-1}, is splitted into 3 or more components within 0.33 cm^{-1}. For heavier atoms lines are more separated and the splitting is easier to observe. Sommerfield extended the simple Bohr's model by including elliptical orbits for same energies, as suggested by Kepler's law in gravitation. To distinguish circular and elliptical orbits he introduced a new quantum number.

The principal quantum number n determines the major semi-axis of the ellipse, and the secondwould be determined by imposing that the angular momentum is a multiple k ofh/2π, with k=n,k<n.



2.08Overview of Progress in Atomic Models

- In 1803, John Dalton, proposed his atomic theory. He suggested that atoms were indivisible solid spheres.
- J.J. Thomson proposed that an atom was a solid sphere of positively charged material and negatively charged

particles, electrons were embedded in it like the seeds in a guava fruit. But later this concept was proved wrong.

- Rutherford suggested the planetary model, but this model was rejected.
- In 1913, Neils Bohr proposed that electrons revolve around the nucleus in a definite orbit with a particular energy. Based on the facts obtained from spectra of hydrogen atom, he introduced the concept of energy levels of atom.
- In 1916 Sommerfeld modified Bohr's model by introducing elliptical orbits for electron path. He defined sub energy levels for every major energy level predicted by Bohr.
- The concept of Quantum numbers was introduced to distinguish the orbital on the basis of their size, shape and orientation in space by using principal, azimuthal, magnetic and spin quantum numbers.
- From the study of quantum numbers, various rules are put forward for filling of electrons in various orbitals by following:
- Aufbau principle
- Pauli's exclusion principle and
- Hund's rule of maximum multiplicity
- In 1921 Burry and Bohr gave a scheme for the arrangement of electrons in an atom. Further the nature of electron (s) is studied.

2.09 Dual properties of electrons

In case of light, some phenomena like interference, diffraction etc., can be explained if light is supposed to have wave character. However certain other phenomena such as black body radiation and photo electric effect can be explained only if it is believed to be a stream of photons i.e., has particle character. Thus light is said to have a dual character. Such studies on light were made by Einsteinin 1905.

Louis de Broglie, a French Physicist, in 1924, advanced the idea that likephotons, all material particles such as electron, proton, atom, molecule, a pieceof chalk, a piece of stone or iron ball possessed both wave character as well asparticle character. The wave associated with a particle is called a matter wave.

Difference between a particle and a wave

The concept of a particle and a wave can be understood by the differentpoints of distinction between them.

S. No.	Particle	Wave
1.	A particles occupies a well-defined position in space i.e. a particle is localized in space e.g. a grain of sand, cricket ball, etc.	A wave is spread out in space, i.e. on throwing a stone in a pond of water,the waves start moving out in the form of concentric cycles. Similarly the sound reaches everybody in the audience. Thus a wave is delocalized in space.
2.	When a particular space is occupied by one particle, the same space cannot be occupied simultaneously by another particle. In other words, particles do not interfere.	Two or more waves can co-exist in the same region of space and hence interfere.
3.	When a number of particles are present in a given region of space, their total value is equal to their sum i.e. it is neither less nor more.	When a number of waves are present in a given region of space, due to interference, the resultant wave can be larger or smallerthan the individual waves i.e. interference may be constructive or destructive

(1) In 1924, the French physicist, Louis de Broglie suggested that if light has electron, behaves both as a material particle and as a wave.

(2) This presented a new wave mechanical theory of matter. According to this theory, small particles like electrons when in motion possess wave properties.

(3) According to de-broglie, the wavelength associated with a particle of mass m, moving with velocity v is given by the relation $\lambda = h/mv$ where h = Planck's constant.

(4) This can be derived as follows according to Planck's equation,

$E = hv = hc/\lambda \;\therefore v = c/\lambda$ (energy of photon)

(on the basis of Einstein's mass energy relationship) $E = mc^2$,

Equating both $hc/\lambda = mc^2$ or $\lambda = h/mc$ which is same as de-Broglie relation. ($\therefore mc = p$)

(5) This was experimentally verified by Davisson and Germer by observing diffraction effects with an electron beam. Let the electron is accelerated with a potential of V than the Kinetic energy is

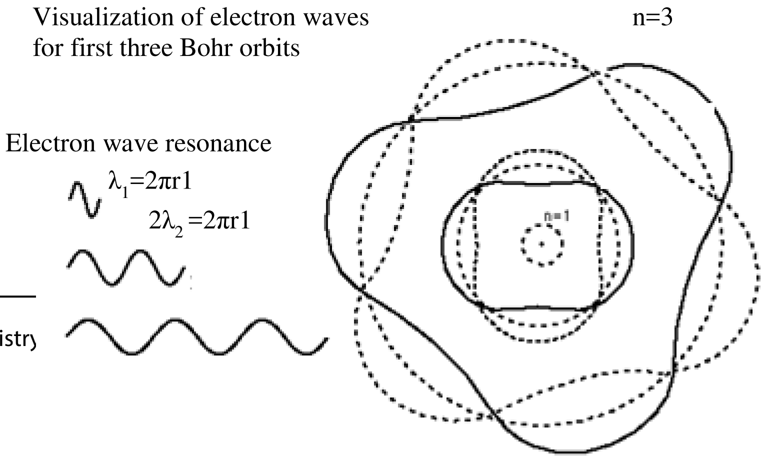
$$\mathbf{(1/2)\, mv^2 = eV;\; m^2V^2 = 2eVm}$$

$$\mathbf{mv = \sqrt{2eVm} = P; \lambda = h/\sqrt{2eVm}}$$

(6) If Bohr's theory is associated with de-Broglie's equation then wave length of an electron can be determined in bohr's orbit and relate it with circumference and multiply with a whole number $2\pi r = n\lambda$ or $\lambda = (2\pi r/2\pi)$ From de-Broglie equation, $\lambda = (h/mv)$.

$$\mathbf{Thus\ h/mv = (2\pi r/n)\ or\ mvr = (nh/2\pi)}$$

(7) The de-Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles. Since, we come across macroscopic objects in our everyday life, de-broglie relationship has no significance in everyday life.



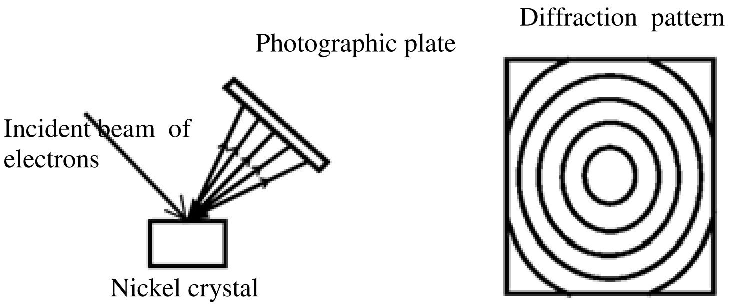
Experiments to prove particle and wave property of Electrons

a) Verification of Wave character

i) Davisson and Germer's Experiment

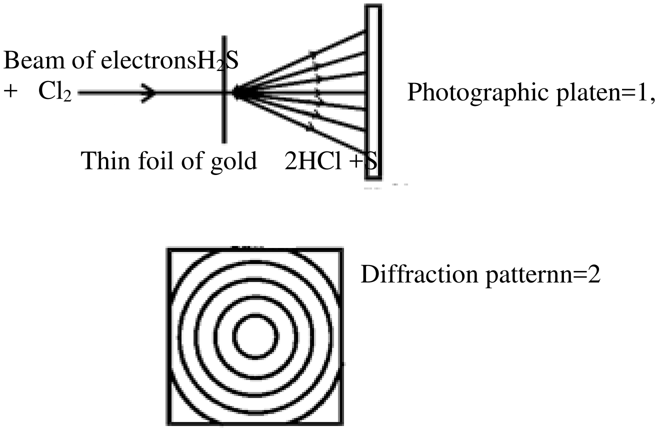
In 1927 Davisson and Germer observed that, a beam of electrons obtainedfrom a heated tungsten filament is accelerated by using a high positive potential.When this fine beam of accelerated electron is allowed to fall on a large singlecrystal of nickel, the electrons are scattered from the crystal in different directions.The diffraction pattern so obtained is similar to the diffraction pattern obtainedby Bragg's experiment on diffraction of X-rays from a target in the same way.

Since X-rays have wave character, therefore, the electrons must also have wave character associated with them. Moreover, the wave length of the electrons as determined by the diffraction experiments were found to be in agreement with the values calculated from de-Broglie equation. From the above discussion, it is clear that an electron behaves as a wave.



Electron diffraction experiment by Davisson and Germer

ii) Thomson’s experiment



Diffraction of electron beam by thin foil of gold n=2,

G.P. Thomson in 1928 performed experiments with thin foil of gold in place of nickel crystal. He observed that if the beam of electrons after passing through the thin foil of gold is received on the photographic plate placed perpendicular to the direction of the beam, a diffraction pattern is observed as before. This again confirmed the wave nature of electrons.

b) Verification of the particle character

The particle character of the electron is proved by the following different experiments:

a) When an electron strikes a zinc sulphide screen, a spot of light known asscintillation is produced. A scintillation is localized on the zinc sulphide screen.Therefore the striking electron which produces it, also must be localizedand is not spread out on the screen. But the localized character is possessedby particles. Hence electron has particle character.

b) Experiments such as J.J.Thomson’s experiment for determination of the ratioof charge to mass (i.e. e/m) and Milliken oil drop experiment fordetermination of charge on electron also show that electron has particlecharacter.

c) The phenomenon of Black body radiation and Photoelectric effect also provethe particle nature of radiation.

2.10 De-Broglie relation

The wavelength of the wave associated with any material particle was calculated by analogy with photon as follows:

In case of a photon, if it is assumed to have wave character, its energy is given by $E = h\nu$ (according to the Planck's quantum theory), where ν is the frequency of the wave and h is Planck's constant.

If the photon is supposed to have particle character, its energy is given by $E = mc^2$ (according to Einstein equation) where m is the mass of photon and c is the velocity of light.

By equating the above two equations, we get,

$$h\nu = mc^2$$

But $\nu = c / \lambda$

$$\therefore h(c/\lambda) = mc^2$$

Or

$$\lambda = h / mc$$

de Broglie pointed out that the above equation is applicable to any material particle. The mass of the photon is replaced by the mass of the material particle and the velocity "c" of the photon is replaced by the velocity v of the material particle. Thus, for any material particle like electron, we may write

$$\lambda = h / mv \text{ or } \lambda = h / p$$

Where $mv = p$ is the momentum of the particle. The above equation is called de Broglie equationand 'λ' is called *de Broglie wavelength.*

Thus the significance of de Broglie equation lies in the fact that it relates the particle character with the wave character of matter. Louis de-Broglie's concept of dual nature of matter finds application in the construction of electron microscope and in the study of surface structure of solids by electron diffraction. The de-Broglie's concept can be applied not only to electrons but also to other small particles like neutrons, protons, atoms, molecules, etc.

Significance of de-Broglie waves

The wave nature of matter, however, has no significance for objects of ordinary size because wavelength of the wave associated with them is too small to be detected. This can be illustrated by the following examples.

i) Suppose we consider an electron of mass 9.1 x 10^{-31} kg and moving with a velocity of 10^7 ms^{-1}. Its de-Broglie wavelength will be;

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{9.1 \times 10^{-31}\ \text{kg} \times 10^7\ \text{ms}^{-1}} = 0.727 \times 10^{-10}\text{m} = 7.27 \times 10^{-11}\text{m}$$

This value of λ can be measured by the method similar to that for thedetermination of wave length of X-rays.

ii) Let us now consider a ball of mass 10-2 kg moving with a velocity of 102 ms-1. Its de-Broglie wave length will be;

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{10^{-2}\ \text{kg} \times 10^2\ \text{ms}^{-1}} = 6.62 \times 10^{-34}\text{m}$$

This wavelength is too small to be measured, and hence de-Broglie relation has no significance for such a large object. Thus, de-Broglie concept is significant only for sub-microscopic objects in the range of atoms, molecules or smaller sub-atomic particles.

2.11 Heisenberg's Uncertainty Principle

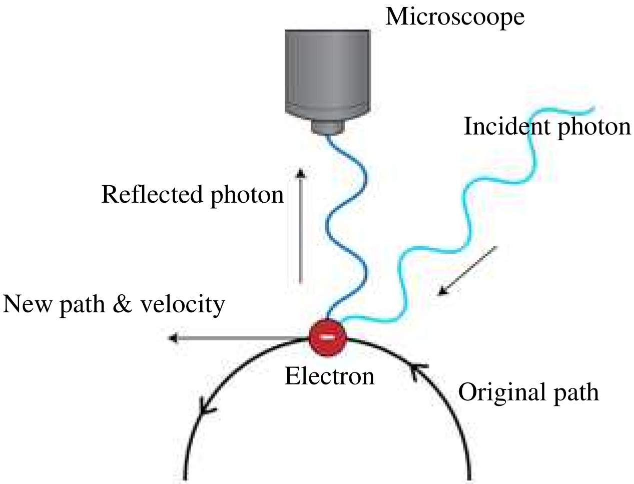
The consequences of de Broglie's concept are the Heisenberg uncertainty principle. According to him — *It is impossible* *to specify at any given moment both the position and momentum (velocity) of an electron."*

In view of Heisenberg uncertainty principle it is more correct to say that an electron is associated with a definite energy, i.e. it belongs to a definite energy levels and not that it belongs to a particular orbit. Mathematical representation of Heisenberg principle is,

$$\Delta x.\Delta p = h/2\pi$$

Let Δx is the uncertainty in position and $\Delta p$is the uncertainty in momentum, then these two quantities can be related as follows.

Explanation of Uncertainty Principle



Heisenberg uncertainty principle can be understood by following description.

1. For measuring the position and momentum of electron, a light phenomenon is used.
2. To know the position of electron, a photon of light is become strike on the electron.
3. The microscope is used to see the reflected photon.

4. Due to hitting with photon, both the position and momentum of electron is disturbed.
5. The electron has wave particle duality. It shows an intrinsic uncertainty position and momentum.
6. Due to small and light weight of electron, the incident photon changes the motion of electron after interacting with the electron.

2.12 Wave nature of an electron

It has been made clear that, if a substance is divided into finer and finerpieces, we reach molecules and atoms, then we realize that the atoms consist ofelectrons and nuclei. It has been clarified that matter is a collection of ultra-microscopic particles. Upto the 19th century, these particles were considered tomove obeying Newtonian mechanics and Maxwellian electromagnetism.However, this view point has become doubtful after the proposal of the Bohrmodelof the atomic structure (Bohr's quantum theory).

On the other hand, light had been considered to be electromagnetic waves.However, after the discovery of light quanta (photons), it was clarified that the light has wave nature at one time and particle nature at another time. Therefore,light has a kind of duality.

The idea of deBroglie wave nature waves or deBroglie matter waves isbased on the fact that light has both wave and particle nature. Hence particle likeelectron or proton can also be considered to be 'particle' with 'wave nature'**.**Einstein's relations which connect the particle and wave aspects in light quanta,would be satisfied for de Broglie matter wavesas well.

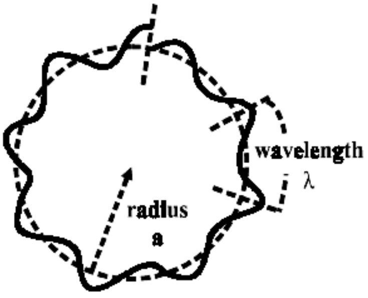
$$E = h\nu, \qquad p = \frac{h}{\lambda}$$

Therefore the relations, the above equation are often called **Einstein-de Broglie's relations.**

If we apply these relations to the case of the Bohr model of the hydrogenatom, we can well understand its possibility as follows. If we consider that theelectron in a hydrogen atom moves at constant speed along a circular orbit aroundthe nucleus (proton), the **quantum condition** in Bohr's quantum theory is writtenas the following equation. By using Einstein's relation p = h/λ in this equation, the quantumcondition is written

$$2\pi a = n\lambda \ (n = 1, 2, 3 \ldots.)$$

This equation means that the circumference of the circular orbit of the electronmust be an integral multiple of the wavelength of de Broglie wave. In other word,de-Broglie wave accompanying the motion of the electron should be continuous.Therefore, we can easily understand the quantum condition that determines thestationary states by considering the continuity of de Broglie waves (See thefollowing figure).



Bohr's quantum condition: The conditionfor stationary states

The circumference of the circular orbit ofthe electron should be an integral multiple ofthe wavelength of de Broglie wave,otherwise the wave cannot be smoothlycontinuous.

Energy of electron in an atom: By applying Schrodinger wave equationto hydrogen atom, the energy of electron (En) was found as:

$$E_{n} = -\frac{2\pi me^{4}}{n^{2}h^{2}}$$

Where n is the principal quantum number. This expression is same as Bohr's equation for energy of electron in a hydrogen atom. Substituting the values of m, e and h in the above relation (1), we get,

$$E_{n} = -\frac{1312}{n^{2}} \text{ kJmol}^{-1}$$

Significance of negative electronic energy

The energy of an electron at infinity is arbitrarily assumed to be zero. This state is called zero-energy state. When an electron moves and comes under the influence of nucleus, it does some work and spends its energy in this process. Thus, the energy of the electron decreases and it becomes less than zero i.e. it acquires a negative value.

2.13 The Schrödinger wave equation

In 1926, Schrodinger proposed a wave equation to describe the motion of the subatomic particle in a similar manner to that used for the macroscopic particles. In three dimensions, the Schrödinger equation is,

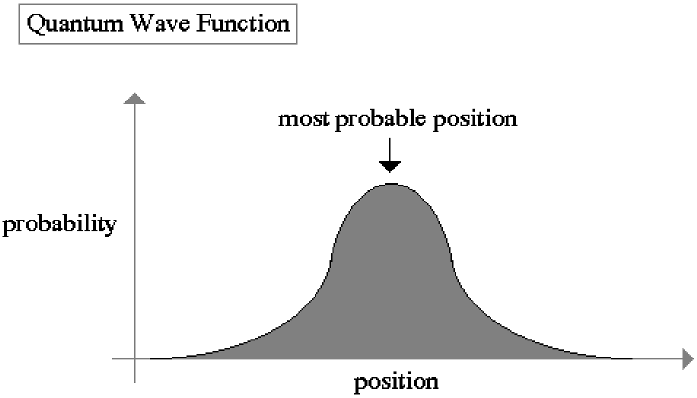
$$\frac{\partial^2\varphi}{\partial x^2}+\frac{\partial^2\varphi}{\partial y^2}+\frac{\partial^2\varphi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\varphi=0$$

Where m is the mass of the particle, *E* and *V* are the total energy and the potential energy of the particle, and *h* is the Planck's constant. Hence, the Schrödinger's equation is valid for a particle executing simple harmonic motion. This however does not prove the equation, but merely shows that it is applicable to material system.

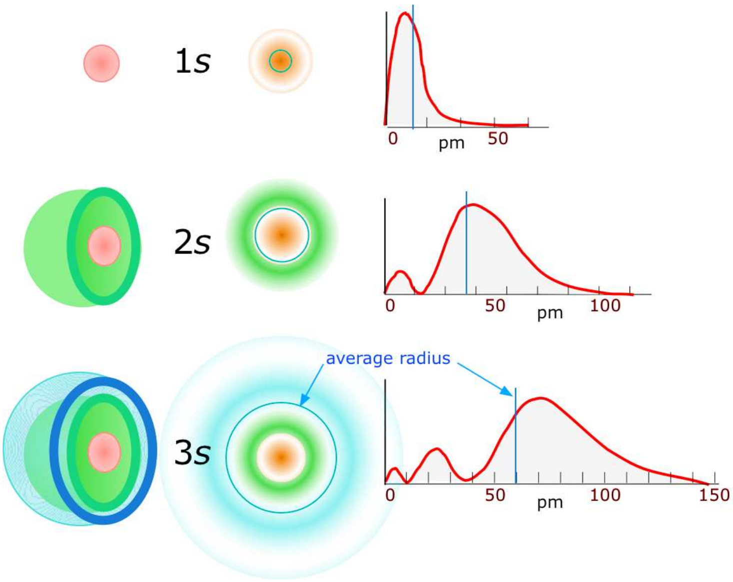
Significance of wave functions

The wave function used in the Schrödinger equation play the role of Newton's laws and conservation of energy in classical mechanics – i.e., it predicts the future behavior of a dynamic system. It predicts analytically and precisely the probability of the events or outcome. The detailed outcome depends on chance, but given a large number of events, the Schrödinger equation will predict the distribution of results.

Wave function**,** in quantum mechanics, is a variable quantity that mathematically describes the wave characteristics of a particle. It is designated by the Greek letter psi, Ψ. Each "particle" is represented by a wave function Ψ (position, time) such that Ψ*Ψ is equal to the probability of finding the particle at that position at that time. Following are the significance of the wave function Ψ.



Wave functions of various *s* orbitals are provided below:



Ψ – Does not have a physical meaning, but a simple mathematical function.

Ψ – It is a function of r, the distance from the nucleus.

Ψ – Allows energy calculations via the Schrödinger equation.

Ψ – Permits calculation of the effective average value (expectation value) of a given variable.

Ψ – For a free particle, it is a sine wave, implying a precisely determined momentum and a totally uncertain position.

Ψ – Contains all the measurable information about the particle.

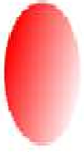
Ψ – Established the probability distribution in three dimensions.

Ψ – Continuous.

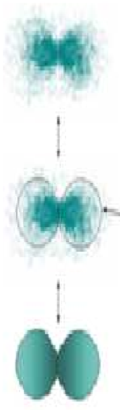
Ψ – Ψ*Ψ summed over all space = 1 (if the particle exists, the probability of finding it somewhere must be one).

The value of the wave function of a particle at a given point of space and time is related to the likelihood of the particle’s being there at the time. By analogy with waves such as those of sound, a wave function, may be thought of as an expression for the amplitude of the particle wave (or de Broglie wave), although for such waves amplitude has no physical significance. The square of the wave function, Ψ^2, however, does have physical significance: the probability of finding the particle described by a specific wave function Ψ at a given point and time is proportional to the value of Ψ^2.

The shape of thewave function when l=1 (p rbital)



The shape of the wave function when l=0 (s orbital)



The electron density in an electron wave

90% of electron density is inside the two lobes drawn on the electron waven=3,2 $\lambda_3 = 2\pi r3$

This balloons represent the region of space which contains 90% of electron density for this particular electron wave.Expected path

2.14 Orbit, Orbital and its importance

Orbit, orbital are not synonymous. An orbit, as proposed by Bohr, is a circular path around the nucleus in which the electron moves. A precise description of this path of the electron is impossible according to Heisenberg's Uncertainty principle. Bohr orbits, therefore, have no real meaning and their existence can never be demonstrated experimentally. An atomic orbital, on the other hand, is a quantum mechanical concept and refers to the one electron wave function Ψ in an atom. It is characterized by three quantum numbers (*n*, *l* and *m*) and its value depends upon the coordinates of the electron. Ψ has, by itself, no physical meaning. It is the square of the wave function i.e. $|\Psi|^2$ which has no physical meaning. $|\Psi|^2$at any point in an atom gives the value of probability density at that point. Probability density ($|\Psi|^2$)is the probability per unit volume and the product of $|\Psi|^2$ and a small volume (called a volume element) yields the probability of finding the electron in that volume [the reason for specifying a small volume is that $|\Psi|^2$ varies from one region to another in space but its value can be assumed to be constant within a small volume element]. The total probability of finding the electron in a given volume can then be calculated by the sum of all the products of $|\Psi|^2$ and the corresponding volume elements. It is thus possible to get the probability distribution of an electron in an orbital.

2.15 Orbital and quantum numbers

A large number of orbitals are possible in an atom. These orbitals are designated by a set of numbers known as quantum numbers. The quantum numbers are nothing but the details that are required to locate an electron in an atom. Qualitatively these orbitals can be distinguished by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly shape and orientation mean that there is more probability of finding the electron along certain directions than along others. Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labeled as *n, l* and $m_{l.}$

1. The principal quantum number (n)

The electrons inside an atom are arranged in different energy levels called electron shells or orbits. Each shell is characterized by a quantum number called principal quantum number. This is represented by the letter 'n' and 'n' can have values, 1,2,3,4 etc. The first level is also known as K level, Second as L level, third as M level, fourth as N level and so on. The first or K level is the orbit nearest to the nucleus and next one is second or L level and so on.

2. The subsidiary or azimuthal quantum number (*l*)

According to Sommerfield, the electron in any particular energy level could have circular path or a variety of elliptical paths about the nucleus resulting in slight differences in orbital shapes with slightly differing to the differences in the attraction exerted by the nucleus on the electron. This concept gave rise to the idea of the existence of sub-energy levels in each of the principal energy levels of the atom. This is denoted by the letter '*l*' and have values from 0 to n-1.

Thus, if,

$n = 1, l = 0$ only one value (one level only) *s* level.

$n = 2, l = 0$ and 1 (2 values or 2 sub- levels) *s* and *p* level.

$n = 3, l = 0, 1$ and 2 (3 values or 3 sub-levels) *s, p* and *d* level.

$n = 4, l = 0, 1, 2$ and 3 (4 values or 4 sub-levels) *s, p, d* and *f* level.

3. Magnetic quantum number (m)

In a strong magnetic field a sub-shell is resolved into different orientations in space. These orientations called orbitals have slight differences in energy. This explains the appearance of additional lines in atomic spectra produced when atoms emit light in magnetic field. Each orbital is designated by a magnetic quantum number m and its values depends on the value of '*l*'. The values are -'*l*' through zero to +'*l*' and thus there are $(2l+1)$ values.

Thus, when,

$l = 0, m = 0$ (only one value or one orbital)

$l = 1, m = -1, 0, +1$ (3 values or 3 orbitals)

$l = 2, m = -2, -1, 0, +1, +2$ (5 values or 5 orbitals)

l = 3, m = -3,-2, -1, 0, +1, +2, +3 (7 values or 7 orbitals).

The three quantum numbers labeling an atomic orbital can be used equally well to label electron in the orbital. However, a fourth quantum number, the spin quantum number, (*s*) is necessary to describe an electron completely.

4. Spin quantum number (*s*)

The electron in the atom rotates not only around the nucleus but also around its own axis and two opposite directions of rotation are possible (clock wise and anti-clock wise). Therefore the spin quantum number can have only two values +1/2 or –1/2. For each values of m including zero, there will be two values for *s*.

To sum up, the four quantum numbers provide the following information:

1. n identifies the shell, determines the size of the orbital and also to a large extent the energy of the orbit.
2. There are n subshells in the nth shell. *l*identifies the subshell and determines the shape of the orbital. There are (2*l*+1) orbitals of each type in a subshell i.e., one s orbital (*l*=0), three p orbitals (*l*=1), and five d orbitals (*l*=2) per subshell. To some extent *l* also determines the energy of the orbital in a multi-electron atom.
3. m*l*designates the orientation of the orbital. For a given value of *l*, m*l* has (2*l*+1) values, the same as the number of orbitals per subshell. It means that the number of orbitals is equal to the number of ways in which they are oriented.
4. ms refers to orientation of the spin of the electron.

Example 1: What is the total number of orbitals associated with the principal quantum number n = 3?

Solution

For n = 3, the possible values of *l* are 0,1 and 2. Thus, there is one 3s orbital (n = 3, *l* = 0 and m*l* = 0); there are three p orbitals (n = 3, *l* = 1 and m*l* = -1, 0, 1) there are five 3d orbitals (n = 3, *l* = 2, m*l* = -2, -1, 0, 1, 2). Therefore, the total number of orbitals is 1+3+5 = 9.

Example 2

Using s, p, d, f notations, describe the orbital with the following quantum numbers (a) n=2, *l* = 1 (b) n = 4, *l* = 0 (c) n = 5, *l* = 3 (d) n = 3, *l* = 2.

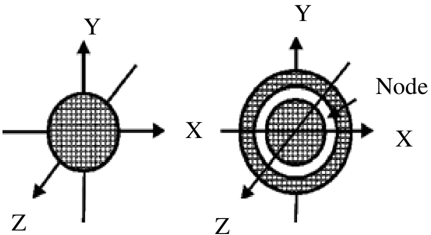
	n	*l*	orbital
(a)	2	1	2p
(b)	4	0	4s
(c)	5	3	5f
(d)	3	2	3d

2.16 Shapes of s, p and d orbitals

An orbital is the region of space around the nucleus within which the probability of finding an electron of given energy is maximum .The shape of thisregion (electron cloud) gives the shape of the orbital. The plot of angular wavefunctions or square of angular wave functions (probability functions) give us theshapes of orbitals.These two plots differ only slightly. Let us consider the individualshapes.

Shape of s-orbitals

For s-orbitals, when *l* = 0, the value of m is 0 i.e., there is only one possibleorientation. This means that the probability of finding an electron is the same in alldirections at a given distance from the nucleus. It should, therefore, be sphericalin shape. Hence all s-orbitals are non-directional and spherically symmetricalabout the nucleus.



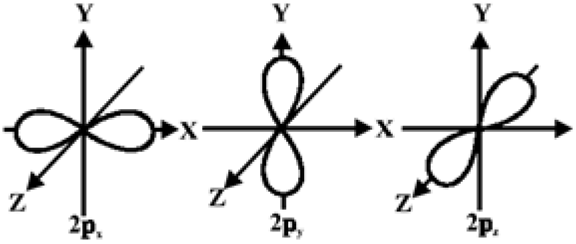
1s orbital 2s orbital

Shapes of 1s and 2s orbitals

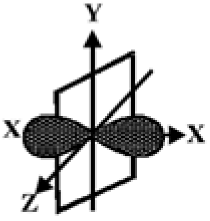
The size of an s-orbital depends upon value of the principal quantum numbern. Greater the value of 'n' larger is the size of the orbital.
An important feature of the 2s-orbital is that there is a spherical shell withinthis orbital where the probability of finding the electron is zero (nearly). This iscalled a node or nodal surface. In 2s orbital there is one spherical node. Thenumber of nodal surfaces or nodes in s-orbital of any energy level is equal to(n-1), where n is the principal quantum number.

Shape of p-orbitals

For p-subshell $l = 1$, there are three values of m namely -1, 0, +1. It means that p orbitals can have three possible orientations. These three p-orbitalsare equal in energy (degenerate state) but differ in their orientations. Eachp-orbital consists of two lobes symmetrical about a particular axis. Dependingupon the orientation of the lobes, these are denoted as $2p_x$, $2p_y$and $2p_z$, accordingly as they are symmetrical about X,Y and Z - axis respectively.



Shapes of $2p_x$, $2p_y$ and $2p_z$ orbitals



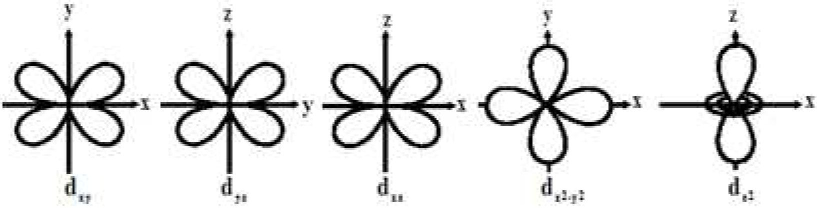
Nodal plane for $2p_z$ orbital

The lines in the figure represent the cross-section of the three dimensionalboundary surfaces of p-orbitals. The boundary surface means the surface whichencloses 90 percent of the dots representing the electrons. Two lobes of each porbitals are separated by a nodal plane (a plane having zero electron density). Forexample, for $2p_x$orbital, YZ plane is the nodal plane x.

Thus, p-orbitals have dumb-bell shape and have directional character. Theprobability of finding the electron is equal in both the lobes. The p-orbitals ofhigher energy levels have similar shapes although their size are bigger.

Shape of d-orbitals

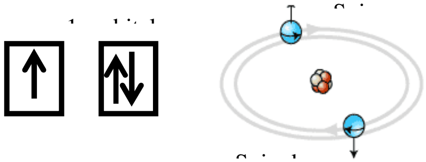
For d-subshell, $l = 2$, there are five values of m namely -2, -1, 0, 1, 2. It means d- orbitals can have five orientations. These are represented by d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}; for example, $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$ and $3d_{z^2}$. The d_{xy}, d_{yz}, and d_{zx} orbitals have same shape i.e., clover leaf shape but they lie in XY, YZ and ZXplanesrespectively.The d_{z^2} orbital is symmetrical about Z-axis and has a dumb - bell shape with a doughnut shaped electron cloud in the center. The $d_{x^2-y^2}$ orbital is also clovar leaf shaped but its leaves are directed along the X and Y- axis. The reason for the presence of four lobes in any nd orbital lies in the fact thatthe d - orbitals have two nodes, and hence two changes in algebraic sign of ψ,which lead to four lobes.



Shapes of d-orbitals

2.17 Pauli's exclusion principle

The Pauli Exclusion Principle states that, in an atom, no two electrons can have the **same** four electronic quantum numbers.

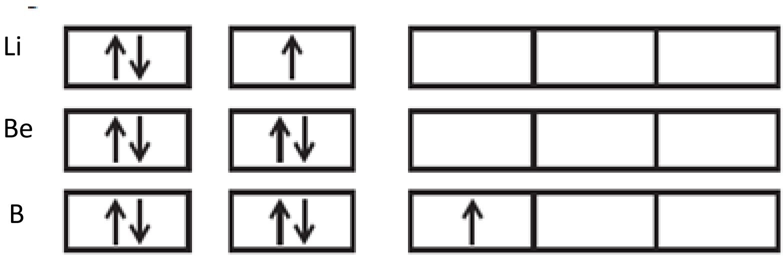


The two electrons in an orbital may have the same *n*, *l*, and *m* values, but atleast they differ in the value of spin quantum number.That means one of the electron in the orbital would spin up (+1/2) and the other would spin down (-1/2).

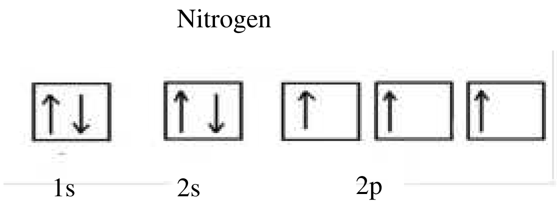
2.18 Hund’s rule

Hund's Rule states that: *„Every orbital in a sublevel is singly occupied before any orbital is doubly occupied. All of the electrons in singly occupied orbitals have the same spin (to maximize total spin)”.*

When assigning electrons in orbitals, each electron will first fill all the orbitals with similar energy (also referred to as degenerate) before pairing with another electron in a half-filled orbital. Atoms at ground states tend to have as many unpaired electrons as possible. When visualizing this process, think about how electrons are exhibiting the same behavior as the same poles on a magnet would if they came into contact; as the negatively charged electrons fill orbitals they first try to get as far as possible from each other before having to pair up.



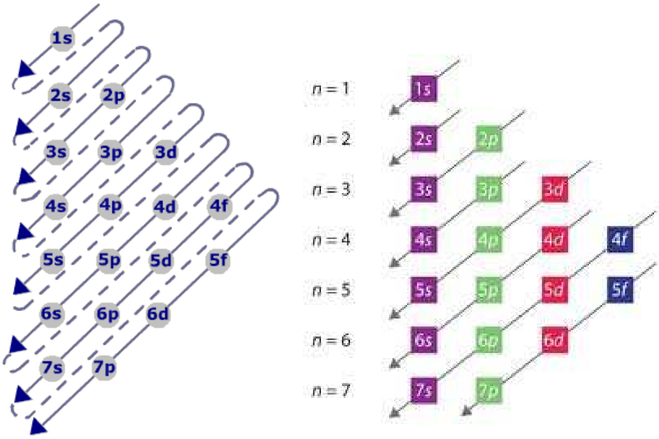
Example: Nitrogen atom



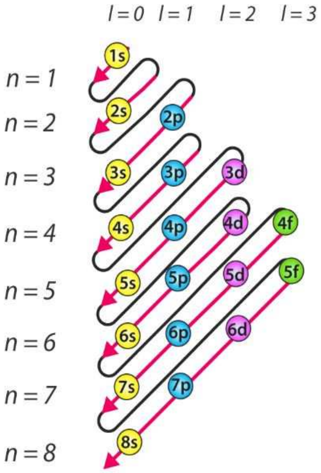
If we look at the correct electron configuration of the nitrogen (Z = 7) atom: $1s^2\ 2s^2\ 2p^3$. We can clearly see that *p* orbitals are half filled as there are three electrons and three *p* orbitals. This is because the three electrons in the 2*p* subshell will fill all the empty orbitals first before pairing with electrons in them. Keep in mind that elemental nitrogen is found in nature typically as di-nitrogen, N_2, which would require the filling in of molecular orbitals instead of atomic orbitals as demonstrated above.

2.19 Sequence of energy levels (Aufbau principle)

Aufbau comes from the German word "Aufbauen" which means "to build". In essence when writing electron configurations we are building up electron orbitals as we proceed from atom to atom. As we write the electron configuration for an atom, we will fill the orbitals in order of increasing atomic number.



"The Aufbau principle originates from the Pauli's exclusion principle which says that no two fermions *(e.g., electrons) in an atom can have the same set of quantum numbers, hence they have to "pile up" or "build up" into higher energy levels".*



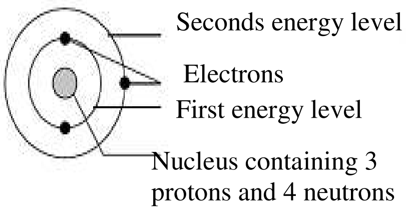
How the electrons build up is a topic of electron configurations. If we follow the pattern across a period from B (Z=5) to Ne (Z=10) the number of electrons increase and the subshells are filled. Here we are focusing on the p subshell in which as we move towards Ne, the p subshell becomes filled.

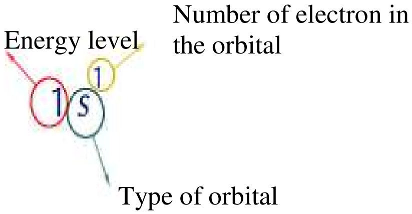
2.20 Electronic configuration of atoms

It is known that atoms consist of a positively charged nucleus with protons and neutrons in it. Negatively charged particles called electrons constantly revolve around the nucleus in set of orbits. The electron orbits are numbered as 1, 2, 3, etc., starting from the orbit closest to the nucleus. These orbits are also called K, L, M, Nshells, as mentioned in the atom model proposed by Niel's Bohr. The maximum number of electrons in an orbit is given by $2n^2$, where nis the orbit number.

For the first orbit n = 1,

and the number of electrons it can hold is 2 x 1^2 = 2electrons.
For the second orbit n = 2,
and it can hold a maximum of 2 x 2^2 = 8electrons.
For the third orbit n = 3,
and it can hold a maximum of 2 x 3^2 = 18electrons.





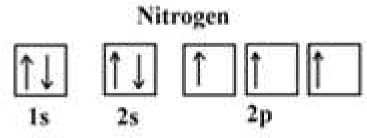
It must be understood that the second orbit begins only after the first orbit is filled. The third orbit begins to fill only after the second orbit is filled. But the fourth orbit commences even before the third orbit is completely filled. The reason for this lies in the concept of quantum numbers. Thus the term electronic configuration or electronic structure refers to the way the electrons are arranged around the nucleus. Most of the properties of elements and their compounds depend on their electronic configurations.

To write electronic configuration, the principal quantum number of the shells must be known. This number describes the number of orbits present in the atom.

The electronic configuration of atoms can be represented in two

With orbitals or Ways S, p, d or f

With orbital picture



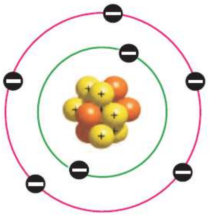
Let us consider sodium atom. Atomic number of **sodium is 11 i.e.** Total number of electrons in sodium = **11**

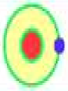
Orbit wise distribution of electrons in a sodium atom

Orbit Number of electrons

1. **(K-Shell)**	$2n^2$ =	2×1^2	= 2 electrons
2. **(L-Shell)**	$2n^2$ =	2×2^2	= 8 electrons
3. **(M-Shell)**	Remaining		= 1 electron

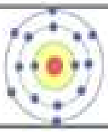
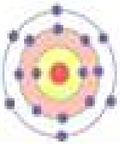
Thus the electronic distribution in sodium is **2, 8, 1**.Similarly the electronic configuration of nitrogen is **2, 5**. The electronic configurations of some of the elements with their distributions in orbitals are shown below:



Element	Atomic Number	Electronic dot structure	Electron distribution
Hydrogen H	1		1
Helium He	2		2
Lithium Li	3		2,1
Beryllium Be	4		2,2
Boron B	5		2,3

Element	Atomic Number	Electronic dot structure	Electron distribution
Carbon C	6		2,2
Nitrogen N	7		2,5
Oxygen O	8		2,6
Fluorine F	9		2,7
Neon N	10		2,8

Element	Atomic Number	Electronic dot structure	Electron distribution
Sodium Na	11		2,2,1
Magnesium Mg	12		2,8,2
Aluminium Al	13		2,8,3
Silicon Si	14		2,8,4

Element	Atomic Number	Electronic dot structure	Electron distribution
Phosphorus P	15		2,2,5
Sulphur S	16		2,2,6
Chlorine Cl	17		2,2,7
Argon Ar	18		2,2,8

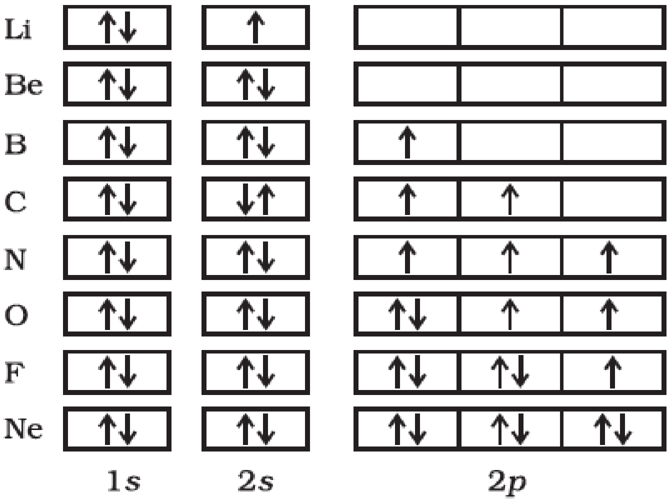
The distribution of electrons into orbitals ofan atom is called its electronicconfiguration. If one keeps in mind the basicrules which govern the filling of differentatomic orbitals, the electronic configurationsof different atoms can be written very easily.The electronic configuration of differentatoms can be represented in two ways. Forexample:

(i) $s^a p^b d^c$ ...... notation

(ii) Orbital diagrams *p d*

In the first notation, the subshell isrepresented by the respective letter symboland the number of electrons present in thesubshell is depicted, as the super script, likea, b, c, etc. The similar subshell representedfor different shells is differentiated by writingthe principal quantum number before therespective subshell. In the second notationeach orbital of the subshell is represented bya box and the electron is represented by anarrow (↑) a positive spin or an arrow (↓) anegative spin. The advantage of second notationover the first is that it represents all the fourquantum numbers.

The hydrogen atom has only one electronwhich goes in the orbital with the lowestenergy, namely 1*s*. The electronicconfiguration of the hydrogen atom is $1s^1$meaning that it has one electron in the 1*s*orbital. The second electron in helium (He)can also occupy the 1*s* orbital. Itsconfiguration is, therefore, $1s^2$. As mentionedabove, the two electrons differ from each otherwith opposite spin, as can be seen from theorbital diagram.The third electron of lithium (Li) is notallowed in the 1*s* orbital because of Pauli's exclusion principle. It, therefore, takes thenext available choice, namely the 2*s* orbital.The electronic configuration of Li is $1s^2 2s^1$.The 2*s* orbital can accommodate one moreelectron. The configuration of beryllium (Be) atom is, therefore, $1s^2 2s^2$.In the next six elements-boron(B, $1s^2 2s^2 2p^1$), carbon (C, $1s^2 2s^2 2p^2$), nitrogen(N, $1s^2 2s^2 2p^3$), oxygen (O, $1s^2 2s^2 2p^4$), fluorine(F, $1s^2 2s^2 2p^5$) and neon (Ne, $1s^2 2s^2 2p^6$), the2*p* orbitals get progressively filled. Thisprocess is completed with the neon atom. Theorbital picture of these elements can berepresented as follows:

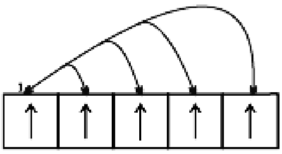


The electronic configuration of the elementssodium (Na, $1s^22s^22p^63s^1$) to argon(Ar,$1s^22s^22p^63s^13p^6$), follow exactly the same pattern as the elements from lithium to neonwith the difference that the 3*s* and 3*p* orbitalsare getting filled now. This process can besimplified if we represent the total number ofelectrons in the first two shells by the nameof element neon (Ne). The electronicconfiguration of the elements from sodium toargon can be written as (Na, [Ne]$3s^1$) to (Ar,[Ne] $3s^23p^6$). The electrons in the completelyfilled shells are known as core electrons andthe electrons that are added to the electronicshell with the highest principal quantumnumber are called valence electrons. Forexample, the electrons in Ne are the coreelectrons and the electrons from Na to Ar arethe valence electrons. In potassium (K) andcalcium (Ca), the 4*s* orbital, being lower inenergy than the 3*d* orbitals, is occupied byone and two electrons respectively.A new pattern is followed beginning withscandium (Sc). The 3*d* orbital, being lower inenergy than the 4*p* orbital, is filled first.Consequently, in the next ten elements,scandium (Sc), titanium (Ti), vanadium (V),chromium (Cr), manganese (Mn), iron (Fe),cobalt (Co), nickel (Ni), copper (Cu) and zinc(Zn), the five 3*d* orbitals are progressivelyoccupied. We may be puzzled by the fact thatchromium and copper have five and tenelectrons in 3*d* orbitals rather than four andnine as their position would have indicatedwith two-electrons in the 4s orbital. Thereason is that fully filled orbitals and half-filledorbitals have extra stability (that is,lower energy). Thus p^3, p^6, d^5, d^{10},f^7, f^{14} etc.configurations, which are either half-filled orfully filled, are more stable. Chromium and copper therefore adopt the d^5 and d^{10}configuration. With the saturation of the 3*d* orbitals, thefilling of the 4*p* orbital starts at gallium (Ga)and is complete at krypton (Kr). In the nexteighteen elements from rubidium (Rb) to xenon(Xe), the pattern of filling the 5*s*, 4*d* and 5*p*orbitals are similar to that of 4*s*, 3*d* and 4*p*orbitals as discussed above. Then it is theturn of the 6*s* orbital. In Caesium (Cs) and thebarium (Ba), this orbital contains one and twoelectrons, respectively. Then from lanthanum(La) to mercury (Hg), the filling up of electronstakes place in 4*f* and 5*d* orbitals. After this,filling of 6*p*, then 7*s* and finally 5*f* and 6*d*orbitals takes place. The elements afteruranium (U) are all short-lived and all of themare produced artificially. One may ask what is the utility of knowingthe electron configuration? The modernapproach to the chemistry, infact, dependsalmost entirely on electronic distribution tounderstand and explain chemical behavior.For example, questions like why two or moreatoms combine to form molecules, why someelements are metals while others are nonmetals,why elements like helium and argonare not reactive but elements like the halogensare reactive, find simple explanation from theelectronic configuration. These questions haveno answer in the Daltonian model of atom. Adetailed understanding of the electronicstructure of atom is, therefore, very essentialfor getting an insight into the various aspectsof modern chemical knowledge.

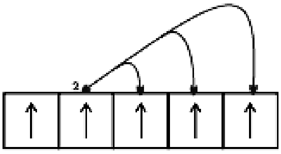
Stability of Completely Filled and Half Filled Subshells

The ground state electronic configuration ofthe atom of an element always correspondsto the state of the lowest total electronicenergy. The electronic configurations of mostof the atoms follow the basic rules provided in the earlier discussion. However, in certain elementssuch as Cu, or Cr, where the two subshells(4*s* and 3*d*) differ slightly in their energies,an electron shifts from a subshell of lowerenergy (4*s*) to a subshell of higher energy (3*d*),provided such a shift results in all orbitals ofthe subshell of higher energy getting eithercompletely filled or half filled. The valenceelectronic configurations of Cr and Cu,therefore, are $3d^5 4s^1$ and $3d^{10} 4s^1$ respectivelyand not $3d^4 4s^2$ and $3d^9 4s^2$. It has been foundthat there is extra stability associated withthese electronic configurations.

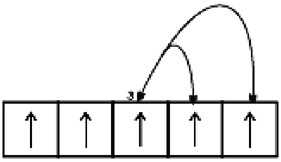
The completely filled and completely half-filled sub-shells are stable due to thefollowing reasons:



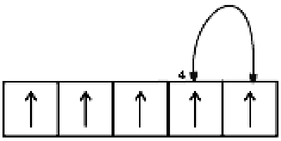
4 exchange by electron 1



3 exchange by electron 2



2 exchange by electron 3



1 exchange by electron 4

1. Symmetrical distribution ofelectrons:

It is well known that symmetryleads to stability. The completely filled orhalf-filled subshells have symmetricaldistribution of electrons in them and aretherefore more stable. Electrons in thesame subshell (here *3d*) have equal energybut different spatial distribution.

Consequently, their shielding of oneanotheris relatively small and theelectrons are more strongly attracted bythe nucleus.

2. Exchange Energy:

The stabilizingeffect arises whenever two or moreelectrons with the same spin are presentin the degenerate orbitals of a subshell.These electrons tend to exchange theirpositions and the energy released due tothis exchange is called exchange energy. These electrons tend to exchange theirpositions and the energy released due tothis exchange is called exchange energy.The number of exchanges that can takeplace is maximum when the subshell iseither half-filled or completely filled. As a result the exchange energy ismaximum and so is the stability.You may note that the exchangeenergy is at the basis of Hund's rule thatelectrons which enter orbitals of equalenergy have parallel spins as far aspossible. In other words, the extrastability of half-filled and completely filledsubshell is due to: (i) relatively smallshielding, (ii) smaller coulombic repulsionenergy, and (iii) larger exchange energy.(Possible exchange of d^5 electrons are shown in the above figure).

Chapter III

Periodic Classification of Elements and s block elements

Brie history of periodic classification - IUPAC periodic table and IUPAC nomenclature of elements with atomic number greater than 100 – Electronic configuration and periodic table - Periodicity of properties - Anomalous periodic properties of elements. Review of periodic properties - Calculation of atomic radii – Calculation of ionic radii - Method of determination of Ionization potential - Factors affecting ionization potential - Method to determine the electron affinity - Factors affecting EA - Various scales on electro negativity values.

s Block elements: Isotopes of hydrogen - Nature and application - Ortho and para hydrogen - Heavy water - Hydrogen peroxide - Liquid hydrogen as a fuel - Alkali metals - General characteristics - Chemical properties - Basic nature of oxides and hydroxides - Extraction of lithium and sodium - Properties and uses - General characteristics - Magnesium - Compounds of alkaline earth metals.

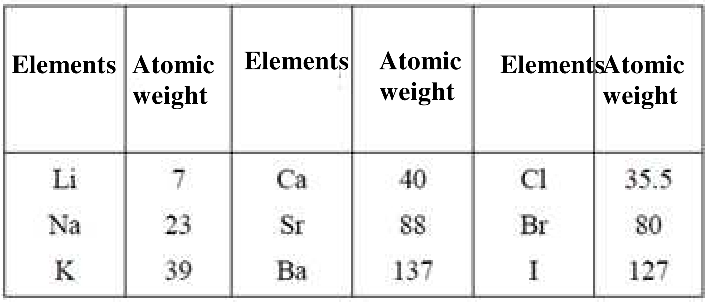
3.01 Brief history of periodic classification

More than one hundred and nine elements are known today. Theperiodic table of elements is an important landmark in the history ofchemistry. It would be difficult to study individually the chemistry of allthe elements and their numerous compounds. The periodic table providesa systematic and extremely useful framework for organizing a lot ofinformation available on the chemical behavior of the elements into afew simple and logical patterns. This gave rise to the necessity ofclassifying the elements into various groups or families having similarproperties. This classification has resulted in the formulation of periodictable. Periodic table may be defined as the arrangements of variouselements according to their properties in a tabular form.

All earlier attempts on the classification of elements were based onatomic mass. Several chemists have for long tried to classify the elementsand to find patterns in their properties.

Dobereiner's Triads

In 1829, *John Dobereiner* (German Chemist) classified elementshaving similar properties into groups of three. These groups were calledtriads. According to this law when elements are arranged in the order ofincreasing atomic mass in a triad, the atomic mass of the middle elementwas found to be approximately equal to the arithmetic mean of the othertwo elements.



Elements	Atomic weight	Elements	Atomic weight	Elements	Atomic weight
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

For example lithium, sodium and potassium constitutedone triad. However, only a limited number of elements could be groupedinto triads.

Newlands Law of Octaves

In 1865, John Newlands (English Chemist) observed that if the elements were arranged in order of their increasing atomic weights, the eighth element starting from a given one, possessed properties similar to the first, like the eighth note in an octave of music. He called it the law of octaves. It worked well for the lighter elements but failed when applied to heavier elements.

Lother-Meyer's Arrangement

In 1869, J. Lother-Meyerin Germany gave a more detailed and accurate relationship among the elements. Lother-Meyer plotted atomic volumes versus atomic weights of elements and obtained a curve. He pointed out that elements occupying similar positions in the curve possessed similar properties.

Mendeleev's Periodic Table

In 1869, Dimitriv Mendeleev (Russian Chemist) arranged the 63 chemical elements, then known, according to their increasing order of atomic weights. He gave his famous scheme of the periodic classification of elements known as the periodic law. The law states that "the properties of the elements are the periodic function of their atomic weights". It means that when elements are arranged in order of increasing atomic weights, the elements was similar properties recur after regular intervals. On the basis of this periodic law Mendeleev constructed a periodic table in such a way that the elements were arranged horizontally in order of their increasing atomic weights. Mendeleev, while studying his periodic table had found that in certain cases the regularity in behavior between two succeeding elements was not observed. In order to overcome this he had kept gaps between such elements and had predicted that the gaps would be filled by new elements, to be discovered in future, For example, both gallium and germanium were not discovered at the time when Mendeleev proposed the periodic table. Mendeleev named these elements as eka-aluminium and eka-silicon because he believed that they would be similar to aluminium and silicon respectively. These elements were discovered later and Mendeleev's prediction proved remarkably correct. The discoveries / synthesis of new elements have continued even to the present day, raising their number to 120. The elements with atomic numbers upto 92 (i.e. uranium) are found in nature. The rest known as transuranium elements have been synthesized in the laboratories, which are highly unstable. They decay radioactively.

The modified periodic table is essentially similar to that of Mendeleev with a separate column added for noble gases, which were not discovered until the closing years of the nineteenth century. The general plan of the modified Mendeleev's periodic table is improved.

The Mendeleev's modified periodic table consists of:

(1) Nine vertical columns called groups. These are numbered from I to VIII and zero. (The members of zero

groups were not discovered at the time of Mendeleev). Each group from I to VII is further sub-divided into two sub-groups designated as A and B. Group VIII consists of three sets, each one containing three elements. Group zero consists of inert gases.

(2) Seven horizontal rows, called periods. These are numbered from 1 to 7. First period contains two elements. Second and third periods contain eight elements each. These periods are called short periods. Fourth and fifth contains eighteen elements each. These periods are called long periods. Sixth period contains thirty two elements and is called longest period. Seventh period is incomplete and contains nineteen elements according to early classification.

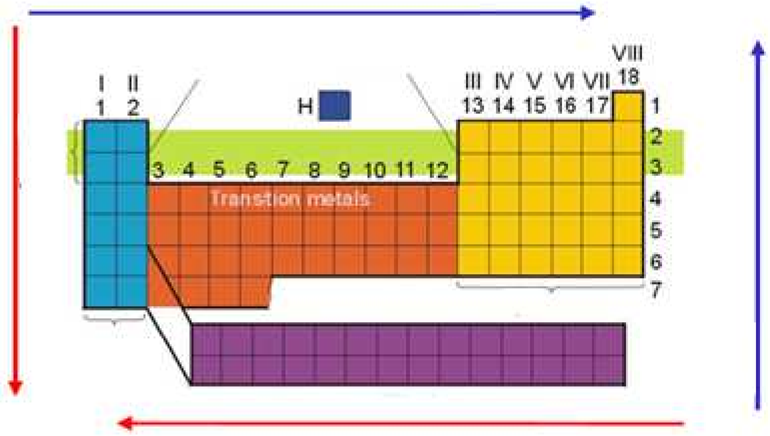
3.02 IUPAC periodic table and IUPAC nomenclature of elements with atomic number greater than 100

Modern Periodic Law

In 1913, a British Physicist Henry Moseley showed that the atomic number is a more fundamental property of an element than its atomic weight. This observation led to the development of modern periodic law. The modern periodic law states that "the physical and chemical properties of the elements are periodic function of their atomic numbers."

This means that when the elements are arranged in order of increasing atomic numbers, the elements with similar properties recur after regular intervals. The periodic repetition is called periodicity. The physical and chemical properties of the elements are related to the arrangement of electrons in the outermost shell. Thus, if the arrangement of electrons in the outermost shell (valence shell) of the atoms is the same, their properties will also be similar. For example, the valence shell configurations of alkali metals show the presence of one electron in the *s* orbital of their valence shells.

Similar behavior of alkali metals is attributed to the similar valence shell configuration of their atoms. Similarly, if we examine the electronic configurations of other elements, we will find that there is repetition of the similar valence shell configuration after certain regular intervals with the gradual increase of atomic number. Thus we find that the periodic repetition of properties is due to the recurrence of similar valence shell configuration after certain intervals. It is observed that similarity in properties is repeated after the intervals of 2, 8, 18, or 32 in their atomic numbers.



Long form of the Periodic Table:

The periodic table is constructed on the basis of repeating electronic configurations of the atoms when they are arranged in the order of increasing atomic numbers. Readers are advised to follow the periodic table closely while studying the structural features of the long form of the periodic Table.

Structural Features of the Long form of the periodic Table:

The long form of the periodic table consists of horizontal rows called periodsand vertical columns called groups.

Periods:

In terms of electronic structure of the atom, a periodconstitutes a series of elements whose atoms have the same number of electron shell i.e., principal quantum number (n). There are seven periodsand each period starts with a different principal quantum number.

The first period corresponds to the filling of electrons in the firstenergy shell (n = 1). Now this energy level has only one orbital (1*s*) and,therefore, it can accommodate two electrons. This means that there canbe only two elements (hydrogen, $1s^1$ and helium, $1s^2$) in the first period.

The second period starts with the electron beginning to enter the second energy shell (n = 2). Since there are only four orbitals (one 2*s*andthree 2*p* orbitals) to be filled, it can accommodate eight electrons.

Thus, second period has eight elements in it. It starts with lithium (Z = 3)in which one electron enters the 2s-orbital. The period ends with neon(Z = 10) in which the second shell is complete ($2s^2 2p^6$).

The third period begins with the electrons entering the third energy shell (n = 3). It should be noted that out of nine orbitals of this energy level (one *s*, three *p* and five *d*) the five 3*d*-orbitals have higher energythan 4s-orbitals. As such only four orbitals (one 3*s* and three 3*p*)corresponding to n = 3 are filled before fourth energy level begins to befilled. Hence, third period contains only eight elements from sodium(Z = 11) to argon (Z = 18).

The fourth period corresponding to n = 4 involves the filling of one4*s* and three 4p-orbitals (4*d* and 4*f* orbitals have higher energy than 5*s*orbitaland are filled later). In between 4s and 4p-orbitals, five 3*d*-orbitalsare also filled which have energies in between these orbitals. Thus,altogether nine orbitals (one 4s, five 3d and three 4p) are to be filled andtherefore, there are eighteen elements in fourth period from potassium(Z = 19) to krypton (Z = 36). The elements from scandium (Z = 21) tozinc (Z = 30) are called 3d- transition series.

The fifth period beginning with 5*s*-orbital (n=5) is similar to fourth period. There are nine orbitals (one 5s, five 4d and three 5p) to be filledand, therefore, there are eighteen elements in fifth period from rubidium (Z = 37) to xenon (Z = 54).

The sixth period starts with the filling of 6*s*-orbitals (n= 6). There are sixteen orbitals (one 6*s*, seven 4*f*, five 5*d*, and three 6*p*) in which fillingof electrons takes place before the next energy level starts. As such thereare thirty two elements in sixth period starting from cesium (Z = 55) andending with radon (Z = 86). The filling up of 4f orbitals begins withcerium (Z = 58) and ends at lutetium (Z = 71). It constitutes the first finnertransition series which is called lanthanide series.

The seventh period begins with 7s-orbital (n = 7). It would also have contained 32 elements corresponding to the filling of sixteen orbitals(one *7s*, seven *5f*, five *6d* and three *7p*), but it is still incomplete. Atpresent there are 23 elements in it. The filling up of 5f-orbitals begins with thorium (Z = 90) and ends up at lawrencium (Z = 103). It constitutessecond *f*-inner transition series which is called actinide series. It mostlyincludes man made radioactive elements. In order to avoid undueextension of the periodic table the 4f and 5f-inner transition elements areplaced separately.The number of elements and the corresponding orbitals being filledare given below.

Period	Principal Valence shell (=n)	Orbitals being filled up	Electrons to be accomodated	Number of electrons
First	n=1	1s	2	2
Second	n=2	2s, 2p	2+6	8
Third	n=3	3s, 3p	2+6	8
Fourth	n=4	4s, 3d, 4p	2+10+6	18
Fifth	n=5	5s, 4d, 5p	2+10+6	18
Sixth	n=6	6s, 4f, 5d, 6p	2+14+10+6	32
Seventh	n=7	7s, 5f, 6d, 7p	2+14+10+6	32

The first three periods containing 2, 8 and 8 elements respectively are called short periods, the next three periods containing 18, 18 and 32 elements respectively are called long periods.

Groups

A vertical column in the periodic table is known as group. A group consists of a series of elements having similar configuration of the outerenergy shell. There *are* eighteen vertical columns in long from of theperiodic table. According to the recommendations of the **InternationalUnion of Pure and Applied Chemistry** (IUPAC), these groups arenumbered from 1 to 18. Previously, these were numbered from I to VII asA and B, VIII and zero groups elements. The elements belonging to thesame group are said to constitute a family. For example, elements ofgroup 17 (VII A) constitute halogen family.

IUPAC Nomenclature for Elements with Z > 100

The elements beyond uranium (Z = 92) are all synthetic elements and are known as transuranium elements. The elements beyond fermium areknown as transfermium elements. These elements fermium (Z = 100),mendelevium (Z = 101), nobelium (Z = 102) and lawrencium (Z = 103)arenamed after the names of famous scientists. Although names andsymbols to many of these elements have been assigned by these are stillnot universally accepted. Also some of these elements have beenassigned two names/symbols. For example, element with atomic number104 is called either Kurchatovium (Ku) or Rutherfordium (Rf) whileelement with atomic number 107 is called Neilsbohrium (Ns) or Borium(Bh). But the following elements have been assigned only one officialname. For example element with atomic number 105 is called Dubnium,with atomic number 106 as Seaborgium, with atomic number 108 asHassnium and with atomic number 109 is named as Meiternium. Toovercome all these difficulties, IUPAC nomenclature has beenrecommended for all the elements with Z > 100. It was decided byIUPAC that the names of elements beyond atomic number 100 shoulduse Latin words for their numbers. The names of these elements arederived from their numerical roots.

	0	1	2	3	4	5	6	7	8	9
Numerical roots	nil	un	bi	tri	quad	pent	hex	sept	octen	

Atomic number	Name of the element	Symbol
101	Unnilunnium	Unu
102	Unnilbium	Unb
103	Unniltrium	Unt
104	Unnilquadium	Unq
105	Unnilpentium	Unp
106	Unnilhexium	Unh
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilennium	Une
110	Ununnilium	Uun
111	Unununium	Uuu
112	Ununbium	Uub
113	Ununtrium	Uut
114	Ununquadium	Uuq
115	Ununpentium	Uup
116	Ununhexium	Uuh
117	Ununseptium	Uus
118	Ununoctium	Uuo
119	Ununennium	Uue
120	Unbinilium	Ubn

3.03 Electronic configuration and periodic table

There is a close connection between the electronic configuration of the elements and the long form of the Periodic Table. We have already learnt that an electron in an atom is characterized by a set of four quantum numbers and the principal quantum number (n) defines the main energy level known as the Shell. The electronic configuration of elements can be best studied in terms of variations in periods and groups of the periodic table.

(a) Electronic Configuration in periods

Each successive period in the periodic table is associated with thefilling up of the next higher principal energy level (n=1, n=2,etc.). It canbe readily seen that the number of elements in each period is twice thenumber of atomic orbitals available in the energy level that is beingfilled. The first period starts with the filling of the lowest level (1s) andhas thus the two elements-hydrogen ($1s^1$) and helium ($1s^2$) when the firstshell (K) is completed. The second period starts with lithium and thethird electron enters the 2s orbital. The next element, beryllium has fourelectrons and has the electronic configuration $1s^22s^2$. Starting from thenext element boron, the 2p orbitals are filled with electrons when the Lshell is completed at neon ($2s^22p^6$). Thus there are 8 elements in thesecond period. The third period (n=3) begins at sodium, and the addedelectron enters a 3s orbital. Successive filling of 3s and 3p orbitals givesrise to the third period of 8 elements from sodium to argon.

The fourth period (n=4) starts at potassium with the filling up of 4sorbital. Now you may note that before the 4p orbital is filled, filling upof 3d orbitals becomes energetically favourable and we come across theso-called 3d Transition Series of elements. The fourth period ends atkrypton with the filling up of the 4p orbitals. Altogether we have 18elements in this fourth period. The fifth period (n=5) beginning withrubidium is similar to the fourth period and contains the 4d transitionseries starting at yttrium (Z=39). This period ends at xenon with fillingup of the 5p orbitals. The sixth period (n=6) contains 32 elements andsuccessive electrons enter 6s, 4f, 5d and 6p orbitals, in that order. Fillingup of the 4f orbitals begins with cerium (Z=58) and ends at lutetium(Z=71) to give the 4f-inner transition series, which is called theLanthanoid Series. The seventh period (n=7) is similar to the sixth period with the successive filling up of the 7s, 5f, 6d and 7p orbitals andincludes most of the man-made radioactive elements. This period willend at the element with atomic number 118 which would belong to thenoble gas family. Filling up of the 5f orbitals after actinium (Z=89) givesthe 5f-inner transition series known as the Actinoid Series. The 4f- and5f- transition series of elements are placed separately in the periodic tableto maintain its structure and to preserve the principle of classification bykeeping elements with similar properties in a single column.

(b) Groupwise/electronic configuration

Elements in the same vertical column or group have similar electronic configuration, have the same number of electrons in the outerorbitals, and similar properties. Group 1 (the alkali metals) is anexample.Thus it can be seen that the properties of an element have periodicdependence upon the atomic number and not on relative atomicmass (Table).

Atomic number	Symbol	Electronic configuration
3	Li	$1s^2 2s^1$ or [He] $2s^1$
11	Na	$1s^2 2s^2 2p^6 3s^1$ or [Ne]$3s^1$
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or [Ar]$4s^1$
37	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$ or [Kr]$5s^1$
55	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$ or [Xe]$6s^1$

Types of elements: *s-, p-,d-, f-* Blocks

The Aufbau principle and the electronic configuration of atomsprovide a theoretical foundation for the periodic classification. Theelements in a vertical column of the periodic table constitute a group orfamily and exhibit similar chemical behavior. Strictly, helium belongsto the s-block but its positioning in the p-block along with other group 18elements is justified because it has a completely filled valence shell ($1s^2$)and as a result, exhibits properties characteristic of other noble gases.The other exception is hydrogen. It has a lone s-electron and hence canbe placed in group 1 (alkali metals). It can also gain an electron toachieve a noble gas arrangement and hence it can behave similar to agroup 17 (halogen family) elements. Because it is a special case, weshall place hydrogen separately at the top of the Periodic Table. We willbriefly discuss the salient features of the four types of elements markedin the periodic table.

The *s*-Block Elements

The elements of group 1 (alkali metals) and group 2 (alkaline earthmetals) which have ns^1 and ns^2 outermost electronic configuration belongto the *s*-block elements**.** They are all reactive metals with low ionizationenthalpies. They lose the outermost electron(s) readily to form 1+ (in thecase of alkali metal) or 2+ ions (in the case of alkaline earth metals). Themetallic character and the reactivity increase as we go down the group.The compounds of the *s*-block elements, with the exception of those ofberyllium are predominantly ionic.

The *p*-Block Elements

The *p*-Block Elementscomprise those belonging to groups 13 to 18 and together with the s-block elements are called the RepresentativeElements or Main Group Elements**.** The outermost electronicconfiguration varies from ns^2np^1 to ns^2np^6 in each period. Each periodends in a noble gas with a closed shell ns^2np^6 configuration. All theorbitals in the valence shell of the noble gasesare completely filled byelectrons and it is very difficult to alter this stable arrangement by theaddition or removal of electrons. The noble gases thus exhibit very lowchemical reactivity. Preceding the noble gas family are two chemicallyimportant groups of nonmetals. They are the halogens(groups 17) and $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^1$ or $[Kr]5s^1$(group 16). These two groups of elements have highernegative electron gain enthalpies and readilyw add one or two electronsrespectively to attain the stable nobleq gas configuration. The nonmetallic character increases as we move from laaaaaaaaaeft to right across a period andmetallic character increases as we go down the group.

The *d*-block Elements (Transition Elements)

These are the elements of group 3 to 12 in the center of the periodic table. These elements are characterized by filling of inner d orbitals byelectrons and are therefore referred to as *d*-Block Elements. These elements have the outer electronic configuration (n-1)d^{1-10} ns^{1-2}. They are all metals. They mostly form colored ions and exhibit variable valencies. However, Zn, Cd and Hg, which have the (n-1)d^{10} ns^2 electronicconfiguration, do not show most of the properties of transition elementsin __-a way, transition metals form a bridge between the chemically activemetals of s-block elements and less active metals of groups 13 and 14and thus take their familiar name “transition elements”.

The *f*-Block Elements (Inner-Transition elements)

The two rows of elements at the bottom of the periodic table, calledthe Lanthanoids $_{58}$Ce-$_{71}$Lu and Actinoids**.** $_{90}$Th-$_{103}$Lr are characterizedby the outer electronic configuration (n-2)f^{1-14} (n-1)$^{0-10}$$ns^2$. The lastelectron added to each element is an f-electron. These two series ofelements are hence called the inner transition elements (f-BlockElements). They are all metals within each series, the properties of theelements are quite similar. The chemistry of the early actinoids is morecomplicated than the corresponding lanthanoids, due to the large numberof oxidation states possible for these actinoid elements. Actinoidelements are radioactive. Many of the actinoid elements have been madeonly in nanogram quantities or less by nuclear reactions and theirchemistry is not fully studied. The elements coming after uranium arecalled transuranium elements.

Example 1

The elements Z=117 and 120 have not yet been discovered. In which family / group would you place these elements and also give theelectronic configuration in each case.

Solution

We see from the periodic table that element with Z=117, wouldbelong to the halogen family (group 17) and the electronic configuration would be. $[Rn]4f^{14}5d^{10}7s^{2}7p^{5}$, the element with Z=120, will be placedin group 2 (alkaline earth metals), and will have the electronicconfiguration $[Uuo]8s^{2}$.

In addition to displaying the classification of elements into s-, p-, d- ,and f-blocks, the periodic table shows another broad classification ofelements based on their properties. The elements can be divided intoMetals and Non-metals. Metals comprise more than 75% of all knownelements and appear on the left side of the Periodic Table. Metals areusually solids at room temperature (Mercury is an exception); they havehigh melting and boiling points. They are good conductors of heat andelectricity. They are malleable (can be flattened into thin sheets byhammering) and ductile (can be drawn into wires). In contrast nonmetalsare located at the top right hand side of the periodic table. Nonmetalsare usually solids or gases at room temperature with low meltingand boiling points. They are poor conductors of heat and electricity.Most non-metallic solids are brittle and are neither malleable nor ductile.The elements become more metallic as we go down a group; the nonmetalliccharacter increases as one goes from left to right across the periodic table. The change form metallic to non-metallic character isnot abrupt as shown by the thick zig-zag line in the periodic table. Theelements (e.g. germanium, silicon, arsenic, antimony and tellurium)bordering this line and running diagonally across the periodic tableshow properties that are characteristic of both metals and non-metals.These elements are called Semi Metals or Metalloids.

Example 2

Arrange the following elements in the increasing order of metalliccharacter: Si, Be, Mg, Na, P.

Solution

Metallic character increases down a group and decreases along aperiod as we move from left to right. Hence the order of increasingmetallic character is, P<Si<Be<Mg<Na.

3.04 Periodicity of properties

Repetition of properties of elements at regular intervals is calledperiodicity in properties. The periodicity is due to similar electronic configuration of outer-most shells. Some of the properties are discussedbelow.

(i) Atomic and ionic radii

The size of an atom can be visualized from its atomic radius. Theterm atomic or ionic radius is generally defined as the distance betweenthe centers of the nucleus and the outermost shell of electrons in an atomor ion. For example, the atomic radius of hydrogen atom is equal to 74/2pm = 37 (bond distance in hydrogen molecule (H_2) is 74pm).Atomic and ionic radii both decrease from left to right across a periodin the periodic table when we consider only normal elements, e.g. in theelements of 2nd period the covalent radii decrease as we move from Li toF as shown below:

Elements of 2nd period:

Li Be B C N O F

Covalent radii Values decreasing →

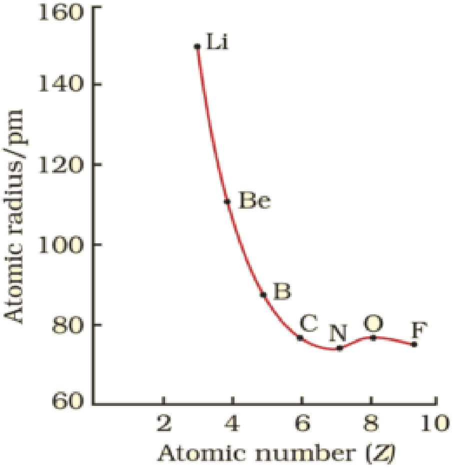
Thus in any period the alkali metals (that are present at the extremeleft of the periodic table) have the largest size while the halogens (that are present at the extreme right, excluding the zero group elements) havethe smallest size.

Explanations

We know that as we proceed from left to right in a period, theelectrons are added to the orbitals of the same main energy level.Addition of different electrons to the same main energy level puts theelectrons, on the average, no farther from the nucleus and hence the sizecannot be increased. But with the addition of each electron, the nuclearcharge (i.e. atomic number) increases by one. The increased nuclearcharge attracts the electrons more strongly close to the nucleus and thusdecreases the size of the atoms.

Atomic radii across the periods

Atom	Atomic radius	Atom	Atomic radius
Li	152	Na	186
Be	111	Mg	160
B	88	Al	143
C	77	Si	117
N	70	P	110
O	74	S	104
F	72	Cl	99



Variation of atomic radius with atomic number across the Second period

(b) **In a group**

On moving down a group of regular elements both atomic and ionicradii increase with increasing atomic number, e.g. in the elements of IAGroup both covalent and ionic radii of M^+ ions increase when we passfrom Li to Cs.

Elements of IA Group: Li Na K Rb Cs

Covalent radii/Ionic radii

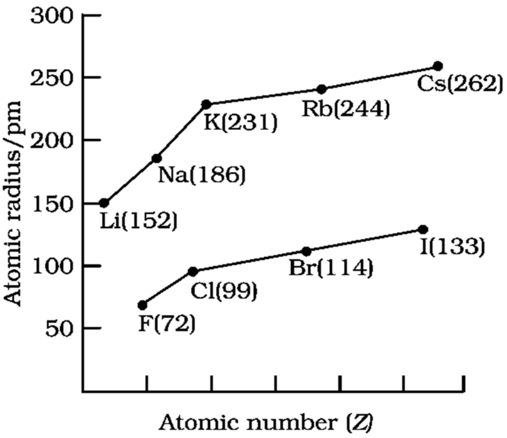
Values increasing →

Explanation

On proceeding downwards in a group the electrons are added tohigher main energy levels, which are, on the average, farther from thenucleus. This effect decreases the electrostatic attraction between thenucleus and the valence-shell electrons and this decreased electrostaticattraction increases the atomic and ionic radii.

Atomic Radii / pm Down the Group Across a Family

Atom	Atomic radius	Atom	Atomic radius
Li	152	F	72
Na	186	Cl	99
K	231	Br	114
Rb	244	I	133
Cs	262	Ar	140



Variation of atomic radius with atomic number for Alkali metals and halogens

When we find some atoms and ions, which contain the same number of electrons, we call them **isoelectronic**. For example, O^{2-}, F^-, Na+ and Mg^{2+} have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The cation with thegreater positive charge will have a smaller radius because of the greaterattraction of the electrons to the nucleus. Anions with the greaternegative charge will have the larger radius. In this case, the net repulsionof the electrons will outweigh the nuclear charge and the ion will expandin size.

Example

Which of the following species will have the largest and the smallest size Mg, Mg^{2+}, Al, Al^{3+}?

Solution

Atomic radii decrease across a period. Cations are smaller than their parent atoms. Among isoelectronic ions, the one with the large positivenuclear charge will have a smaller radius.

Hence the largest species is Mg; the smallest one is Al^{3+}. The size of an anion greater while that of the cation is smaller thanthat of its parent atom, e.g. F^- (=1.36 Å)>F(=0.72 Å); Cl^-(=1.81Å)>Cl(=0.99Å); Na^+(=0.95Å)<Na(=1.90Å); Ca^{2+}(=0.99 Å)<Ca(=1.97Å).

Explanation

Let us consider the radii of Na, Na^+, Cl and Cl^-. The reason of the fact that Na^+ ion is smaller than Na atom is that Na^+ion has 10 electrons ($Na^+ \rightarrow 1s^2,2s^2p^6$) while Na atom has 11electrons (Na $1s^22s^2p^63s^1$). The nuclear charge (charge on the nucleus) in each case is the same, i.e.equal to +11 (atomic number of Na). This nuclear charge of +11 can pull10 electrons of Na^+ ion inward more effectively than it can pull a greaternumber of 11 electrons of Na atom. Thus Na^+ ion is smaller than Naatom.The reason why Cl^- ion is bigger than Cl atom can also be explainedon a similar basis. The Cl^- ion has 18 electrons ($Cl^- \rightarrow 1s^22s^2p^63s^23p^6$)while Cl atom has only 17 electrons ($Cl \rightarrow 1s^22s^2p^63s^23p^5$). The nuclearcharge in each case is +17, which cannot pull 18 electrons of Cl^- ion aseffectively as it can pull 17 electrons of Cl atom inward. Thus Cl^- ion isbigger than Cl atom.

(ii) Ionization Energy: (Ionization Potential**)**

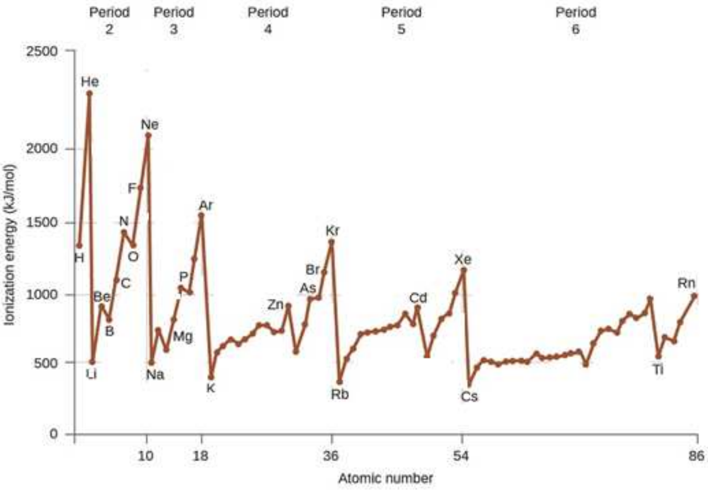
In modern terminology, ionization energy is known as ionization enthalpy. The energy required to remove an electron from an atom isknown as ionization enthalpy (IE). The first ionization enthalpy may bedefined as the amount of energy required to remove the most looselybound electron from the isolated gaseous atom.

$$\text{Atom}_{(g)} + \text{Energy} \rightarrow \text{Positive ion}_{(g)} + \text{Electron}$$

For example,

$$Li_{(g)} + 520\text{ kJ mol}^{-1} \rightarrow Li+_{(g)} + e^-$$

Ionization enthalpy is also called *ionization potential* because it is measured as the amount of potential required to remove the most looselyheld electron from the gaseous atom. It is expressed in terms of eitherkJ/mol or electron Volts/atom.



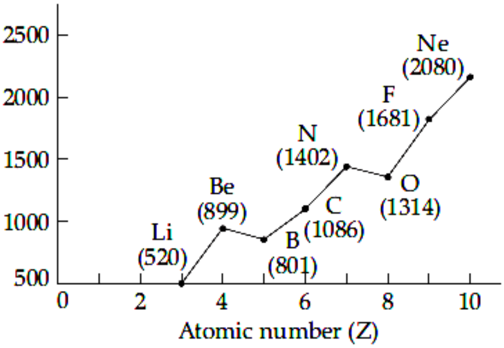
If a second electron is to be removed from the same element the energy required will be higher than that required for removal of the firstelectron because it is more difficult to remove an electron from a positively charged species than from a neutral atom.

$$Li^{+}_{(g)} + 7297\ kJ\ mol^{-1} \longrightarrow Li^{2+} + e^{-}$$

Similarly the third ionization enthalpy will be higher than the second and so on. Figure shows a plot of first ionization enthalpy of some elements.

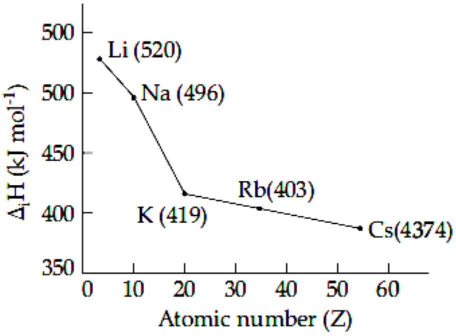
Variation of Ionization Energy in the periodic Table

It is seen from the above figure that the ionization enthalpy of an elementdepends on its electronic configuration. Ionization potentials of noblegases are found to be maximum and those of alkali metals are found tominimum. The high values of noble gases are due to completely filledelectronic configurations in their outermost shells and the low values ofalkali metals are due to their large size and a single electron in theoutermost shell.



First ionization enthalpies of elements of the second period as a function of atomic number

The ionization potential increases from left to right in a period. This trend can be explained in terms of increase in nuclear charge anddecrease in size from left to right in a period. Generally the firstionization enthalpy decreases down a group in the periodic table. As wemove down the group, the outer electrons, which are to be removed, arefarther from the nucleus and there is an increasing screening of thenuclear charge by the electrons in the inner shells. Consequently theremoval of electrons becomes easier down the group.



First ionization enthalpies of alkali metals as a function of atomic number

Factors Influencing Ionization Enthalpy

The ionization enthalpy of an atom depends on the following factors.

(i) Size of the atom

As the distance between the electron and the nucleus increases, i.e., as the size of the atom increases, the outermost electrons are less tightlyheld by the nucleus. Thus, it becomes easier to remove an outermost electron. Thus ionization enthalpy decreases with increases in atomic size.

(ii) Charge on the nucleus

Ionization enthalpy increases with increase in nuclear charge because of the increase in the attractive force between the nucleus and the electron.

(iii) Screening effect of inner electrons

Ionization enthalpy decreases when the shielding effect of inner electrons increases. This is because when the inner electron shells increases, the attraction between the nucleus and the outermost electron decreases.

(iv) Penetration effect of electrons

The penetration power of the electrons in various orbitals decreases in a given shell (same value of n) in the order: s>p>d> f. Since the penetration power of s-electron towards the nucleus is more, it will be closer to the nucleus and will be held firmly. Thus, for the same shell, the ionization enthalpy would be more to remove the s-electrons in comparison with the p-electron which in turn would be more than that for d-electron and so on.

(v) Effect of half-filled and completely filled sub-levels

If an atom has half-filled or completely filled sub-levels, itsionization enthalpy is higher than that expected normally from itsposition in the periodic table. This is because such atom, have extrastability and hence it is difficult to remove electrons from these stableconfigurations.

(iii) Electron affinity

In modern terminology, electron affinity is known as the electrongain enthalpy. Electron gain enthalpy is the amount of energy releasedwhen an isolated gaseous atom accepts an electron to form a monovalentgaseous anion.

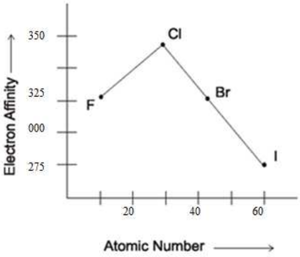
$$\text{Atom}_{(g)} + \text{Electron} \rightarrow \text{Anion}_{(g)} + \text{energy}$$

Example, $Cl_{(g)} + e^{-} \rightarrow Cl^{-}_{(g)} + EA$

If an atom has high tendency to accept an electron, large energy willbe released. Consequently, electron gain enthalpy will be high. On theother hand if an atom has less tendency to accept the electron smallamount of energy will be released, leading to small value of electron gainenthalpy. The values of electron gain enthalpy are expressed either inelectron volt per atom or kilo joules per mole of atoms. For example,electron gain enthalpy of,

F = 322 kJ mol^{-1}
Cl = 349 kJ mol^{-1}
Br = 324 kJ mol^{-1} and
I =295 kJ mol^{-1}

Halogens (elements of group 17) can take up an electron to acquire the stable noble gas configuration. Their values for electron gain enthalpy are thus very high. Electron gain enthalpy values for the halogens are as in figure.



Electron gain enthalpies generally decrease on moving down the group. This is expected on account of the increase in size of atoms, the effective nuclear attraction for electrons decreases. As a result, there isless tendency to attract additional electrons with an increase in atomicnumber down the group.

From the electron gain enthalpy data of halogens it is clear that, contrary to expectation, the electron gain enthalpy of fluorine is lower than that of chlorine. This is because the fluorine atom has a verycompact electronic shell due to its small size. The compactness of the fluorine shell results in electron repulsion whenever an electron isintroduced into its 2p-orbital. This is why its electron gain enthalpy is less than the expected value. In Cl atom, 3p-orbitals are not as compactas the 2p-orbitals in fluorine atom. The incoming electron is morereadily accepted by the chlorine atom because of weaker electron-electronrepulsion. The electron gain enthalpy of chlorine is, therefore,higher than that of fluorine.

In the case of noble gases, the outer s-and p-orbitals are completely filled. No more electrons can be accommodated in these orbitals. Noblegases, therefore, show no tendency to accept electrons. Their electrongain enthalpies are zero.

Electron gain enthalpies generally increase as we move across a period from left to right. This is due to the increase in the nuclear charge,which results in greater attraction for electrons.

The second electron gain enthalpy refers to a process in which theelectron is added to a negative ion. For example:

$$O^{-}_{(g)} + e- \rightarrow O^{2-}_{(g)}$$

Since a negative ion O- and an electron repel each other, energy is required and not released by the process. Therefore the second electrongain enthalpy is negative in this case.

Factors influencing the magnitude of electron affinity

The magnitude of EA is influenced by a number of factors such as (i) Atomic size; (ii) Effective nuclear charge; and (iii) Screening effect by inner electrons.

Example

Which of the following will have the most negative electron gainenthalpy and which has the least negative? P, S, Cl, F.Explain your answer.

Solution

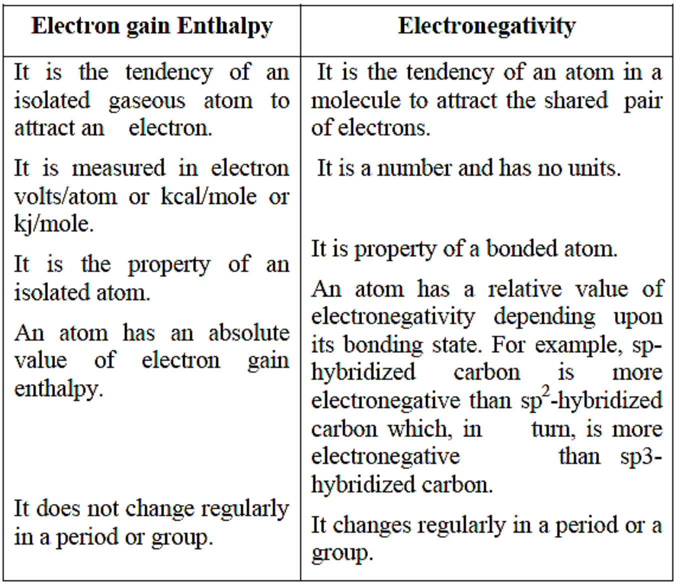
Electron gain enthalpy generally becomes more negative across aperiod as we move from left to right. Within a group, electron gainenthalpy becomes less negative down a group. However, adding anelectron to the 2p orbital leads to greater repulsion than adding anelectron to the larger 3p orbital. Hence the element with most negativeelectron gain enthalpy is chlorine; the one with the least negative electrongain enthalpy is phosphorus.

(iv) Electronegativity

Electronegativity may be defined as the tendency of an atom in amolecule to attract towards itself the shared pair of electrons. The mainfactors, which the electronegativity depends, are effective nuclear chargeand atomic radius. Greater the effective nuclear charge greater is theelectronegativity. Smaller the atomic radius greater is theelectronegativity.

In a period electronegativity increases in moving from left to right.This is due to the reason that the nuclear charge increases whereas atomicradius decreases as we move from left to right in a period. Halogens havethe highest value of electronegativity in their respective periods.In a group electronegativity decreases on moving down the group.This is due to the effect of the increased atomic radius. Among halogensfluorine has the highest electronegativity. In fact fluorine is the mostelectronegative element and is given a value of 4.0 (Pauling's scale)whereas cesium is the least electronegative element (E.N. = 0.7) becauseof its largest size and maximum screening effect. In other words, cesiumis the most electropositive element and hence is the most metallicelement in the periodic table.

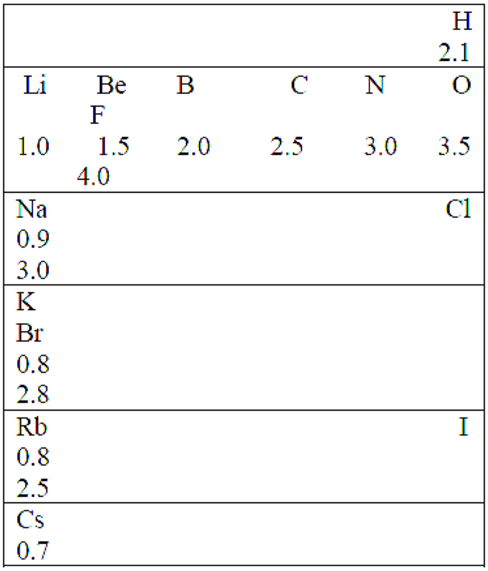
The main differences between Electron gain enthalpy (electroaffinity) and electronegativity are given below:



Electron gain Enthalpy	Electronegativity
It is the tendency of an isolated gaseous atom to attract an electron.	It is the tendency of an atom in a molecule to attract the shared pair of electrons.
It is measured in electron volts/atom or kcal/mole or kj/mole.	It is a number and has no units.
It is the property of an isolated atom.	It is property of a bonded atom.
An atom has an absolute value of electron gain enthalpy.	An atom has a relative value of electronegativity depending upon its bonding state. For example, sp-hybridized carbon is more electronegative than sp^2-hybridized carbon which, in turn, is more electronegative than sp3-hybridized carbon.
It does not change regularly in a period or group.	It changes regularly in a period or a group.

Electronegativity of an element is important in determining the bondcharacter. If two atoms have the same electronegativities the bondbetween the two will be covalent, while a large difference inelectronegativity leads to ionic bond. Between the extremes the purelycovalent bond and purely ionic, the bonds will have different degrees ofionic character. As a rough estimate it is seen that a difference of 1.7 inelectronegativities, the bond has 50% ionic character. If the difference isless than 1.7, the bond is considered covalent, and greater than 1.7 it isconsidered ionic.

Pauling's Electronegativity coefficients (for the mostcommon oxidation states of the elements)



					H 2.1
Li 1.0	Be F 1.5 4.0	B 2.0	C 2.5	N 3.0	O 3.5
Na 0.9 3.0					Cl
K Br 0.8 2.8					
Rb 0.8 2.5					I
Cs 0.7					

3.05 Anomalous periodic properties of elements

According to Hund's rule atoms having half-filled or completelyfilled orbitals are comparatively more stable and hence more energy isneeded to remove an electron from such atoms. The ionization potentialsof such atoms are, therefore, relatively higher than expected normallyfrom their position in the periodic table.

Example

A few irregularities that are seen in the increasing values ofionization potential along a period can be explained on the basis of theconcept of half-filled and completely filled orbitals, e.g., Be and N in thesecond period and Mg and P in the third period have slightly highervalues of ionization potentials than those normally expected. This isexplained on the basis of extra stability of the completely-filled 2s-orbital in Be(Be → $2s^2$) and 3s-orbital in Mg (Mg → $3s^2$) and of half-filled 2porbitalin N (N → $2s^2p^6$) and 3p-orbital in P (P → $3s^2p^3$).

Another example for irregularity in Ionization potential is observed in the case of B and Be.Ionization energy of boron ($B \rightarrow 2s^2 2p^1$) is lower than that ofberyllium ($Be \rightarrow 2s^2$) [B = 8.3 eV, Be = 9.3 eV], since in case of boronwe have to remove a $2p^1$ electron to get B^+[B (2s2p1) → $B^+(2s^2) + e^-$]while in case of Be we have to remove a $2s^1$ electron of the same mainenergy level to have Be^+ ion. [Be ($2s^2$) → $Be^+(2s^1)$ $+e^s$].There is an exception to the vertical trend of ionization potential. Thisexception occurs in the case of those elements whose atomic numbers aregreater than 72. Thus the ionization potentials of the elements from $Ta_{73}$to Pb_{82} are greater than those of the elements of the same sub-group above them as shown below: (First ionization potential values are givenin electron volts, eV).

VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA
Nb_{41} 6.8	Mo_{42} 7.1	Tc_{43} 7.2	Ru_{44} 7.3	Rh_{45} 7.4	Pd_{46} 8.3	Ag_{47} 7.5	Cd_{48} 8.9	In_{49} 5.7	Sn_{50} 7.3
Ta_{73} 7.7	W_{74} 7.8	Re_{75} 7.8	Os_{76} 8.7	Ir_{77} 9.2	Pt_{78} 9.0	Au_{79} 9.2	Hg_{80} 10.4	Tl_{81} 6.1	Pb_{82} 7.4

The reason for the abnormal behavior (i.e. an increase in the value of I1 from Nb → Ta, Mo → W, …..,Sn →Pb) shown by the elements from Ta_{73} to Pb_{82} is due to the lanthanide contraction as a result of whichthere occurs an increase in the nuclear charge without a correspondingincrease in size through the rare earths. In fact, the size actually decreasesin this region.

Periodic Variations

Similarly in moving down a group electron affinity values generally decrease, e.g. $E_{Cl} > E_{Br} > E_I$. This is due to the steady increase in the atomic radius of the elements.

Exceptions

There are, however, some exceptions to this general rule as is evidentfrom the following examples:It is known that $E_F < E_{Cl}$ (E_F = 322 kJ mol^{-1}, E_{Cl} = 349 kJ mol^{-1}). Thelower value of E for F is probably due to the electron-electron repulsionin relatively compact 2*p*-orbital of F-atom.

In period, electron affinity values generally increase on moving from left to right in a period in the periodic table.

Exceptions

There are, however, exceptions also to this general rule; e.g.Be and Mg have their EA values equal to zero. Since Be and Mghave completely filled *s*-orbitals (Be → $2s^2$, Mg → $3s^2$), the additional electron will be entering the 2*p*-orbital in case of Be and 3*p*-orbital in case of Mg which are of considerably higher energy than the 2*s*-and 3sorbitals respectively.

3.06 Horizontal, vertical, and diagonal relationships in the periodic table and General properties of atoms

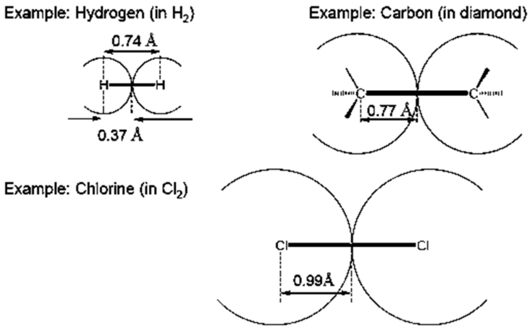
The periodicity of these properties follows trends as you move across a row or period of the periodic table or down a column or group:

Ionization Energy Increases,Electronegativity Increases, Atomic Radius Decreases.

Ionization Energy Decreases, Electronegativity Decreases, Atomic Radius Increases.

Size of atoms and ions

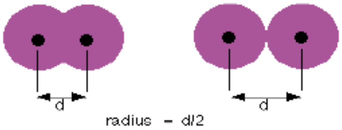
The *size* of an isolated atomcan't be measured because we can't determine the location of the electrons that surround the nucleus. We can estimate the sizeof an atom, however, by assuming that the radius of an atom is half the distance between adjacent atomsin a solid.



Atomic radii

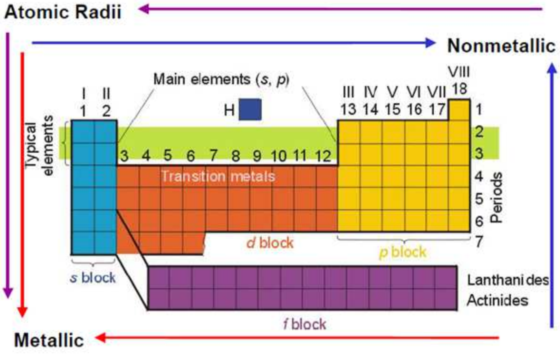
The atomic radius of a chemical element is a measure of the sizeof its atoms, usually the mean or typical distance from the center of the nucleus to the boundary of the surrounding cloud of electrons.

The atomic radius is simply the distance from the nucleus to the outermost electron. Since the position of the outermost electron can never be known precisely, the atomic radius is usually defined as half the distance between the nuclei of two bonded atoms of the same element:

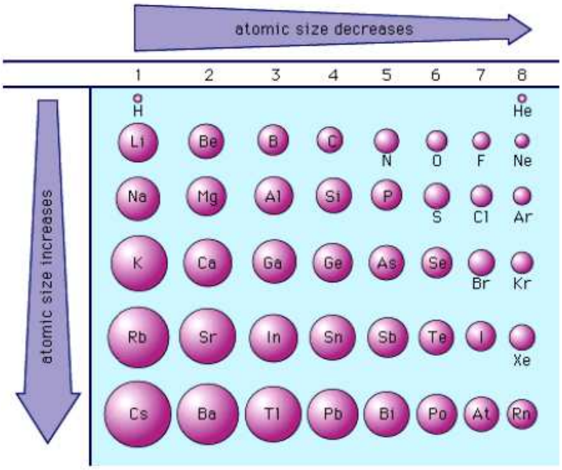


As a group is descended, the outermost electron is in a higher energy level which is further from the nucleus so the radius increases.

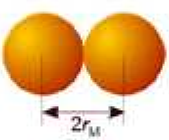
Across a period, electrons are being added to the same energy level, but the number of protons in the nucleus increases. This attracts the energy level closer to the nucleus and the atomic radius decreases across a period.



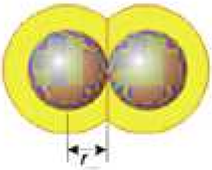
The following graph shows the trend in atomic radius:



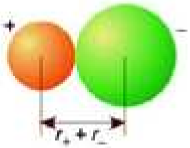
Atomic Radius to refer to both covalent or metallic radius depending on whether the element is a non-metal or a metal.



1 metallic radius



2 Covalent radius



3 Ionic radius

Ionic radii and Trend in ionic radii

Similar to atomic radius, the ionic radius of an element increases in size down a group as the number of electron shells increase.

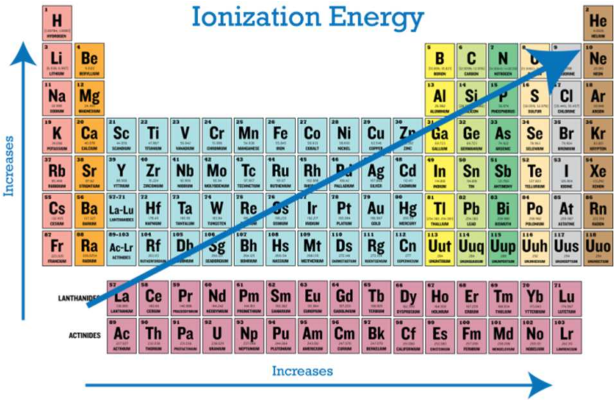
However, going across a period, the ionic radius decreases from Group 1 to Group 3 as with atomic radius, but then increases and decreases again as the large negative ions are formed from Groups 5 to 7. (Recall that Group 4 elements do not typically form ions). An example showing the relative ion sizes from Period 3 are shown above.

The cations (Na^+, Mg^{2+} and Al^{3+}) contain fewer electrons than protons so the electrostatic attraction between the nucleus and the outermost electron is greater and the ion is smaller than the parent atom. It is also smaller because the number of electron shells has decreased by one. Across the period the ions contain the same number of electrons but an increasing number of protons so the ionic radius decreases in size. The anions (P^{3-} and S^{2-}) contain more electrons than protons and therefore are larger that the parent atom. Across a period, the ionic size decreases because the number of electrons remains the same but the numbers of protons increase, pulling the outer shell closer to the nucleus.

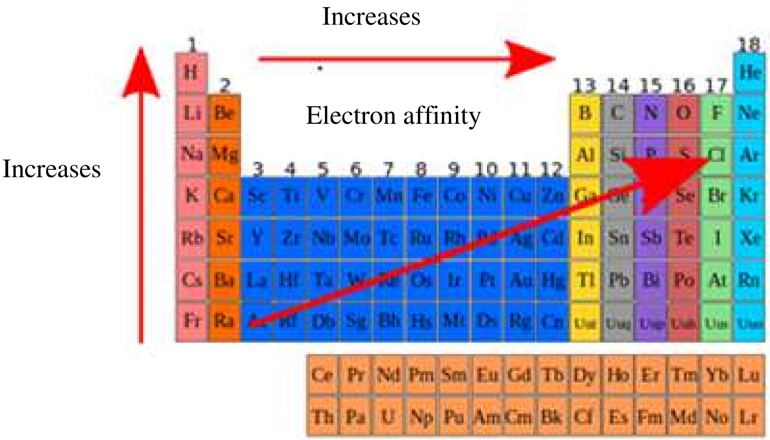
***Note:** The size of an atom always decreases when being converted to a positive ion because it loses an electron and therefore there is less electron repulsion. The size of an atom always increases when being converted to a negative ion because since there is an increase in repulsion between electrons.

Ionization potential

A quantitative measure of the tendency of an element to lose electron is given by its Ionization Enthalpy. It represents the energy required to remove an electron from an isolated gaseous atom (X) in its ground state.



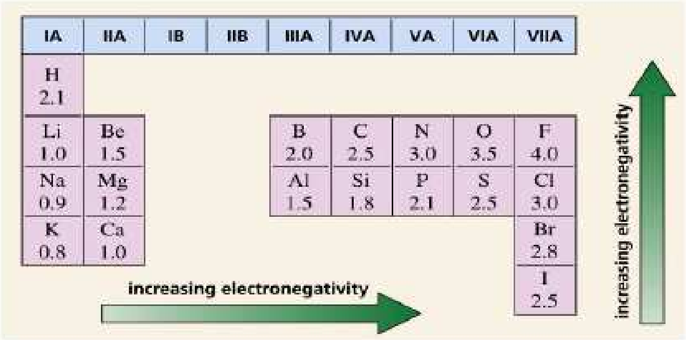
Electron affinity



An atom‘s electron affinityis the amount of energy released when an electron is added to the atom in its gaseous state—when an electron is added to an atom, the atom forms a negative ion. Most often, energy is releasedas an electron is added to an atom, and the greater the attraction between the atom and the electron added, the more negative the atom's electron affinity.

Electronegativity

Electronegativity is a relative measure of the attraction that an atom has for a shared pair of electrons when it is covalently bonded to another atom. The electronegativity decreases as you go down a group. This is due to the shielding effect where electrons in lower energy levels shield the positive charge of the nucleus from outer electrons resulting in those outer electrons not being as tightly bound to the atom. Electronegativity increases as you go from left to right across a period. This is because there is more electron-attracting power of the nucleus with the increasing nuclear charge as the number of protons increase form left to right across the periodic table.



IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
Li 1.0	Be 1.5			B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2			Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0							Br 2.8
								I 2.5

a) Pauling

The most common and widely used scale for electronegativities is the Pauling scale, devised by Linus Pauling in 1932. This is the scale commonly presented in general chemistry textbooks. Pauling based his scale on thermochemical data, particularly bond energies, which allowed him to calculate differences in electronegativity between atoms in a covalent bond. He assigned a value of 4.0 to fluorine, the most electronegative element, and calculated other values with respect to that. Thus the Pauling scale runs from 0 to 4, with 4 being the most electronegative. The least electronegative element is francium. Recently, the scale was revised a little—fluorine was assigned an electronegativity value of 3.98, and some minor changes were made to other reported values.

b) Mulliken-Jaffe

In 1934, shortly after Pauling proposed his approach for measuring electronegativity, Robert S. Mulliken proposed a different approach. Mulliken suggested that an atom's electronegativity should be the average value of the atom's electron affinity (EAv) and ionization energy (IEv). Mulliken electronegativities, C_M, may be estimated by the following equation.

$C_M = 0.168 (IE_V + EA_v -1.23)$

In this equation, the values for electron affinity and ionization energy (reported in electron volts) must be calculated for the atom as it exists within the molecule—they are not the experimentally determined values for the neutral atom.

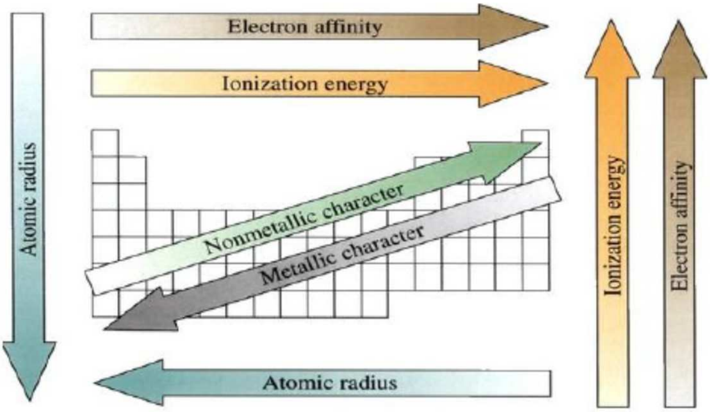
c) Allred-Rochow definitions

In 1958, A. L. Allred and E. G. Rochow proposed a separate method, based on atomic size and charge, to calculate electronegativities. They defined electronegativity as the electrostatic force exerted by theatomic nucleus on the valence electrons (outermost electrons involved in chemical bonding). When calculated using the following equation, the electronegativity values (C_{AR}) on this scale agree well with those on the Pauling scale.

$C_{AR} = 0.744 + 0.359Z_{eff}/r^2$

Where Z_{eff} is the effective nuclear charge experienced by a valence electron, and r is the distance between the electron and the atomic nucleus (covalent radius).

Summary of periodic trends



The s Block elements

3.10 Isotopes of hydrogen

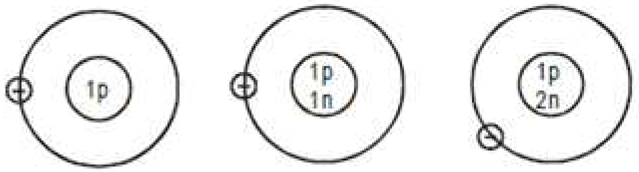
Hydrogen is the first element in the periodic table. It has the simplest electronic configuration 1s1. It contains one proton in the nucleus and oneelectron.

Isotopes: Atoms of the same element having same atomic number but different mass number are called isotopes.There are three isotopes for hydrogen with mass numbers 1, 2 and 3,each possessing an atomic number of one.

Name	Symbol	Atomic number	Mass number	Relative abundance	Nature radioactive or non radioactive
Protium or	${}_{1}^{1}H$ or H	1	1	99.99 %	Non radioactiv

Hydrogen					e
Deuterium	$^{2}_{1}H$ or D	1	2	0.015%	radioactive
Tritium	$^{3}_{1}H$ or T	1	3	10-18%	radioactive

The structures of three isotopes of hydrogen are:



Protium Deuterium Tritium

1. Protium or ordinary hydrogen:

It is the common form of hydrogen. It consists of one proton in its nucleus and one electron revolving around it. It constitutes 99.984% of total hydrogen available in nature. Its mass number is one.

2. Deuterium or heavy hydrogen:

$^{1}H_{2}$ or $^{1}D_{2}$. It occurs naturally in very small traces. The proportion present in naturally occurring hydrogen is in the approximate ratio: D:H ~ 1:6000. It's nucleus consists of a proton and a neutron. However, only a solitary electron is revolving around the nucleus. Its chemical properties are similar to those of protium but their reaction rates are different.

3. Tritium, $^{1}H_{3}$ or $^{1}T_{3}$:

It occurs in the upper atmosphere only where it is continuously formed by nuclear reactions induced by cosmic rays.Unlike deuterium, it is radioactive, with a half-life of ~ 12.3 years. It'snucleus consists of one proton and two neutrons.They will have same similar chemical properties, however, theirreaction rates will be different and their physical properties differappreciably.

3.11 Nature and application of isotopes of hydrogen

Methods of Preparation of deuterium

1. By Diffusion Process:

It is possible to obtain deuterium directly from hydrogen gas by taking advantage of different rates of diffusion of thetwo isotopes. The lighter hydrogen diffuses more quickly than deuteriumthrough a porous partition under reduced pressure. Lower the pressure,higher is the efficiency of the process.The process of diffusion has been carried out in various diffusionchambers called Hertz diffusion units. Each diffusion units consists of aporous membrane.

When the mixture is led into the diffusion units under reduced pressureby the help of mercury diffusion pumps, the heavier deuterium diffuses lessreadily while lighter hydrogen diffuses at faster rates. This process isrepeated several times till hydrogen gets collected on the left whiledeuterium on the right. The efficiency of this process could be increased byincreasing the number of diffusion units.

2. By fractional distillation of liquid hydrogen:

By fractional distillation of liquid hydrogen, it is possible to result in enrichment of thelast fraction in deuterium because deuterium boils at 23.5K while hydrogenboils at lower temperature of 20.2K.

3. By electrolysis of heavy water:

As water contains about one part of heavy water in 6000 parts, at first, the concentration of heavy water isincreased by fractional electrolysis of water containing an alkali betweennickel electrodes. For example 1 ml of heavy water is obtained from about20litres by this method.From heavy water, it is possible to get deuterium by decomposing it with sodium, red hot iron or tungsten or by its electrolysis containingsodium carbonate.

$$2D_2O \xrightarrow{\text{Electrolysis}} 2D_2 + O_2$$

$$D_2O + 2Na \longrightarrow NaOD + D_2$$

Sodium deuteroxide

Physical properties

Like hydrogen, deuterium is a colorless, odorless and tasteless gas which is insoluble in water and bad conductor of heat and electricity. Thevalues of boiling point, melting point, vapor pressure, dissociation energyand latent heat of fusion are found to be lower for protium than deuterium.

Chemical properties

By virtue of its larger mass, deuterium reacts slower than hydrogen.

1. Burning in oxygen: Like hydrogen, it is combustible and burns in oxygen or air to give deuterium oxide which is also known as heavy water.

$$2D_2 + O2 \longrightarrow 2D_2O$$

2. Reaction with halogens: Like hydrogen, it combines with halogens under suitable conditions to form their deuterides.

$$D_2 + Cl_2 \xrightarrow{\text{in light}} 2\,DCl$$

Deuterium chloride

$$D_2 + F_2 \xrightarrow{\text{in dark}} D_2\,F_2$$

Deuterium fluoride

3. Reaction with nitrogen: Like hydrogen, it combines with nitrogen in the presence of a catalyst to form nitrogen deuteride which are also known as heavy ammonia or deutero ammonia.

$$3D_2 + N_2 \longrightarrow 2ND_3$$

4. Reaction with metals: Like hydrogen, it reacts with alkali metals at high temperatures (633K) to form deuterides.

$$2\,Na + D_2 \longrightarrow 2\,NaD$$

5. Addition reactions: Like hydrogen, it gives addition reactions with unsaturated compounds. For example, a mixture of deuterium and ethylenewhen passed over heated nickel, gives Ethylene deuteride which issaturated hydrocarbon like ethane.

$$C_2H_4 + D_2 \xrightarrow[535\,K]{Ni} CH_2D\text{-}CH_2D$$

6. Exchange reactions: Deuterium and hydrogen atoms undergo ready exchange with H_2, NH_3, H_2O and CH_4 deuterium slowly exchanges their hydrogens partially or completely at high temperatures.

$$H_2 + D_2 \rightleftharpoons 2\,HD$$

$$2NH_3 + 3D_2 \rightleftharpoons 2ND_3 + 3H_2$$

$$H_2O + D_2 \rightleftharpoons D_2O + H_2$$

$$CH_4 + 2D_2 \rightleftharpoons CD_4 + 2H_2$$

$$C_2H_6 + 3D_2 \rightleftharpoons C_2D_6 + 3H_2$$

Uses of deuterium

1. It is used as tracers in the study of mechanism of chemicalreactions.
2. High speed deuterons are used in artificial radioactivity.
3. Its oxide known as heavy water (D_2O) which is employed asmoderator in nuclear reactor to slow down the speed of fast movingneutrons.

Tritium $_1H^3$: It is a rare isotope of hydrogen. Its traces are found innature due to nuclear reactions induced by cosmic rays.Tritium is prepared by:

i) By bombarding lithium with slow neutrons

$${}_3Li^6 + {}_0n^1 \longrightarrow {}_1T^3 + {}_2He^4$$

ii) By bombarding beryllium with deuterons

$${}_4Be^9 + {}_1D^2 \longrightarrow {}_1T^3 + {}_4Be^8$$

$${}_4Be^9 + {}_1D^2 \longrightarrow {}_1T^3 + 2\,{}_2He^4$$

Properties: It is radioactive with a half-life of 12.4 years. It decays into helium-3 with the emission of beta radiation.

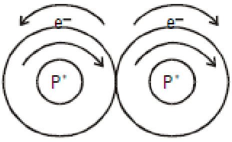
Uses

(i) It is used as a radioactive tracer in chemical research.

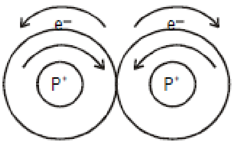
(ii) It is used in nuclear fusion reactions.

3.12 Ortho and para hydrogen

The nucleus of the hydrogen atom spins about an axis like a top. Whentwo hydrogen atoms combine, they form molecular hydrogen.Thus depending on the direction of the two protons in the nucleus thefollowing two types of hydrogen molecules are known. Hydrogen moleculein which both the protons in the nuclei of both H-atoms are known to spinin same direction is termed as ortho hydrogen. If the protons in the nuclei ofboth H-atoms spin in opposite direction, it is termed as para-hydrogen.



Orthohydrogen



Parahydrogen

At room temperature ordinary hydrogen consists of about 75% ortho and 25% para form. As the temperature is lowered, the equilibrium shifts infavor of para hydrogen at 25K. There is 99% para and 1% orthohydrogen.

The change in the proportion of the two forms of hydrogenrequires a catalyst such as platinum or atomic hydrogen or silent electric discharge. The para form was originally prepared by absorbing ordinary hydrogenin activated charcoal in a quartz vessel kept at a temperature of 20K. Thecharcoal absorbs almost pure para hydrogen. By this method, pure parahydrogen can be isolated.

Conversion of para into ortho hydrogen

Ortho hydrogen is more stable than para hydrogen. The para form is transformed into ortho form by the following methods.

1. By treatment with catalysts like platinum or iron.
2. By passing an electric discharge.
3. By heating to 800 ^{o}C or more.
4. By mixing with paramagnetic molecules like O_2, NO, NO_2.
5. By mixing with nascent hydrogen or atomic hydrogen.
6.

Properties: Ortho and para hydrogen are similar in chemical propertiesbut differ in some of the physical properties.

a) Melting point of para hydrogen is 13.83K while that of ordinaryhydrogen is 13.95 K.

b) Boiling point of para hydrogen 20.26K while that of ordinaryhydrogen is 20.39K.

c) The vapor pressure of liquid para hydrogen is higher than that ofordinary liquid hydrogen.

d) The magnetic moment of para hydrogen is zero since the spins neutralize each other while in the case of ortho, it is twice than that of aproton.

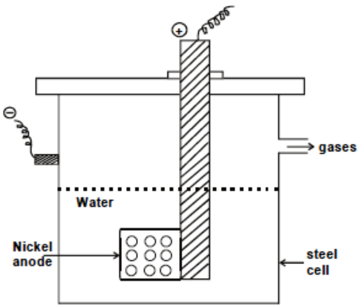
e) Para hydrogen possesses a lower internal molecular energy thanortho form.

3.13 Heavy water

It is also called as deuterium oxide. The oxide of heavy hydrogen(deuterium) is called heavy water. Heavy water was discovered by Urey in1932. By experimental data he showed that `ordinary water', H_2O containssmall proportion of heavy water, D_2O (about 1 part in 5000).

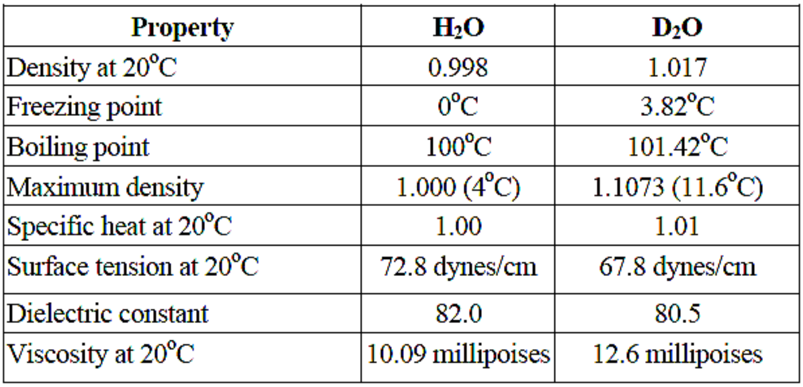
Preparation: The main source of heavy water is the ordinary water from which it is isolated. Generally it is prepared by exhaustive electrolysis.

Principle: The heavy water is isolated either by prolonged electrolysis or by fractional distillation of water containing alkali. Taylor, Eyring andFirst in 1933 formulated the electrolysis of water in seven stages using N/2-NaOH solution and strip nickel electrodes.



The cell consists of a steel cell 18 inches long and 4 inches in diameter.The cell itself serves as the cathode while the anode consists of a cylindricalsheet of nickel with a number of holes punched in it. A large number of such cells are used for electrolysis of water in several stages. The gasesobtained from each stage are separately burnt and the water thus formed isreturned to the previous stage. The heavy water gradually concentrates inthe residue left behind. The process usually consists of five stages.A partial separation of heavy water from ordinary water can be affectedby fractional distillation. This method utilizes the small difference inboiling points of protium oxide (H_2O) and deuterium oxide (D_2O).

Comparison of water and heavy water



Property	H_2O	D_2O
Density at 20°C	0.998	1.017
Freezing point	0°C	3.82°C
Boiling point	100°C	101.42°C
Maximum density	1.000 (4°C)	1.1073 (11.6°C)
Specific heat at 20°C	1.00	1.01
Surface tension at 20°C	72.8 dynes/cm	67.8 dynes/cm
Dielectric constant	82.0	80.5
Viscosity at 20°C	10.09 millipoises	12.6 millipoises

The solubilities of substances in heavy water also differ from those inordinary water. Thus sodium chloride is about 15% less soluble in heavywater than in ordinary water.

Physical Properties

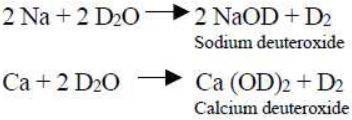
Heavy water is a colorless, odorless and tasteless mobile liquid.Higher viscosity of heavy water is responsible for lower solubility of ionicsolids like NaCl and smaller mobilities of ions.

Chemical Properties

The difference in chemical behavior between H_2O and D_2O is very slight. However, the reaction velocity in general is slightly less in case ofD_2O reactions.

Important reactions of heavy water

1. With metalsD_2O reacts slowly with alkali and alkaline earth metals liberating heavyhydrogen.



$$2\,Na + 2\,D_2O \longrightarrow \underset{\text{Sodium deuteroxide}}{2\,NaOD} + D_2$$

$$Ca + 2\,D_2O \longrightarrow \underset{\text{Calcium deuteroxide}}{Ca\,(OD)_2} + D_2$$

2. With metallic oxides: Metals like sodium and calcium dissolve in D_2O and form heavyalkalies.

$$Na_2O + D_2O \rightarrow 2\ NaOD$$
$$CaO + D_2O \rightarrow Ca(OD)_2$$

3. With acid anhydrides, D_2O forms corresponding acids containing heavy hydrogen.

$$SO_3 + D_2O \rightarrow \underset{\text{Deutero sulphuric acid}}{D_2\ SO_4}$$

$$P_2O_5 + 3D_2O \rightarrow \underset{\text{Deuterophosphoric acid}}{2D_3\ PO_4}$$

4. Upon electrolysis, heavy water containing dissolved P_2O_5,decomposesinto deuterium and oxygen which are liberated at the cathode and anoderespectively.

$$2D_2O \rightarrow 2D_2 + O_2$$

5. With salt and other compounds they form deuterates.

$$Cu\ SO_4.\ 5\ D_2O,\ Na_2\ SO_4.\ 10D_2O,\ NiCl_2.6D_2O$$

6. Exchange reactions: When compounds containing hydrogen are treated with D_2O, hydrogenundergoes an exchange for deuterium.

$$NaOH + D_2O \rightarrow NaOD + HOD$$
$$NH_4\ Cl + 4D_2O \rightarrow ND_4\ Cl + 4HOD$$

Biological properties

In general heavy water retards the growth of living organisms like plants and animals. The tobacco seeds do not grow in heavy water. Also,pure heavy water kills small fish, tadpoles and mice when fed upon it.Certain molds have been found to develop better in heavy water.

Uses of heavy water

1. As a neutron moderator, in nuclear reactors.
2. It is used as a tracer compound in the study of reactions occurring inliving organisms.
3. It is used for the preparation of deuterium.

3.13 Hydrogen peroxide

Hydrogen peroxide was first prepared by L.J.Thenard, in 1813 by the action of dilute acid on barium peroxide. Traces of $H_2O_2$are found in atmosphere and in certain plants.

Laboratory preparation of hydrogen peroxide

1. By the action of dilute sulphuric acid on sodium peroxide. Calculated quantity of Na_2O_2 is added in small proportions to a 20% icecold solution of sulphuric acid.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

30% solution of H2O2 is obtained by this process.

2. Pure H_2O_2 is obtained by reacting BaO_2 with an acid.

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$
$$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 3H_2O_2$$

3. H_2O_2 is manufactured by the electrolysis of 50% sulphuric acid followed by vacuum distillation. The distillate is 30% solution of pure H_2O_2.

Reactions

$$\begin{aligned}
&H_2SO_4 &&\rightleftharpoons H^+ + HSO_4^-\\
&2HSO_4^- &&\rightleftharpoons H_2S_2O_8 + 2e^- \text{ (At anode)}\\
&H_2S_2O_8 + H_2O &&\rightleftharpoons H_2SO_4 + H_2SO_5\\
&H_2SO_5 + H_2O &&\rightleftharpoons H_2SO_4 + H_2O_2\\
&2H^+ + 2e^- &&\rightleftharpoons H_2 \text{ (At cathode)}
\end{aligned}$$

Concentration of hydrogen peroxide solution

The impurities like organic material or metallic ions, may catalyze its explosive decomposition.

i) By careful evaporation of the solution obtained above on a water bath preferably under reduced pressure using fractionating column.

ii) By distillation under reduced pressure at temperatures below 330K, the concentration up to 90% solution is used till crystallization formed.

Strength of Hydrogen peroxide

The strength of a sample of hydrogen peroxide solution is expressed in terms of the volumes of oxygen at S.T.P that one volume of H_2O_2 gives on heating.

Properties

Physical

H_2O_2 is a colorless, odorless, syrupy liquid in the anhydrous state. It is miscible with water, alcohol, and ether in all proportions.

Chemical

Pure H_2O_2 is unstable and decomposes on standing. On heating when water and oxygen are formed.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Oxidizing Properties

H_2O_2 is a powerful oxidizing agent. It functions as an electron acceptor.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2\ H_2O$$

(In acidic solution)

$$H_2O_2^- + 2e^- \rightarrow 2OH^-$$

(In alkaline solution)

i) It oxidizes PbS to $PbSO_4$

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

ii) It oxidizes ferrous salts into ferric salts .

$$2Fe^{2+} + 2H^+ + H_2O_2 \rightarrow 2\ Fe^{3+} + 2H_2O$$

Due to its oxidizing property, it is a valuable bleaching agent, powerfulbut harmless disinfectant and germicide. Delicate materials like silk, wool,hair which will be destroyed by chlorine, are bleached with H_2O_2.

Reducing Properties

With powerful oxidizing agents, H_2O_2 acts as a reducing agent. Moistsilver oxide, acidified KMnO4, ozone, chlorine and alkaline solutions offerricyanides are reduced.

$$Ag_2O + H_2O_2 \rightarrow 2\ Ag + H_2O + O_2$$

Uses

i) It destroys bacteria and hence it is used as an antiseptic and germicide for washing wounds, teeth and ears.

ii) It destroys the color of some organic compounds and is used inbleaching delicate things like hair, wool, silk ivory and feathers.

iii) It is used as an oxidizing agent.

iv) It is also used as a propellant in rockets.

3.14 Liquid hydrogen as a fuel

The hydrogen atom has become a model for the structure of atom. Hydrogen as a substance however, has an equally important place in chemistry. Hydrogen is normally a colorless, odorless gas composed ofH_2 molecules. Approximately 40% of the hydrogen produced commerciallyis used to manufacture ammonia and about the same amount is used inpetroleum refining. But the future holds an even greater role for hydrogenas a fuel.

Liquid hydrogen, H_2, is a favorable rocket fuel. On burning, itproduces more heat per gram than any other fuel. In its gaseous form, hydrogen may become the favorite fuel of the twenty first century. Whenhydrogen burns in air, the product is simply water. Therefore, the burningof hydrogen rather than fossil fuels (natural gas, petroleum, and coal) hasimportant advantages.

The burning of fossil fuels is a source of environmental pollutants. They become the source of acid rain and discharge a large amount of toxicgases like SO_2 and CO_2.

Controlling carbondioxide emissions into the atmosphere is a difficultchallenge, but the answer might lie in the conversion to a hydrogeneconomy, hydrogen would become a major energy barrier. Automobiles,for example may be modified to burn hydrogen. At present, in USA theyuse car using a modified piston engine and has a hydrogen storage unit inthe tank. This proves that it is possible to develop hydrogen-burning cars though hydrogen in not a primary energy source. But it is a convenient andnon-polluting fuel, but it would have to be obtained from other energysources.

1) It is produced by heating propane and steam at high temperature and pressure in presence of the catalyst nickel.

$$C_3H_{8(g)} + 3H_2O_{(g)} \xrightarrow{Ni} 3\,CO_{(g)} + 7H_{2(g)}$$

2) Pure hydrogen may be produced by reacting carbonmonoxide with steam in the presence of a catalyst to fix CO_2 and H_2. The CO_2 is removedby dissolving it in a basic aqueous solution.

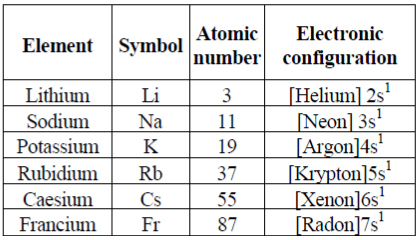
3) Hydrogen can be obtained directly from water that is decomposed by some form of energy. For example, electricity from solar photovoltaic collectors can be used as a source of energy to decompose water byelectrolysis. Researchers use solar energy to convert water directly tohydrogen and oxygen.

3.15 Alkali metals

Position of alkali metals in the periodic table

Alkali metals occupy the group I of the periodic table. Elementslithium, sodium, potassium, rubiduim, caesium and francium constitutealkali metals. They are named so from the Arabic word `Alquili' meaning`plant ashes'. Ashes of plants are composed mainly of sodium andpotassium carbonates.

Electronic configuration of alkali metals



Element	Symbol	Atomic number	Electronic configuration
Lithium	Li	3	[Helium] $2s^1$
Sodium	Na	11	[Neon] $3s^1$
Potassium	K	19	[Argon]$4s^1$
Rubidium	Rb	37	[Krypton]$5s^1$
Caesium	Cs	55	[Xenon]$6s^1$
Francium	Fr	87	[Radon]$7s^1$

General characteristics

1. The alkali metals are shiny white and soft.
2. They can be readily cut with a knife.
3. They are extremely reactive metals and form strong alkaline oxidesand hydroxides.
4. The last metal of this group, francium is radioactive.
5. Since the alkali metals are extremely reactive they occur only ascompounds in nature.
6. All the alkali metals exhibit an oxidation state of +1. This isbecause the metals can easily lose their single outermost electron.

7. The alkali metals give characteristic color in bunsen flame. Thecolors given by Li, Na and K are crimson red, yellow, lilac respectively.

This is because when the alkali metal or any of its compounds are heated ina bunsen flame, the ns' electron gets excited to higher energy levels andwhile returning to their ground state the excitation energy absorbed by themis released as light in the visible region.

Gradation in Physical Properties

1. Density: In general, these elements have high density due to the close packing of atoms in their metallic crystals. Lithium has low densitydue to the low atomic weight of the atom. Density of the elements increaseson moving down the group due to the increase in the mass of the atomswith increasing atomic number. However, K is lighter than Na probablydue to an unusual increase in atomic size.

2. Atomic volume: Atomic volume increases on moving down the group from Li to Cs. Hence there is an increase in atomic and ionic radii inthe same order.

3. Melting and boiling points: All alkali metals have low melting and boiling point due to the weak bonding in the crystal lattice. The weakinteratomic bonds are attributed to their large atonic radii and to thepresence of one valence electron. With the increase in the size of the metalatoms, the repulsion of the non-bonding electron gets increased andtherefore melting and boiling points decreases on moving down the groupfrom Li to Cs.

4. Ionization energy: The first ionization energies of alkali metals are relatively low and decreases on moving down from Li to Cs.

$$M_{(g)} \rightarrow M^+_{(g)} + 1e^-$$

As the atomic radius gets increased on moving down the group, the outer electron gets farther and farther away from the nucleus and thereforeionization energy decreases.

The second ionization energies of alkali metals are fairly high. This implies that the loss of the second electron is quite difficult, because it hasto be pulled out from the noble gas core.

5. Electropositive character: As alkali metals have low ionization energies, they have a great tendency to lose electrons forming unipositive ions. Therefore they:

$$M \rightarrow M^{+} + 1e^{-}$$

have strong electropositive character. Electropositive character increases as we go down the group. The alkali metals are so highly electropositive thatthey emit electrons when irradiated with light. This effect is known asphotoelectric effect. Due to this property, Cs and K are used inphotoelectric cells.

6. Oxidation state: All the alkali metals have only one electron intheir outermost valence shall. As the penultimate shell being complete,these elements lose one electron to get the stable configuration of thenearest inert gas. Thus, they are monovalent elements showing an oxidationstate of +1.

7. Reducing properties: As alkali metals have low ionization energy, they lose their valence electrons readily and thus bring about reductionreaction. Therefore these elements behave as good reducing agents.

Extraction of Lithium and Sodium

Extraction of Lithium

Electrolysis of Lithium chloride

Lithium metal is obtained by the electrolysis of moisture free lithium chloride in a crucible of thick porcelain using gas-coke splinter anode andiron wire cathode. For the preparation of the metal on a large scale, a fusedmixture of equal parts of lithium and potassium chloride is used, as it meltsat a lower temperature of 720 K.Lithium is also obtained by the electrolysis of a concentrated solution oflithium chloride in pyridine or acetone.

Properties of Lithium

Physical: Lithium is a silvery white metal and it is the lightest of allsolid elements. It's vapors impart calamine red color to the flame. It is agood conductor of heat and electricity. It gives alloys with number ofmetals and forms amalgam.

Chemical

1) With air: Lithium is not affected by dry air but in moist air it is readilyoxidized. When heated in air above 450K, it burns to give lithiummonoxide and lithium nitride.

$$4\,Li + O_2 \rightarrow 2Li_2O$$

$$6\,Li + N_2 \rightarrow 2Li_3N$$

2) It decomposes cold water forming lithium hydroxide and hydrogen

$$2Li + 2H_2O \rightarrow 2LiOH + H_2$$

3) Lithium is a strongly electropositive metal and displaces hydrogen from acid with the formation of corresponding lithium salts. Dilute andconcentrated hydrochloric and dilute sulphuric acid react readily whileconcentrated sulphuric acid reacts slowly. With nitric acid, the action isviolent and metal melts and catches fire.

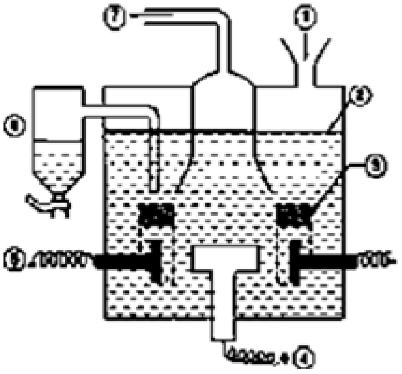
Uses

1) For the manufacture of alloys.
2) As a deoxidizer in the preparation of copper and nickel.
3) Lithium citrate and salicylate are used in the treatment of gout.
4) $LiAlH_4$ is used as a reducing agent.
5) Its compounds are used in glass and pottery manufacture.

Extraction of Sodium

Down's process:

It is now rtfgmanufactured by electrolysis of fused sodium chloride.Down's electrolytic cell, consists of an iron box through the



1. NaCl
2. Fused NaCl
3. Wire gauze shell
4. Graphite anode
5. Iron cathode
6. Sodium
7. Chlorine

Down process

bottomofwhich rises a circular carbon anode. The anode is surrounded by a ringshaped iron cathode enclosed in a wire gauze shell which also acts as apartition and separates the two electrodes.On electrolysis, chlorine is liberated at the anode and let out through anexit at the top. Sodium is liberated at the cathode and remains in the wiregauzeshell. Level of molten sodium rises and it overflows into a receiver.

$$2NaCl \rightarrow 2Na + Cl_2$$

Physical properties

1) It is a silvery white metal when freshly cut but is rapidly tarnished in air. It forms tetragonal crystals.
2) It is a soft metal.
3) It is a good conductor of electricity.
4) It dissolves in liquid ammonia forming an intense blue solution.

Chemical properties

1) Action of air: In moist air a layer of sodium oxide, hydroxide andcarbonate is formed on its surface which loses its lustre.

$$4Na + O_2 \longrightarrow 2\,Na_2O \xrightarrow{2H_2O} 4NaOH \xrightarrow{2CO_2} Na_2CO_3 + 2H_2O$$

When heated in air, it burns violently to form the monoxide and the peroxide.

$$4\,Na + O_2 \longrightarrow 2Na_2O$$
$$2\,Na + O_2 \longrightarrow Na_2O_2$$

2) Action of water: It decomposes water vigorously, liberating hydrogen and forming sodium hydroxide.

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

3) Action of ammonia: Sodium gives sodamide with ammonia liberating hydrogen.

$$2\,Na + 2NH_3 \xrightarrow{570\text{-}670K} 2\,Na\,NH_2 + H_2.$$

Sodium dissolved in liquid ammonia is used as a reducing agent in organic chemistry.

4) Action of acids: It displaces hydrogen from acids.

$$2\,HCl + 2\,Na \longrightarrow 2\,NaCl + H_2.$$

5) Reducing action: Reduces many compounds when heated with them in the absence of air.

$$Al_2O_3 + 6\,Na \longrightarrow 2\,Al + 3\,Na_2O$$
$$SiO_2 + 4Na \longrightarrow Si + 2\,Na_2O.$$

Reduces carbondioxide when heated forming carbon and sodium carbonate.

$$4\,Na + 3\,CO_2 \longrightarrow 2\,Na_2CO_3 + C.$$

6) With Mercury: When heated with mercury, sodium forms an amalgam of varying composition Na_2Hg, Na_3Hg, NaHg etc.

Uses

1) For the preparation of sodium peroxide, sodamide and sodiumcyanide, tetraethyl lead etc.

2) Sodium amalgam is employed as a reducing agent.

3) As a deoxidizing agent in the preparation of light alloys and somerare earth metals from their oxides.

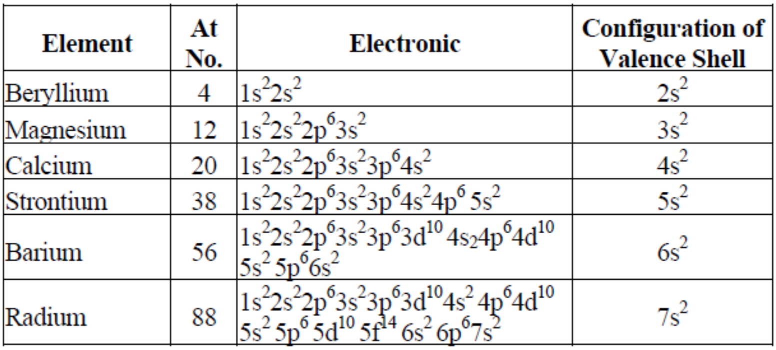
4) It acts as a catalyst in the polymerization of isoprene (C_5H_3) intoartificial rubber.

5) As a reagent in organic chemistry.

3.16 Alkaline earth metals

General characteristics

The second group of the periodic table contains Beryllium (Be),Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium(Ra). These elements are also a known as "Alkaline Earth Metals". Theword earth was applied in old days to a metallic oxide and because theoxides of calcium, strontium and barium produced alkaline solutions inwater and, therefore these metals are called the alkaline earth metals.Radium corresponds to all the alkaline earth metals in its chemicalproperties but being radioactive, it is studied along with other radioactiveelements.Like the alkali metals, they are very reactive and hence never occur innature in free form and react readily with many non-metals.



Element	At No.	Electronic	Configuration of Valence Shell
Beryllium	4	$1s^2 2s^2$	$2s^2$
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	$3s^2$
Calcium	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$4s^2$
Strontium	38	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 5s^2$	$5s^2$
Barium	56	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s_2 4p^6 4d^{10} 5s^2 5p^6 6s^2$	$6s^2$
Radium	88	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^{10} 5f^{14} 6s^2 6p^6 7s^2$	$7s^2$

The electronic configurations show that for each element, the neutral atom has two electrons after inert gas core and two electrons are in acompleted s-subshell. Thus, the outer electronic configuration of eachelement is ns^2 where n is the number of the valence shell. It can be expectedthat the two electrons can be easily removed to give the inert gas electronicconfiguration. Hence these elements are all bivalent and tend to form ionicsalts. Thus ionic salts are less basic than group 1. Due to their alikeelectronic structure, these elements resemble closely in physical andchemical properties.The variation in physical properties are not as regular as for thealkalimetals because the elements of this group do not crystallize with thesame type of metallic lattice.These elements have been sufficiently soft yet less than the alkalimetalsas metallic bonding in these elements has been stronger than in first groupalkali elements.

Beryllium is unfamiliar, partly because it is not very abundant and partly because it is difficult to extract. Magnesium and calcium areabundant and among the eight most common elements in the earth's crust.Strontium and barium are less abundant but are well known, while radiumis extremely scarce and its radioactivity is more important than itschemistry.

Metallic properties

The alkaline earth metals are harder than the alkali metals. Hardness decreases, with increase in atomic number. They show good metallic lustreand high electrical as well as thermal conductivity because the two selectronscan easily move through the crystal lattice.

Melting and Boiling Points

Both melting and boiling points do not show regular trends becauseatoms adopt different crystal structures. They possess low melting and boiling points. These are, however, higher than those of alkali metalsbecause the number of bonding electrons in these elements is twice as greatas group 1 elements.

Atomic radius

The atoms of these elements are somewhat smaller than the atoms ofthe corresponding alkali metals in the same period. This is due to higher nuclear charge of these atoms which tends to draw the orbital electronsinwards. Due to the smaller atomic radius, the elements, are harder, havehigher melting points and higher densities than the elements of group 1.Atomic radius is seen to increase on moving down the group on account ofthe presence of an extra shell of electron at each step.

Ionic radius

The ions are also large but smaller than those of the elements in group:This is due to the fact that the removal of two orbital electrons in theformation of bivalent cations M^{2+}, (Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, etc) increasesthe effective nuclear charge which pulls the electrons inwards and thusreduces the size of the ions. The ionic radius is seen to increase on movingdown the group 2.

Atomic volume

Due to the addition of an extra shell of electrons to each element fromBe to Ra, the atomic volume increases from Be to Ra.

Ionization Energy

As the alkaline earth metals are having smaller size and greater nuclear charge than the alkali metals, so the electrons are more tightly held and hencethe first ionization energy would be greater than that of the alkali metal.The second ionization energy has been to be nearly double than that ofthe first ionization energy.It is interesting to observe that although the IE_2 of the alkaline earthmetals is much higher than the IE_1 they are able to form, M^{2+}ions. This is due to their high heat of hydration in aqueous solution and high latticeenergy in the solid state. As the atomic size gets increased from Be to Ba,the values of IE_1 and IE_2 of these elements would decrease on going downthe group, ie, Be to Ba.

As among second group elements beryllium has the highest ionization energy. It has the least tendency to form Be^{2+} ion.Thus its compounds with nitrogen, oxygen, sulphur and halogens arecovalent whereas the corresponding compounds of Mg, Ca, Sr and Ba areionic.The total energy required to produce gaseous divalent ion for secondgroup elements is over four times greater than the amount needed to ionize alkali metals. This very high energy requirement is more than offset by thehydration energy or the lattice energy being more than four times greater.

Oxidation states

Because of the presence of two s-electrons in the outermost orbital,being high heat of hydration of the di-positive ions and comparatively lowvalue of IE_2, the alkaline earth metals have been bivalent. The divalent ionis having no unpaired electron, hence their compounds are diamagnetic and colorless, provided their anions have been also colorless.

Flame coloration

These elements and their compounds impart characteristic colors to flame. Thus, barium - apple green, calcium - brick red, strontium – crimsonred, radium - crimson red.The reason for imparting the color to flame is that when elements ortheir compounds are put into flame, the electrons get energy and excite tohigher energy levels. When they return to the ground state they emit theabsorbed energy in the form of radiations having particular wavelength.Beryllium and magnesium atoms are smaller and their electrons beingstrongly bound to the nucleus are not excited to higher energy levels.Therefore they do not give the flame test.

Diagonal relationship between Beryllium and Aluminium

In case of beryllium, a member of second period of the periodic table, which resembles more with Aluminium group (13 group) than the memberofits own group (2nd). The anomalousbehavior of beryllium is mainlyascribed to its very small size and partly due to its high electronegativity.These two factors tend to increase the polarizing power of Be^{2+}tend to form ions to such extent that it is significantly equal to the polarizing powerof Al^{3+} ions. Thus the two elements resemble very much.

Magnesium

The magnesium comes from the name of the mineral magnesite, which in turn is believed to stem from the name Magnesia. The

British chemistHumphry Davy discovered the pure element magnesium in 1808.Due to its low density, it is considered to be a structural unit.

Important Ores

Magnesium does not occur in the native state. In the combined state it occurs very abundantly in the earth crust.
Magnesite, $MgCO_3$ Dolomite,$MgCO_3.CaCO_3$
Epsomsalt, $MgSO_4$,.$7H_2O$
Carnallite $MgCl_2.KCl.6H_2O$

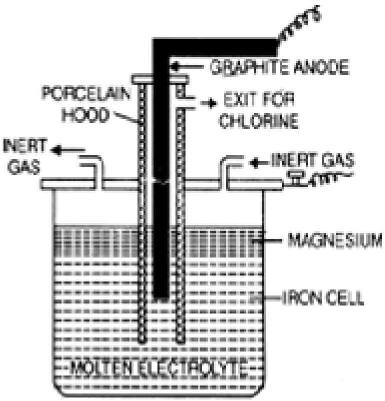
However magnesium ion Mg^{2+}, is the third most abundant dissolved ionin the oceans, after Cl^- and Na^+. The oceans are the best sources formagnesium. It is widely distributed in the vegetable kingdom being presentin chlorophyll, the green coloring matter of the leaves.

Metallurgy

Magnesium is prepared on a large scale by the electrolysis of eitherfused magnesium chloride or magnesia.

1. Electrolysis of fused magnesium chloride

The purified carnallite ore is the principal source for this process. Amixture of equal quantities of carnallite and NaCl is fused to a clear liquidat 973K. The alkali chloride prevents hydrolysis of magnesium chlorideand increases the conductivity of the fused mass.



$$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$$

The electrolysis of the fused mass is carried out in an atmosphere ofcoal gas in air tight iron cell which can hold 6-7 tonnes of the electrolyte.The temperature of the electrolyte bath is maintained at 970K. The iron cellitself acts as a cathode unlike the anode consists of a carbon or graphite rodsurrounded by a porcelain tube through which the liberated chlorineescapes. Molten magnesium being lighter than the electrolyte, rises to thesurface and is periodically removed with perforated ladle. The electrolysisis carried out in an atmosphere of coal gas so as to avoid the oxidation ofmolten magnesium. The metal thus obtained is 99.9% pure. It may befurther purified by re-melting with a flux of anhydrous magnesium chlorideand sodium chloride.

Physical properties

Pure magnesium metal is a relatively active silvery white metal. Atslightly below its melting point, it is malleable and ductile and can bedrawn into wire or rolled into ribbon in which form it is generally sold. It isa very light metal.

Chemical Properties

1. Action of Air: It does not tarnish in dry air but a layer of white oxide isformed on its surface in moist air.

2. With air on burning: It burns in air or oxygen with a dazzling light rich in ultraviolet rays, forming magnesium oxide and magnesiumnitride.

$$2Mg + O_2 \longrightarrow 2MgO$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

3. With CO_2: It continues to burn in CO_2.

$$2Mg + CO_2 \longrightarrow 2MgO + C$$

4. Action of Water: When heated with steam it burns brilliantly producing magnesiumoxide and hydrogen.

$$Mg + H_2O \longrightarrow MgO + H_2$$

5. Action of Acids: Dilute HCl or H_2SO_4 gives hydrogen with magnesium. With diluteHNO$_3$, part of the hydrogen liberated is oxidized by nitric acid, which itselfis reduced to a variety of products depending upon the concentration. Withconcentrated HNO_3, it gives ammonium nitrate.

$$4Mg + 10HNO_3 \longrightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$$

6. Displacement of Metals: It is a strongly electropositive metal and hence Mg displaces nearly allthe metals from the solutions of their salts eg.

$$Mg + 2AgNO_3 \longrightarrow Mg(NO_3)_2 + 2Ag$$

7. Reducing Action: Mg has great affinity for oxygen and it liberates sodium, potassium,boron and silicon from their oxides at high temperatures.

$$K_2O + Mg \longrightarrow MgO + 2K$$

$$B_2O_3 + 3Mg \longrightarrow 3MgO + 2B$$

Uses of Magnesium

1. In flashlight photography, pyrotechnics and in fireworks.
2. As a reducing agent in the preparation of boron and silicon andde-oxidizer in metallurgy.

Compounds of alkaline earth metals

Magnesium sulphate, epsom slat, $MgSO_4.7H_2O$

It is prepared by dissolving magnesium oxide or carbonate in dilute sulphuric acid.

$$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$$

Uses

1) As a purgative.

2) In dyeing and tanning processes and in dressing cotton goods.

3) Platinized $MgSO_4$ is used as a catalyst.

Calcium oxide, CaO, quicklime

It is prepared by burning limestone in specially designed kilns.

$$CaCO_3 \xrightarrow{1070K} CaO + CO_2$$

Properties

1. Lime is a white porous solid.
2. On adding water it gives a hissing sound and becomes very hot. Thefine powder obtained is known as slaked lime and consists of calciumhydroxide $Ca(OH)_2$. This process is called slaking of lime.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

The paste of lime in water is called milk of lime whereas the filtered and clear solution is known as lime water.

3. With chlorine it gives bleaching powder $CaOCl_2.H_2O$.
4. With carbondioxide, it forms calcium carbonate while withsulphurdioxide, calcium sulphite is obtained.
5. Moist hydrochloric acid gas reacts with it to give calcium chloride butthere is no action with the dry gas.

$$CaO + 2\ HCl \longrightarrow CaCl_2 + H_2O$$

Uses

1. For the manufacture of calcium chloride, cement, mortar and glass.
2. For drying gases and alcohol.
3. As milk of lime, used in refining sugar and white washing.
4. As lime water, used as a reagent in laboratory and in medicine.

Calcium sulphate, $CaSO_4$

It occurs as Anhydrite, $CaSO_4$ and Gypsum $CaSO_4 .2H_2O$. It may be prepared by adding dilute sulphuric acid to the solution of a calcium salt.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO4 + H_2O + CO_2$$

Uses of Gypsum

It is used for preparing plasters and as a retardant for the setting of cement.

Plaster of Paris

When Gypsum is heated to about 393K it loses 1½ molecules of waterand forms plaster of paris with the formula $CaSO_4\ \frac{1}{2}H_2O$, CalciumSulphate hemihydrate. The substance is known as plaster of paris becausethe large deposits of Gypsum used for the manufacture of plaster are atMontmeite (Paris).When plaster of paris is wetted with, it forms a plastic mass which setsin from 5 to 15 minutes to a white porous hard mass. A slight expansionoccurs during the setting so that it will take sharp impression of a mould.The process of setting takes place in two steps, the setting step and thehardening step. The final product of setting is gypsum.

$$CaSO_4.\tfrac{1}{2}H_2O \xrightarrow[\text{setting step}]{3/2\ H_2O} CasO_4.2H_2O \xrightarrow[\text{Step}]{\text{hardening}} CaSO_4.2\ H_2O$$

The setting step may be catalysed by NaCl while it is retarded by boraxor alum.

Uses: It is used

1. In surgery for plastering the fractured bones.
2. In making molds for statues, in dentistry etc.
3. In making false ceilings.

Chapter IV Chemical Bonding and Molecular Structure

Introduction - The Octet rule and its exception - Elementary theories on chemical bonding - Chemical bond - Classification of molecules - Kossel-Lewis approach to Chemical Bonding - Types of Bonds - Ionic (or) Electrovalent bond - Formation of ionic or electrovalent bond - Lattice Enthalpy - Covalent bond - Formation of Covalent bond - Valence Shell Electron Pair Repulsion (VSEPR) model - Effect of bonding and nonbonding electrons on the structure of molecules - Valance Bond theory - Orbital overlap concept - Types of bonds Strength of sigma and pi bonds – overlapping of atomic orbitals - Theory of Hybridisation - Promotion (Excitation) of electrons - Hybridisation (mixing of orbitals) - Concept of Resonance - Salient features of hybridisation - Types of hybridization - Geometry of molecules - Molecular Orbital (MO) theory - LCAO method - Criteria for orbital overlap - Symmetry - Energy - Combination of atomic orbitals and their schematic illustration -Conditions for the Combination of Atomic Orbitals - Types of Molecular Orbitals - Qualitative MO energy level diagram of homo and hetero diatomic molecules – H_2, He, Li, Be_2, CO, NO and HCl - Bond order - Stability of molecules - Co-ordinate-covalent bonding or Dative bonding - Intermolecular forces - Hydrogen bonding - Strength of H-bonding - Types of H-bonds - Importance of H-bonding.

Introduction

Matter is made up of one or different type of elements. Under normal conditions no other element exists as an independent atom in nature, except noble gases. However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule. Obviously there must be some force which holds these constituent atoms together in the molecules. The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.

4.01 The Octet rule and its exception

Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell that could accommodate a maximum of eight electrons. He further assumed that these eight electrons occupy the corners of a cube which surround the 'Kernel'. Thus the single outer shell electron of sodium would occupy one corner of the cube, while in the case of a noble gas all the eight corners would be occupied. This octet of electrons' represents a particularly stable electronic arrangement.

Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as electronic theoryof chemical bonding. According to this, atoms can combine either by transfer of valenelectrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as Octet Rule.

Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.In the case of sodium and chlorine, this can happen by the transfer of an electron from sodium to chlorine thereby giving the Na^+ and Cl^- ions. In the case of other molecules like Cl_2, H_2, F_2, etc., the bond is formed by the sharing of a pair of electrons between the atoms. In the process each atom attains a stable outer octet of electrons.

$$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + e^-$$

$$[\mathrm{Ne}]\,3s^1 \qquad [\mathrm{Ne}]$$

$$\mathrm{Cl} + e^- \longrightarrow \mathrm{Cl}^-$$

$$[\mathrm{Ne}]\,3s^2\,3p^6 \qquad [\mathrm{Ne}]\,3s^2\,3p^6 \text{ or } [\mathrm{Ar}]$$

$$\mathrm{Na}^+ + \mathrm{Cl}^- \longrightarrow \mathrm{NaCl} \text{ or } \mathrm{Na}^+\mathrm{Cl}^-$$

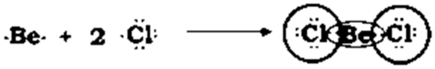
Exceptions to octet rule

It is true that quite a few molecules had non-octet structure. Atoms in these molecules could have a number of electrons in the valence orbit in short of the octer or in excess of the octet.

a) Four electrons around central atom

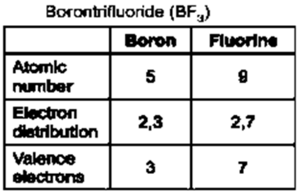
Berylliumdichloride ($BeCl_2$)

	Beryllium	Chlorine
Atomic number	4	17
Electron distribution	2,2	2,8,7
Valence electrons	2	7



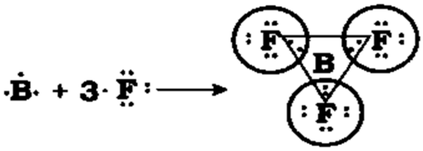
Each chlorine atom is surrounded by **8** electrons, but beryllium is surrounded only by 4 electrons.

b) Six electrons around the central atom



Borontrifluoride (BF_3)

	Boron	Fluorine
Atomic number	5	9
Electron distribution	2,3	2,7
Valence electrons	3	7



Each fluorine atom is surrounded by **8** electrons but boron atom has only **6** electrons.

4.02 Elementary theories on chemical bonding

The study on the "nature of forces that hold or bind atoms together to form a molecule" is required to gain knowledge of the following) to know about how atoms of same element form different compounds combining with different elements.

a) To know why particular shapes are adopted by molecules.

b) To understand the specific properties of molecules or ions and the relation between the specific type of bonding in the molecules.

Chemical bond

Existence of a strong force of binding between two or many atoms is referred to as a Chemical Bondand it results in the formation of a stable compound with properties of its own. The bonding is permanent until it is acted upon by external factors like chemicals, temperature, energy etc. It is known that, a molecule is made up of two or many atoms having its own characteristic properties which depend on the types of bonding present.

Classification of molecules

Molecules having two identical atoms like H_2, O_2, Cl_2, N_2 etc. are called as homonuclear diatomic molecules. Molecules containing two different atoms like CO, HCl, NO, HBr etc., are called as heteronuclear diatomic molecules.Molecules containing identical but many atoms bonded together such as P_4, S_8, etc., are called as homonuclear polyatomics.In most of the molecules, more than two atoms of different kinds are bonded such as in molecules like NH_3, CH_3COOH, SO_2, HCHO and they are called as heteronuclear polyatomics.

Chemical bonds are basically classified into three types consisting of (i) ionic or electrovalent bond (ii) covalent bond and (iii) coordinate covalent bond. Mostly, valence electrons in the outer energy level of an atom take part in the chemical bonding.

In 1916, W. Kossel and G.N. Lewis, separately developed theories of chemical bonding in order to understand why atoms combined to form molecules. According to the electronic theory of valence, a chemical bond is said to be formed when atoms interact by losing, gaining or sharing of valence electrons and in doing so, a stable noble gas electronic configuration is achieved by the atoms. Except Helium, each noble gas has a stable valence shell of eight electrons. The tendency for atoms to have eight electrons in their outer shell by interacting with other atoms through electron sharing or electron-transfer is known as the octet ruleof chemical bonding.

4.03 Kossel-Lewis approach to Chemical Bonding

W. Kossel laid down the following postulates to the understanding of ionic bonding:

- In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases. Therefore one or small number of electrons are easily gained and transferred to attain the stable noble gas configuration.
- The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms.
- The negative and positive ions so formed attains stable noble gas electronic configurations. The noble gases (with the exception of helium which has two electrons in the outermost shell) have filled outer shell electronic configuration of eight electrons (octet of electrons) with a general representation ns^2 np^6.
- The negative and positive ions are bonded and stabilised by force of electrostatic attraction.

Kossel's postulates provide the basis for the modern concepts on electron transfer between atoms which results in ionic or electrovalent bonding. For example, formation of NaCl molecule from sodium and chlorine atoms can be considered to take place according to Kossel's theory by an electron transfer as:

$$\text{(i)}\quad \underset{[Ne]\,3s^1}{Na} \xrightarrow{\text{loss of e}} \underset{[Ne]}{Na^+} + e$$

where [Ne] = electronic configuration of Neon
= $2s^2\,2p^6$

$$\text{(ii)}\quad \underset{[Ne]3s^2\,3p^5}{Cl + e} \xrightarrow{\text{gain of e}} \underset{[Ar]}{Cl^-}$$

[Ar] = electronic configuration of Argon

$$\text{(iii)}\quad Na^+ + Cl^- \xrightarrow[\text{attraction}]{\text{electrostatic}} NaCl\,(\text{or})\,Na^+\,Cl^-$$

NaCl is an electrovalent or ionic compound made up of sodium ions and chloride ions. The bonding in NaCl is termed as electrovalent or ionic bonding. Sodium atom loses an electron to attain Neon configuration and also attains a positive charge. Chlorine atom receives the electron to attain the Argon configuration and also becomes a negatively charged ion. The coulombic or electrostatic attraction between Na^+ and Cl^- ions results in NaCl formation. Similarly formation of MgO may be shown to occur by the transfer oftwo electrons as:

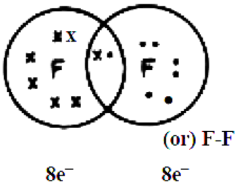
$$\text{(i)}\quad \underset{[Ne]3s^2}{Mg} \xrightarrow{\text{loss of } e^-} \underset{[Ne]}{Mg^{2+}} + 2e$$

$$\text{(ii)}\quad \underset{[He]2s^2\,2p^4}{O + 2e} \xrightarrow{\text{gain of } e^-} \underset{[He]2s^2\,2p^6(\text{or})\,[Ne]}{O^{2-}}$$

$$\text{(iii)}\quad Mg^{2+} + O^{2-} \xrightarrow[\text{attraction}]{\text{electrostatic}} MgO\,(\text{or})\,Mg^{2+}\,O^{2-}$$

The bonding in MgO is also electrovalent or ionic and the electrostaticforces of attraction binds Mg^{2+} ions with O^{2-} ions. Thus, "the binding forcesexisting as a result of electrostatic attraction between the positive andnegative ions", is termed as electrovalent or ionicbond. Theelectro-valency is considered as equal to the number of charges on an ion.Thus magnesium has positive electrovalency of two while chlorine hasnegative electrovalency of one.The valence electron transfer theory could not explain the bonding inmolecules like H_2, O_2, Cl_2 etc., and in other organic molecules that haveions.

G.N. Lewis, proposed the octet rule to explain the valence electron sharing between atoms that resulted in a bonding type with the atoms attaining noble gas electronic configuration. The statement is: "a bond is formed between two atoms by mutual sharing of pairs of electrons to attain a stable outer-octet of electrons for each atom involved in bonding". This type of valence electron sharing between atoms is termed as covalent bonding**.** Generally homonuclear diatomics possess covalent bonds. It is assumed that the atom consists of a `Kernel' which is made up of a nucleus plus the inner shell electrons. The Kernel is enveloped by the outer shells that could accommodate a maximum of eight electrons. The eight outer-shell electrons are termed as octet of electrons and represent a stable electronic configuration. Atoms achieve the stable outer octet when they are involved in chemical bonding. In case of molecules like F_2, Cl_2, H_2 etc., the bond is formed by the sharing of a pair of electrons between the atoms. For example, consider the formation of a fluorine molecule (F_2). The atom has electronic configuration. [He]$2s^2 3s^2 3p^5$ which is having one electron less than the electronic configuration of Neon. In the fluorine molecule, each atom contributes one electron to the shared pair of the bond of the F_2 molecule.In this process, both the fluorine atoms attain the outer-shell octet of a noble gas (Argon) (Figure). Dots (•) represent electrons. Such structures arecalled as Lewis dot structures.



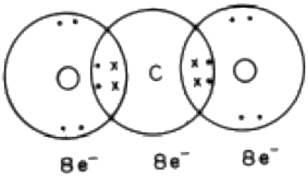
Fluorine molecule

Lewis dot structures can be written for combining of like or different atoms following the conditions mentioned below:

- Each bond is the result of sharing of an electron pair between theatoms comprising the bond.
- Each combining atom contributes one electron to the shared pair.
- The combining atoms attain the outer filled shells of the noble gasconfiguration.

If the two atoms share a pair of electrons, a single bond is said to be formed and if two pairs of electrons are shared a double bond is said to beformed etc. All the bonds formed from sharing of electrons are called ascovalent bonds.

In carbon dioxide (CO_2) two double bonds are seen at the centre carbonatomwhich is linked to each oxygen atom by a double bond. The carbon and the two oxygen atoms attain the Neon electronic configuration.



Carbondioxide molecule

4.04 Types of Bonds

There are more than one type of chemical bonding possible betweenatoms which makes the molecules to show different characteristicproperties. The different types of chemical bonding that are considered toexist in molecules are (i) ionic or electrovalent bondwhich is formed as aresult of complete electron transfer from one atom to the other thatconstitutes the bond; (ii) covalent bondwhich is formed as a result ofmutual electron pair sharing with an electron being contributed by eachatom of the bond and (iii) coordinate - covalent bondwhich is formed as aresult of electron pair sharing with the pair of electrons being donated byonly one atom of the bond. The formation and properties of these types ofbonds are discussed in detail in the following sections.

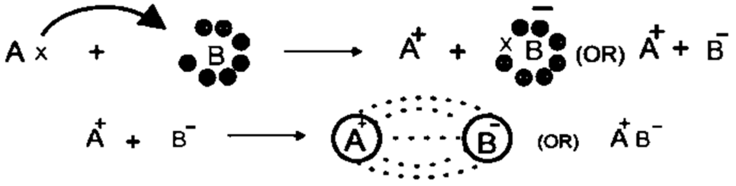
4.05 Ionic (or) Electrovalent bond

The electrostatic attraction force existing between the cation and theanion produced by the electron transfer from one atom to the other isknown as the ionic (or) electrovalent bond. The compounds containing sucha bond are referred to as ionic (or) electrovalent compounds.

Ionic bond is non-directional and extends in all directions. Therefore, insolid state single ionic molecules do not exist as such. Only a network ofcations and anions which are tightly held together by electro-static forcesexist in the ionic solids. To form a stable ionic compound there must be anet lowering of energy. That is, energy is released as a result of electovalentbond formation between positive and negative ions.

Formation of ionic or electrovalent Bond

Let us consider two atoms A and B. The atom A has 1 electron in its valence (outermost) shell. B has 7 electrons in its valence shell. A has 1 electron excess and B has 1 electron lesser than the stable octet configuration. Therefore, A transfers an electron to B. In this transaction both the atoms A and B acquire a stable electron-octet configuration. A becomes a positive ion (cation) and B becomes a negative ion (anion). Both the ions are held together by electrostatic force of attraction. Formation of ionic bond between A and B can be shown as,



The electrostatic attraction between cation (+) and anion (-) produced by electron transfer constitutes an ionic or electrovalent bond. The compounds containing such a bond are referred to as "ionic or electrovalent compound".

When the electronegativity difference between the interacting atoms aregreatly different they will form an ionic bond. In fact, a difference of 2 ormore is necessary for the formation of an ionic bond. Na haselectronegativity 0.9 while Cl has 3.0, thus Na and Cl atoms when broughttogether will form an ionic bond.For example, NaCl is formed by the electron ionization of sodium atomto Na^+ ion due to its low ionization potential value and chlorine atom tochloride ion by capturing the odd electron due to high electron affinity.Thus, NaCl (ionic compound) is formed. In NaCl, both the atoms possessunit charges.

i) $Na(g) \xrightarrow{\text{ionisation}} Na^+_{(g)} + e^-$

$2s^22p^63s^1 \qquad 2s^2sp^6$

sodium cation

ii) $Cl(g) + e^- \xrightarrow{\text{affinity}} Cl^-$

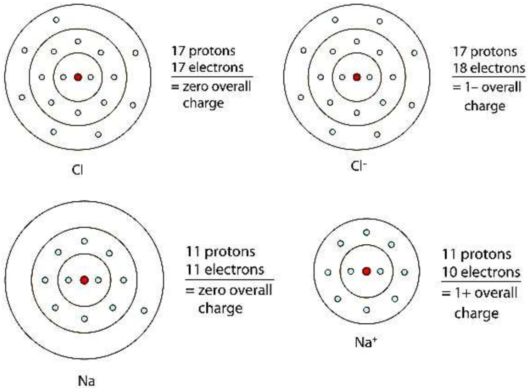
$3s^23p^5 \qquad 3s^2, 3p^6$

chloride anion

iii) $Na^+ + Cl^- \xrightarrow[\text{attraction}]{\text{electrostatic}} NaCl$

Sodium ion   Chloride ion   ionic/crystalline compound is formed

NaCl is formed by the electron ionisation of sodium atom to Na^+ ion due to its low ionisation potential value and chlorine atom to chloride ion by capturing the odd electron due to high electron affinity. Thus, NaCl (ionic compound) is formed. In NaCl, both the atoms possessunit charges.



Lattice Enthalpy

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol^{-1}. This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na^+ (g) and one mole of Cl^- (g) to an infinite distance. This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only.

4.06 Covalent bond

A covalent bond is a chemical bond formed when two atoms mutually share a pair of electron. By doing so, the atoms attain stable octet electronicconfiguration. In covalent bonding, overlapping of the atomic orbitalshaving an electron from each of the two atoms of the bond takes placeresulting in equal sharing of the pair of electrons. Also the interatomic bondthus formed due to the overlap of atomic orbitals of electrons is known as acovalent bond. Generally the orbitals of the electrons in the valency shell ofthe atoms are used for electron sharing. The shared pair of electrons lie inthe middle of the covalent bond. Including the shared pair of electrons theatoms of the covalent bond attain the stable octet configuration. Thus inhydrogen molecule (H_2) a covalent bond results by the overlap of the two s orbitals each containing an electron from each of the two H atoms of themolecule. Each H atom attains '$1s^2$ ' filled K shell.

Formation of covalent bonds

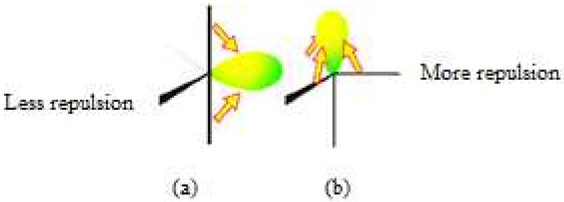
According to G.N. Lewis, two atoms could achieve stable 2 or 8 electrons in the outer shell by sharing electrons between them. Atom A has 1 valence electron and atom B has 1 valence electron. As they approach each other, each atom contributes one electron and the resulting electron pair fills the outer shell of both the atoms.

Thus a shared pair of electrons contributes a covalent bond or electron pair bond. The compounds containing a covalent bond are covalent compounds.

4.07 Valence Shell Electron Pair Repulsion (VSEPR) model

VSEPR theory or model provides a simple procedure to predict the shapes of covalent molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

It is based on the number of regions of high electron density around a central atom. It can be used to predict structures of molecules or ions that contain only non-metals by minimizing the electrostatic repulsion between the regions of high electron density. It can also be used to predict structures of molecules or ions that contain multiple bonds or unpaired electrons.



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The main postulates of VSEPR theory are as follows:

1. The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
2. Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
3. These pairs of electrons tend to occupy such positions in space that minimize repulsion and thus maximize distance between them.

4. The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
5. A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
6. When two or more resonance structure applied to a molecule, the VSEPR model is applicable to any structure.

The repulsive interaction of electron pairs decrease in the order:

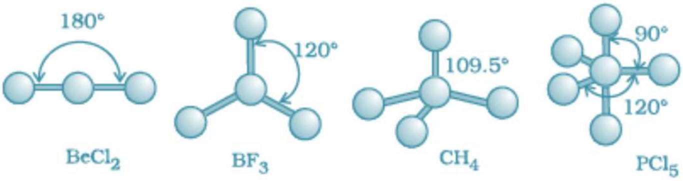
Lone pair (lp) – Lone pair (lp) >
Lone pair (lp) – Bond pair (bp) >
Bond pair (bp) – Bond pair (bp)

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as (i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom has one or more lone pairs.

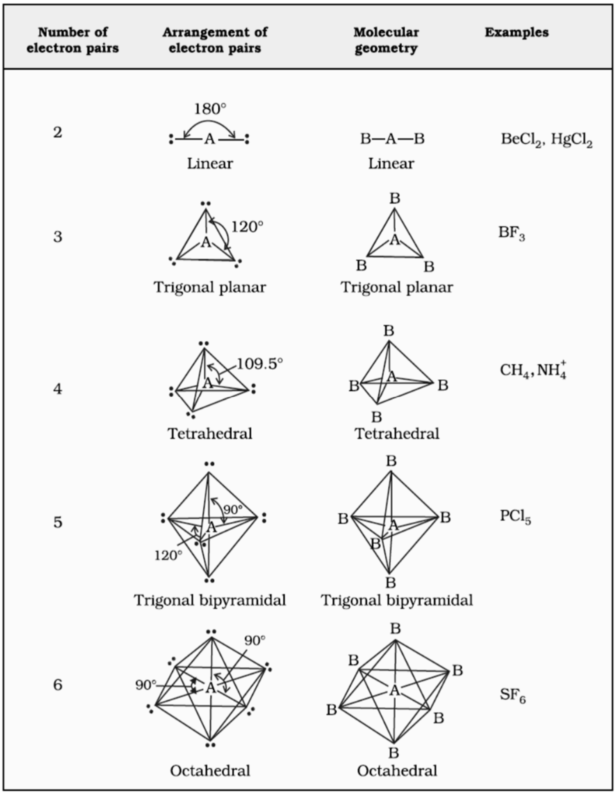
The main postulate of this model is that the structure around a given atom is determined principally by minimizing electron-pair repulsions. The bonding the nonbonding pairs around a given atom should be positioned as far apart as possible.

The following table shows the arrangement of electron pairs about a central atom A (without any lone pairs) and geometries of some molecules/ions of the type AB. Subsequent table shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs. The third table explains the reasons for the distortions in the geometry of the molecule.

As depicted in the above tables, the compounds of AB_2, AB_3, AB_4, AB_5 and AB_6, the arrangement of electron pairs and the B atoms around the central atom A are : linear, trigonal planar, tetrahedral, trigonalbipyramidal and octahedral, respectively. Such arrangement can be seen in the molecules like BF_3 (AB_3), CH_4 (AB_4) and PCl_5 (AB_5) as depicted below by their ball and stick models.

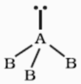
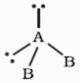
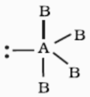
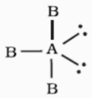
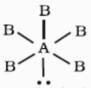
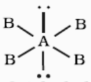


Arrangement of electron pairs about a central atom



Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	180° Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	120° Trigonal planar	Trigonal planar	BF_3
4	109.5° Tetrahedral	Tetrahedral	CH_4, NH_4^+
5	90° 120° Trigonal bipyramidal	Trigonal bipyramidal	PCl_5
6	90° 90° Octahedral	Octahedral	SF_6

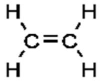
Shapes of molecules having lone pair of electrons

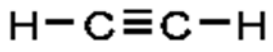
Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1	 Trigonal planar	Bent	SO_2, O_3
AB_3E	3	1	 Tetrahedral	Trogonal pyramidal	NH_3
AB_2E_2	2	2	 Tetrahedral	Bent	H_2O
AB_4E	4	1	 Trigonal bi-pyramidal	See saw	SF_4
AB_3E_2	3	2	 Trigonal bi-pyramidal	T-shape	ClF_3
AB_5E	5	1	 Octahedral	Square pyramid	BrF_5
AB_4E_2	4	2	 Octahedral	Square planar	XeF_4

Shapes of molecules containing bonding pairs and lone pairs with reason for Shapes acquired

Effect of bonding and nonbonding electrons on the structure of molecules

In the ethane Lewis formula shown above all bonds are represented as single lines called single bonds.


The double bond in ethylene


The triple bond in acetylene

Each single bond is made up of two electrons, called bonding electrons. It is also possible for two atoms bonded together to share 4 electrons. This bonding pattern is represented by two lines, each representing two electrons, and is called a double bond. The ethylene molecule shown below is an example. Finally, sharing of 6 electrons between two atoms is also possible. In such case, the representation uses three single lines, an arrangement called a triple bond. The acetylene molecule provides an example of a triple bond.

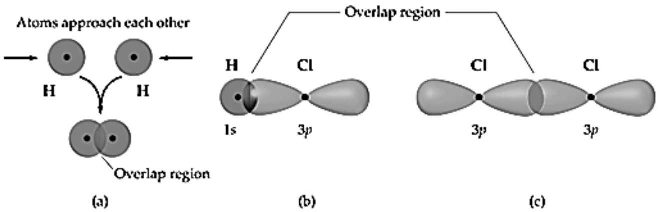
This terminology (single, double, or triple bond) is very loose and informal. The formulas shown above do not do justice to the actual nature of the bonds. All they do is show how many electrons are being shared between the two atoms (2, 4, or 6) but they say nothing about the electronic distribution, or the relative energies of the bonds, or the types of orbitals involved. They are, however, very useful in many situations.

4.08 Valance Bond theory

Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. To start with, let us consider the formation of hydrogen molecule which is the simplest of all molecules.

Valence bond (VB) theory assumes that all bonds are localized bonds formed between two atoms by the donation of an electron from each atom. This is actually an invalid assumption because many atoms bond using delocalized electrons. Valence Bond theory describes covalent bond formation as well as the electronic structure of molecules. The theory assumes that electrons occupy atomic orbitals of individual atoms within a molecule, and that the electrons of one atom are attracted to the nucleus of another atom. This attraction increases as the atoms approach one another until the atoms reach a minimum distance where the electron density begins to cause repulsion between the two atoms. This electron density at the minimum distance between the two atoms is where the lowest potential energy is acquired, and it can be considered to be what holds the two atoms together in a chemical bond.

When a covalent bond is formed, there is shared electron density between the nuclei of thebonded atoms.The simultaneous attraction of the shared electron density for both nuclei holds the atoms together, forming a covalent bond.In valence bond theory, the shared electron density is described as occurring when a valence orbital from one atom overlaps with a valence orbital from another atom.Two electrons with opposite spin are shared in the overlap region, forming a covalent bond. The greater the extent of orbital overlap, the stronger the bond.



Formation of sigma (σ) bonds in H_2, HCl and Cl_2

Consider two hydrogen atoms A and B approaching each other having nuclei NA and NB and electrons present in them are represented by eA and eB. When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate. Attractive forces arise between:

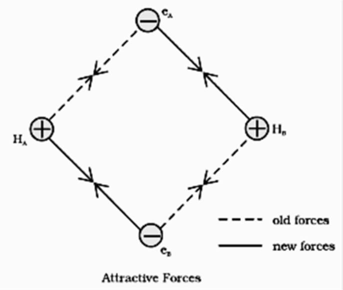
(i) nucleus of one atom and its own electron that is $N_A - e_A$ and $N_B - e_B$.

(ii) nucleus of one atom and electron of other atom i.e., $N_A - e_B$, $N_B - e_A$.

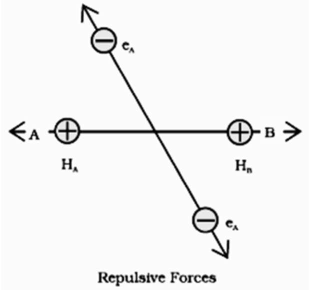
Similarly repulsive forces arise between

(i) electrons of two atoms like $e_A - e_B$,

(ii) nuclei of two atoms $N_A - N_B$.



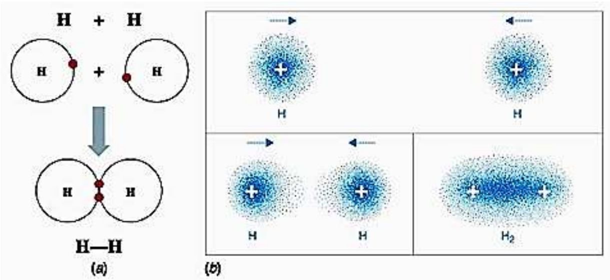
Attractive Forces



Repulsive Forces

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart.

Orbital Overlap Concept



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

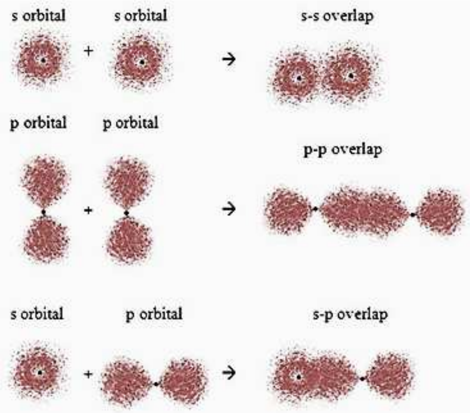
Types of bonds

Sigma bond: This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the inter-nuclear axis. This is called as head on overlap or axial overlap. This can be formed byany one of the following types of combinations of atomic orbitals.

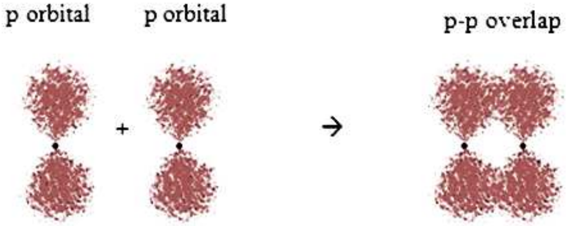
***s-s*overlapping**: In this case, there is overlap of two half-filled *s*-orbitals along the inter-nuclear axis.

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

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



Pi bond: A covalent bond resulting from the formation of a molecular orbital by side-to-side overlap of atomic orbitals along a plane perpendicular to a line connecting the nuclei of the atoms, denoted by the symbol π. Sideways overlap of the formation of π bond is shown below:



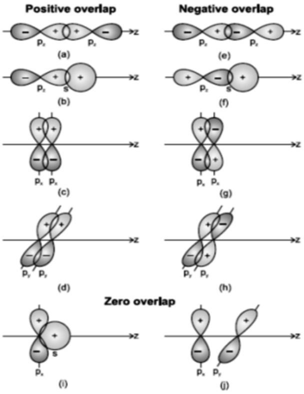
It is important to note that different sources use different terms to define what a sigma and pi bond is. However, once examined carefully, it will be evident that they all try to explain the same thing.

Strength of Sigma and Pi bonds

Basically the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that in the formation of multiple bonds between two atoms of a molecule, pi bond(s) is formed in addition to a sigma bond.

Overlapping of atomic orbitals

When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of amplitude of orbital wave function in space (Figure). Positive and negative sign on boundary surface diagrams in the figure show the sign (phase) of orbital wave function and are not related to charge. Orbitals forming bond should have same sign (phase) and orientation in space. This is called positive overlap. Various overlaps of *s* and *p* orbitals are depicted in the figure below. The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the



homonuclear/heteronuclear diatomic molecules and polyatomic molecules.

We know that the shapes of CH_4, NH_3 and H_2O molecules are tetrahedral, pyramidal and bent respectively. It would be therefore interesting to use VB theory to find out if these geometrical shapes can be explained in terms of the orbital overlaps.

Let us first consider the CH_4 (methane) molecule. The electronic configuration of carbon in its ground state is [He] $2s^22p^2$ which in the excited state becomes [He] $2s^12p_x^12p_y^12p_z^1$. The energy required for this excitation is compensated by the release of energy due to overlap between the orbitals of carbon and the hydrogen. The four atomic orbitals of carbon,each with an unpaired electron can overlap with the 1*s* orbitals of the four H atoms which are also singly occupied. This will result in the formation of four C-H bonds. It will, however, be observed that while the three p orbitals of carbon are at 90° to one another, the HCH angle for these will also be 90°. That is three C-H bonds will be oriented at 90° to one another. The 2*s* orbital of carbon and the 1*s* orbital of H are spherically symmetrical and they can overlap in any direction. Therefore the direction of the fourth C-H bond cannot be ascertained. This description does not fit in with the tetrahedral HCH angles of 109.5°. Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in CH_4. Using similar procedure and arguments, it can be seen that in the case of NH_3 and H_2O molecules, the HNH and HOH angles should be 90°. This is in disagreement with the actual bond angles of 107° and 104.5° in the NH_3 and H_2O molecules respectively.

Theory of Hybridisation

The failures of VB theory based on pure orbital overlaps are explained agreeably based on the concept of hybridisation of orbitals or mixing up of orbitals. There are three major processes that are considered to occur in hybridisation of orbitals. These are:

i) Promotion of electrons to higher or similar energy levels.

ii) Mixing up of various s, p, d and f orbitals to form the same number of new orbitals and

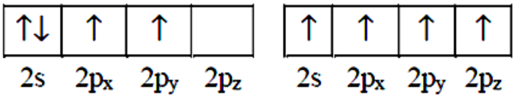
iii) Stabilization of the molecule through bond formations involving hybrid orbitals by release of certain amount of energy which compensates the energy requirement in the electron promotion process.

i) Promotion (Excitation) of Electrons

Atoms of elements like Beryllium, Boron and Carbon have electronic configuration as,

Be (At. no: 4)	: $1s^2 2s^2$
B (At. no: 5)	: $1s^2 2s^2 2p_x^1$
C (At. no: 6)	: $1s^2 2s^2 2p_x^1 2p_y^1$

According to VB theory, Beryllium is expected to behave like a noble gas due to its filled shells, which in practice forms a number of compounds like BeF_2 and BeH_2 proving its bivalency. In case of Boron VB theory predicts univalency due to the presence of one unpaired electron but in practice Boron is trivalent since compounds as BCl_3, BH_3, etc. are found. The stable state (Ground State) electronic configuration of C is (2s22px12py1). Electronic configuration of C suggests only bivalency. But carbon forms over a million compounds in all of which carbon is tetravalent. This suggests only tetravalency. This deficiency is overcome by allowing for promotion (or) the excitationof an electron to an orbital of higher energy. Although for electron promotion energy is needed, if that energy is recovered back during a covalent bond formation, or by a bond with a greater strength or by many number of bonds formation, then the electron promotion becomes energetically allowed and assumed to take place initially. In carbon, promotion of an electron to an orbital which isclose to itself with an empty orbital of only slightly higher energy which isthe $2p_z$ orbital can take place. Then the electron pair is unpaired itself byabsorbing the required energy available by the atom from its surroundingand one of the electrons in the original orbital 2s or 2p shifts to the emptyhigher energy orbital.



Ground state electronic configuration of C

Excited state configuration of C.

Thus promotion of an electron leads to four unpaired electron in theexcited state electronic configuration of carbon atom. Each electron cannow be utilized to form a covalent bond by sharing an electron coming from the combining atom. Thus four σ covalent bonds are possible each with equivalent strength and overlapping tendency. Further, chemical andphysical evidences reveal the four bonds of carbon to be equivalent and thatthey are tetrahedrally oriented. The promotion of an electron from 2s to 2p orbital leads to four half-filled orbitals which can form four bonds leadingto greater energy lowering. This energy is more than the initial energyrequired for the promotion of 2s electron to 2p orbital.

Hybridisation (mixing of orbitals)

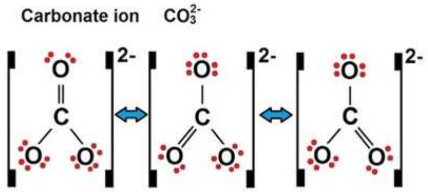
After an electron promotion the 4 electrons are not equivalent, since oneof them involves with an s orbital while the other three involve with porbitals. To explain the equivalence of the four bonds, the concept ofhybridisation is introduced.Dissimilar orbitals like s,p,d with one or many numbers, with nearly thesame energy on the same atom may combine or mix completely to form anequal number of equivalent energy new orbitals with properties of theirown. This is called as hybridisationof orbitals. The new orbitals formedare known ashybrid orbitals and these orbitals possess the properties of thepure orbitals that are mixed to form them. The hybrid orbitals of an atomare symmetrically distributed around it in space. Essentially, mixing up oforbitals to form new orbitals explains the different geometries of manycompounds like CH_4, SF_6, etc.

Concept of Resonance

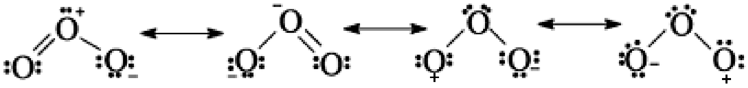
According to the concept of resonance whenever a single Lewisstructure cannot describe a molecular structure accurately, a number ofstructures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are considered to represent the structure. Eachsuch structure is called as canonical structure. A resonance hybrid consistsof many canonical structures. All the canonical structures are equallypossible to represent the structure of the molecule.

For example, in ozone (O_3) molecule, the two canonical structures as shown below and their hybrid represents the structure of O_3 more accurately. Resonance is represented by a double headed arrow placed between the canonical structures. There are two canonical forms of O_3.The resonance structures are possible for molecular ions also. For example, consider resonance in CO_3^{2-} ion.

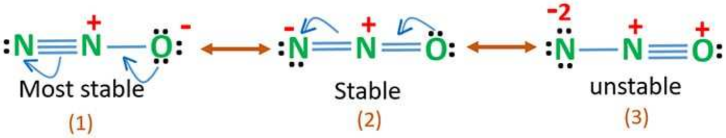
The single Lewis structure based on the presence of two single bondsand one double bond between each carbon and oxygen atoms is adequateto represent the molecule accurately as it represents unequal bonds.According to experimental findings all carbon to oxygen bonds in CO_3^{2-} are equivalent. Therefore the carbonate ion is best described as a resonancehybrid of the canonical forms as shown below.



O_3 molecule



N$_2$O molecule



There are three canonical forms of CO_3^{2-}. Structure of CO_2 molecule is also an example of resonance, theexperimental C-O bond length is found to be shorter than C-O single bondlength and longer than C=O bond length and lies intermediate in valuebetween a pure single and a pure double bond lengths. Also the two C=O bond length in the CO_2 molecule are equivalent and the properties of thetwo bonds are also the same. Therefore, a single lewis structure cannotdepict the structure of CO_2 as a whole and it is best described as aresonance hybrid of the canonical forms given above.

In N_2O molecule which is a linear molecule, structures with charges onatoms can be written similar to CO_2. Here also the experimental bond length of N-N-bond lies between adouble and triple bond and that of N-O bond length lies between asingle and a double bond. Therefore N_2O exists as a hybrid structure of the two canonical forms with a linear geometry.

Salient features of hybridisation:

The main features of hybridisation are as under:

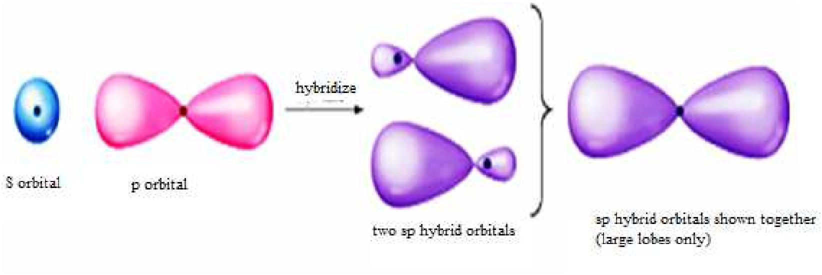
1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridized.
2. The hybridized orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.

4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

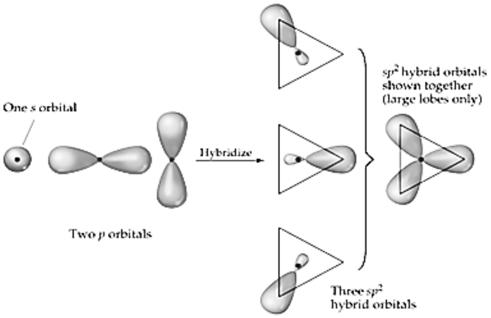
Types of hybridization

How can we use valence bond theory to adequately describe the bonding for polyatomic molecules or ions having electron-domain geometries such as linear, trigonal planar, tetrahedral, trigonal bipyramid oroctahedral? Overlap of atomic s, p and d orbitals will not yield structures with these geometries (exceptlinear)! To explain bonding for these geometries, valence bond theory uses the concept of orbitalhybridization.

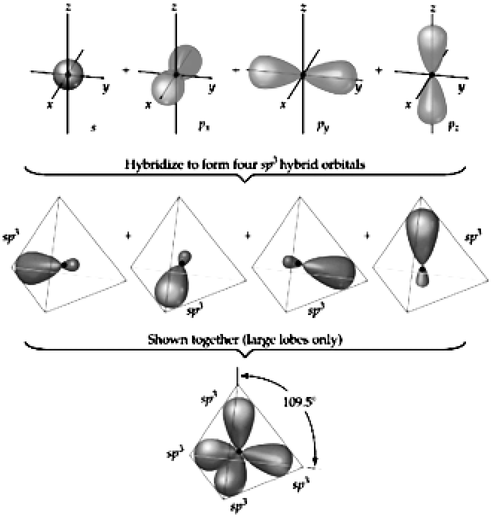
SP hybridization



SP^2 hybridization



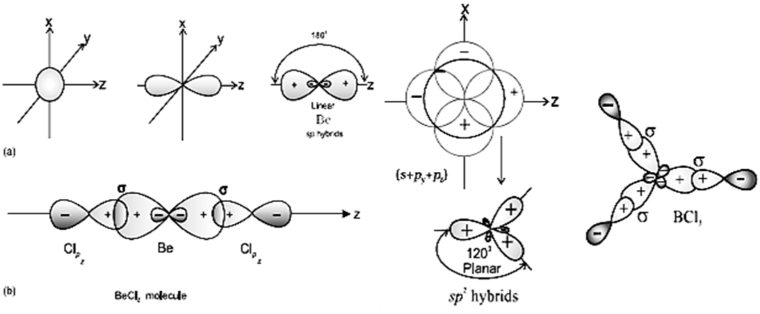
SP^3 hybridization



Geometry of molecules

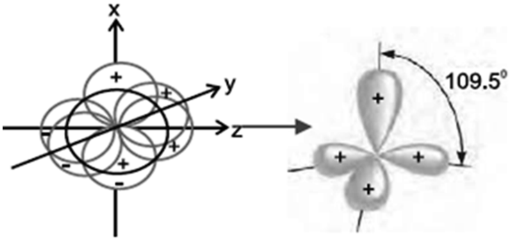
BeCl$_2$:

The ground state electronic configuration of Be is $1s^2 2s^2$. In the exited state one of the 2*s*-electrons is promoted to vacant 2*p* orbital to account for its bivalency. One 2*s* and one 2*p*-orbital gets hybridized to form two *sp* hybridized orbitals. These two *sp* hybrid orbitals are oriented in opposite direction forming an angle of 180°. Each of the *sp* hybridized orbital overlaps with the 2*p*-orbital of chlorine axially and forms two Be-Cl sigma bonds. This is shown in the figure below.

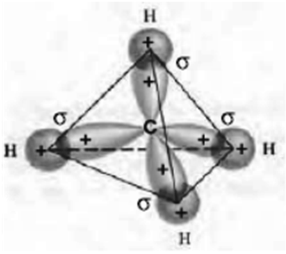


In **BCl_3**molecule, the ground state electronic configuration of central boron atom is $1s^2 2s^2 2p^1$. In the excited state, one of the 2*s* electrons is promoted to vacant 2*p* orbital as a result boron has three unpaired electrons. These three orbitals (one 2*s* and two 2*p*) hybridize to form three *sp*2 hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2*p* orbitals of chlorine to form three B-Cl bonds. Therefore, in BCl_3 (shown in the above figure), the geometry is trigonal planar with ClBCl bond angle of 120°.

In **CH_4** molecule in which there is mixing of one *s*-orbital and three *p*-orbitals of the valence shell to form four sp^3 hybrid orbital of equivalent energies and shape. There is 25% *s*-character and 75% *p*-character in each sp^3 hybrid orbital. The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp^3 hybrid orbitals is 109.5° as shown in figure.



$s+p_x+p_y+p_z$ sp^3 **hybrids**



CH_4

4.10 Molecular Orbital (MO) theory

Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are:

1. The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
2. The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.

3. While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.
4. The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbitalwhile the other is called antibonding molecular orbital.
5. The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
6. Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.
7. The molecular orbitals like atomic orbitals are filled in accordance with the *Aufbau* principle obeying the Pauli's exclusion principle and the Hund's rule.

LCAO method

According to wave mechanics, the atomic orbitals can be expressed by wave functions (ψ) which represent the amplitude of the electron waves. These are obtained from the solution of Schrödinger wave equation.

However, since it cannot be solved for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecules are difficult to obtain directly from the solution of Schrödinger wave equation. To overcome this problem, an approximate method known as linear combination of atomic orbitals (LCAO)has been adopted.

Let us apply this method to the homonuclear diatomic hydrogen molecule. Consider the hydrogen molecule consisting of two atoms A and B. Each hydrogen atom in the ground state has one electron in 1*s* orbital. The atomic orbitals of these atoms may be represented by the wave functions ψ_A and ψ_B. Mathematically, the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave functions of individual atomic orbitals as shown below:

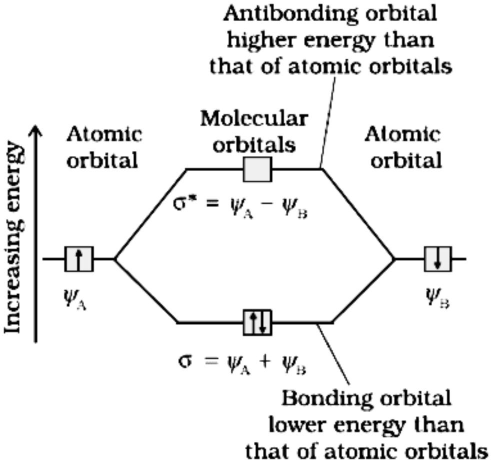
$$\psi_{\mathrm{MO}} = \psi_{\mathrm{A}} \pm \psi_{\mathrm{B}}$$

Therefore, the two molecular orbitals σ and σ* are formed.

$$\sigma = \psi_{\mathrm{A}} + \psi_{\mathrm{B}}$$
$$\sigma^* = \psi_{\mathrm{A}} - \psi_{\mathrm{B}}$$

The molecular orbital σ formed by the addition of atomic orbitals is called the bonding molecular orbitalwhile the molecular orbital σ* formed by the subtraction of atomic orbital is called antibonding molecular orbitalas depicted in the figure shown below.

Qualitatively, the formation of molecular orbitals can be understood in terms of the constructive or destructive interference of the electron waves of the combining atoms. In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other due to constructive interference while in the formation of antibonding molecular orbital, the electron waves cancel each other due to destructive interference. As a result, the electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei.

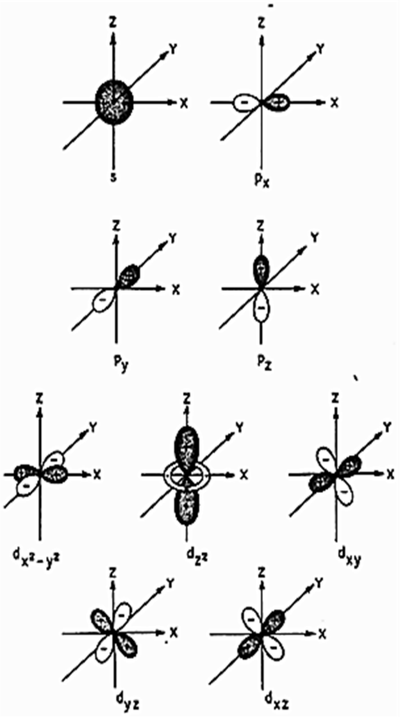


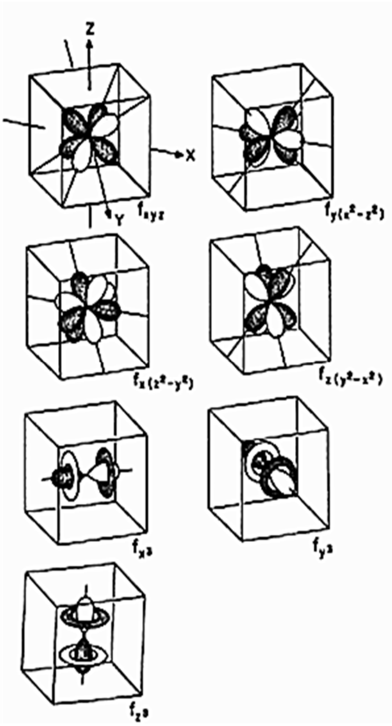
In fact, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilize a molecule. Therefore, a bonding molecular orbital always possesses lower energy than either of the atomic orbitals that have combined to form it. In contrast, the electrons placed in the antibonding molecular orbital destabilize the molecule. This is because the mutual repulsion of the electrons in this orbital is more than the attraction between the electrons and the nuclei, which causes a net increase in energy.

It may be noted that the energy of the antibonding orbital is raised above the energy of the parent atomic orbitals that have combined and the energy of the bonding orbital has been lowered than the parent orbitals. The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

Criteria for orbital overlap

It is not possible for any particular atomic orbital to mix or overlap with just any other orbital. Therefore, certain criteria must be met when constructing a set of molecular orbitals by the use of LCAO method. Particularly the shape and disposition in space with different wave function signs for the atomic orbitals are very important. The shapes of s, p, d and f orbitals are shown for reference.





The three important criteria to be observed are:

1. The atomic orbitals under overlap must be approximately of the same energy, i.e. of comparable magnitude.
2. The atomic orbitals must overlap as extensively as possible, i.e. the overlap must be effective and appreciable.
3. Both the atomic orbitals must have the same symmetry relative to the inter-nuclear axis, i.e. the atomic orbitals must undergo similar changes in symmetry when rotated about the molecular axis.

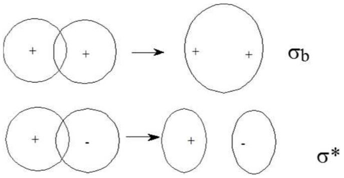
The above features are explained in terms of symmetry and energy.

Symmetry

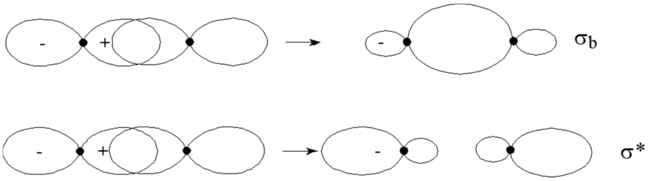
Symmetry either allows or forbids bond formation. If the symmetry is correct then the two orbitals and form bonding and antibonding MOs and if it is wrong the two orbitals will not mix and you get MOs that are only the atomic orbitals you start with. If the orbitals do not have the right symmetry they will have no net overlap. The symmetry is defined alone the line connection to two nuclei. If the two orbitals have the same symmetry relative to this line then the symmetry is correct.

Examples:

Overlap of an s with an s orbital will give significant overlap and you get a bonding and antibonding pair as shown at right side, where the bonding orbital has lower energy then the antibonding orbital.

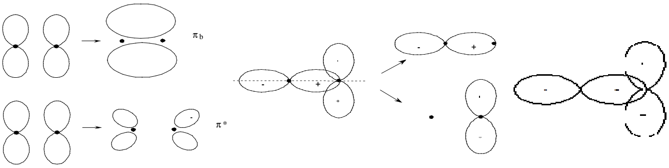


For two p_z orbitals you will also get a σ bonding and σ* antibonding pair with again the bonding orbital having lower energy then the antibonding orbital.



And for two p_y or two p_z orbitals you find similar symmetries and get bonding and antibonding molecular orbitals but they are now π in symmetry. Now what happens when the two orbitals have different symmetries? If we take a p_z with a p_x orbital that the net overlap for the two is zero since the symmetry of the two orbitals is such that any positive overlap the occurs below the dotted line is canceled by negative overlap that occurs above the dotted line.

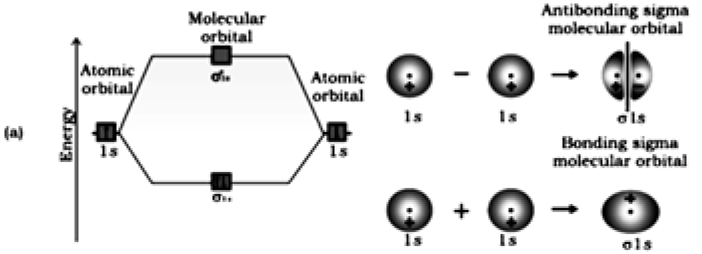
When the net overlap is zero we say the orbitals are nonbonding. This means that the two orbitals will **not** mix. The two atomic orbitals yield two molecular orbitals that look just like the original atomic orbitals thus we get two nonbonding orbitals. Both nonbonding orbitals are shown above and they have the same energies as the original orbitals.

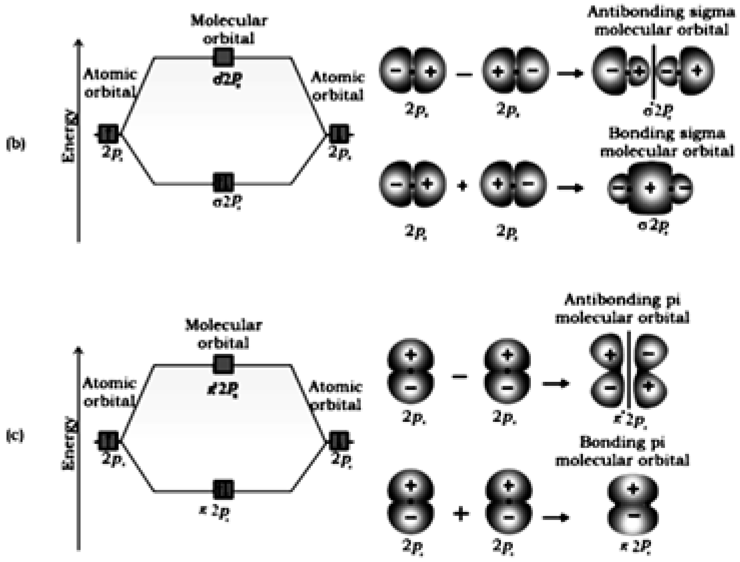


Energy

If the energies of the two orbitals are similar you get better bonding and when they are a lot different they don't interact very well and the orbitals look like they are center on only one of the atoms. Lowest $\sigma_s$orbital is mainly a 2*s* orbital of fluorine and the antibonding σ_s^* is mostly the 2s orbital of nitrogen.

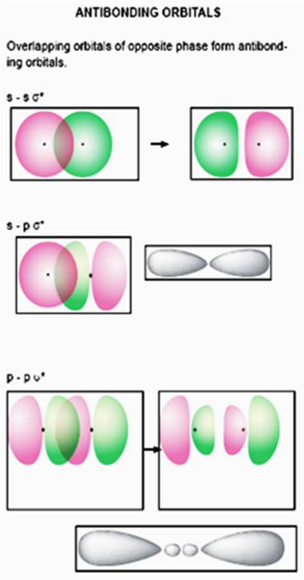
Combination of atomic orbitals and their schematic illustration



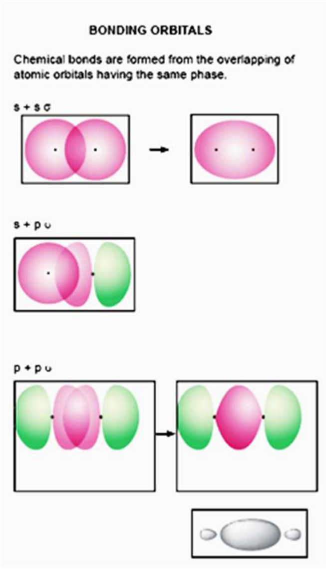


Conditions for the Combination of Atomic Orbitals

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:



Overlapping orbitals of opposite phase form antibonding orbitals.



Chemical bonds are formed from the overlapping of atomic orbitals having the same phase.

1. **The combining atomic orbitals must have the same or nearly the same energy**.

This means that 1*s* orbital can combine with another 1*s* orbital but not with 2*s* orbital because the energy of 2*s* orbital is appreciably higher than that of 1*s* orbital. This is not true if the atoms are very different

2. **The combining atomic orbitals must have the same symmetry about the molecular axis**.

By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, 2$p_z$orbital of one atom can combine with 2$p_z$orbital of the other atom but not with the 2*px* or 2$p_y$orbitals because of their different symmetries.

3. **The combining atomic orbitals must overlap to the maximum extent**.

Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

Types of Molecular Orbitals

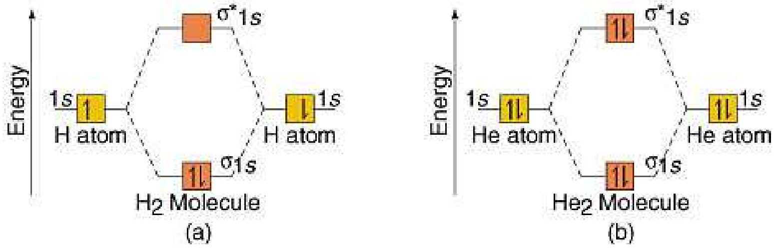
Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pi), δ (delta), etc.In this nomenclature, the sigma (σ) molecular orbitals are symmetrical around the bond-axis while pi (π) molecular orbitals are not symmetrical.

For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbitals are of the σ type and are designated as σ*1s* and σ**1s*. If inter nuclear axis is taken to be in the z-direction, it can be seen that a linear combination of *2pz* orbitals of two atoms also produces two sigma molecular orbitals designated as $\sigma 2p_z$and $\sigma^* 2p_z$.

Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are not symmetrical around the bond axis because of the presence of positive lobes above and negative lobes below the molecular plane. Such molecular orbitals are labeled as π and π*. A π bonding MO has larger electron density above and below the inter-nuclear axis. The π* antibonding MO has a node between the nuclei.

Qualitative MO energy level diagram of homo and hetero diatomic molecules – H_2, He, Li, Be_2, CO, NO and HCl

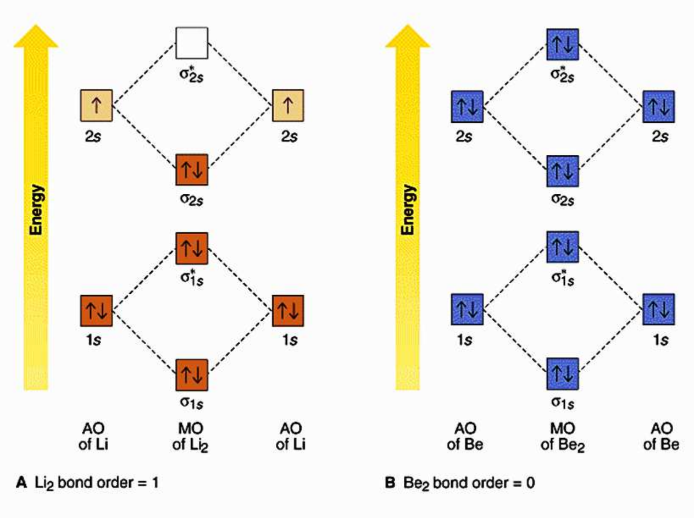
Energy level diagram of hydrogen and helium



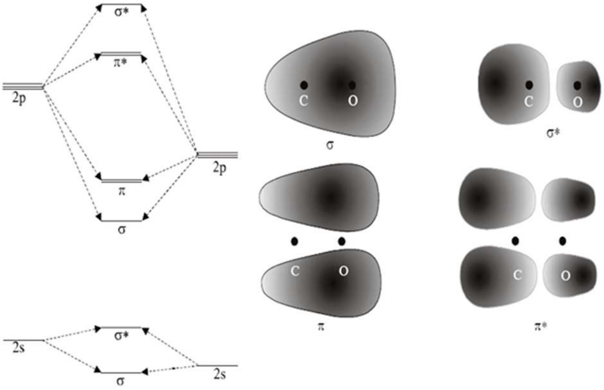
(a)

(b)

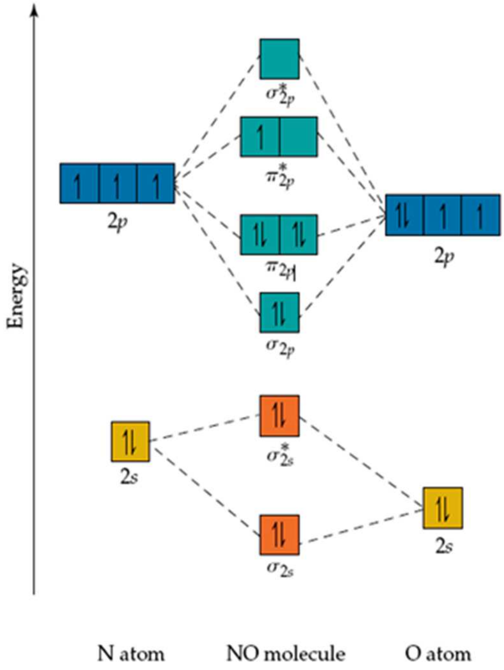
Energy level diagram of lithium and beryllium



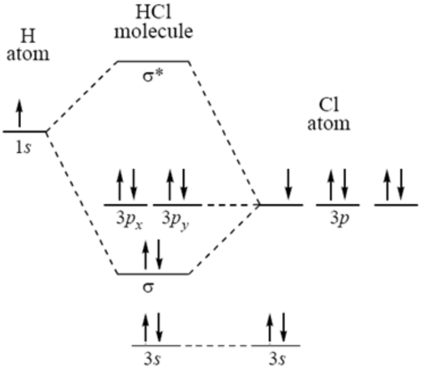
Energy level diagram of CO molecule



Energy Diagram of NO Molecule



Energy Level diagram of HClMolecule



Bond order

Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding (N_b) and the antibonding orbitals (Na).

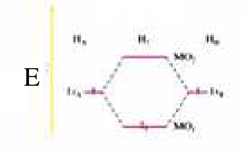
$$Bond\ order\ (b.o) = \frac{Number\ of\ bonding\ orbitals\ (N_a) - Number\ of\ anti\ bonding\ orbitals\ (N_b)}{2}$$

The rules discussed above regarding the stability of the molecule can be restated in terms of bond order as follows: A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b < N_a$) or zero (i.e. $N_b = N_a$) bond order means an unstable molecule.

Bond order :Examples

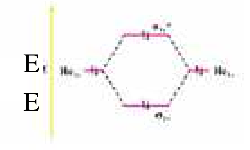
Energy diagram

H_2



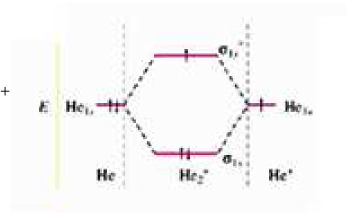
Bond order = (2-0)/2 =1
Single bond
Stable molecule (436 kJ/mol)

He



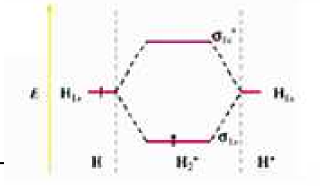
Bond order = (2-2)/2 =0
No bond
Unstable molecule (0kJ/mol)

He_2^+



Bond order =(2-1)/2 -1/2
Half of a single bond
can be made, but its not
very stable (250kJ/mol bond)

H_2^+



Bond order =(1-0)/2 -1/2
Half of a single bond
can be made, but its not
very stable (255kJ/mol bond)

Stability of molecules

If N_b is the number of electrons occupying bonding orbitals and N_a the number occupying the antibonding orbitals, then (i) the molecule is stable if N_b is greater than N_a, and (ii) the molecule is unstable if N_b is less than Na.

In the case of (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. Similarly in the case of (ii) the antibonding influence is stronger and therefore the molecule is unstable.

4.11 Co-ordinate-covalent bonding or Dative bonding

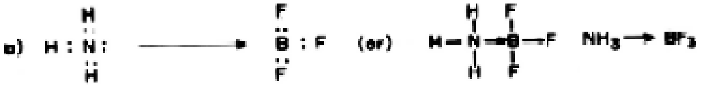
The electron contributions of combining atoms in a covalent bond are generally equal. In each shared pair of electrons one electron is contributed from each atom of the bond. However in some bond formation, the whole of the shared pair of electrons comes from only one of the combining atoms of the bond, which is to referred as the donor atom. The other atom which does not contribute the electron to the shared pair but tries to pull the pair of electron towards itself is called as the acceptor atom. The bond thus formed is between the donor and acceptoratoms is called as the co-ordinate or co-ordinate - covalent or dative bond.

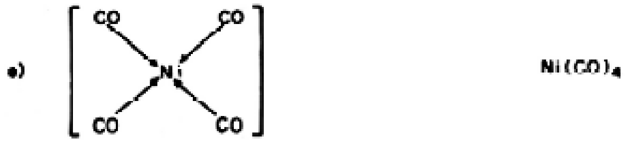
A coordinate bond is showed as an arrow which points from the donor to the acceptor atom. In some cases, the donated pair of electron comes from a molecule as a whole which is already formed to an already formed acceptor molecule as a whole.

For Example, coordination bond between H_3N: and BF_3 molecules. The molecule, ammonia (donor) which gives a pair of electron (lone pair) to BF_3 molecule which is electron deficient (acceptor) has an empty orbital to accommodate the pair of electrons. Thus a dative bond is formed and the molecule as a whole is represented as:

$H_3N \rightarrow BF_3$ (Figure above)

When Proton is added to ammonia, a pair of electron is donated by nitrogen to proton and then proton shares the electron pair to form coordinate covalent bond.





Similarly in (NH_4Cl) ammonium chloride, covalent - coordinate bond exists in NH^{4+} ion only and Cl^- ion exists as it is. Few examples of covalent - coordinate bond:

In nitro methane (CH_3 - NO_2), one of the N-O-bond exists in a covalent coordinate type.

4.12 Intermolecular forces

The ionic, covalent and coordinate bond arises due to attractive forces between atoms. Vander Waal (Dutch physicist, 1873) was the first to proposethe existence of attractive forces between the atoms of inert gases with fully filledorbitals. These forces also exist between non-polar molecules as well as polarmolecules. The attractive interactions between the molecules are responsible forbringing the molecules close together. The attractive interactions between the different molecules of a substance are called intermolecular forces. The magnitudeof these forces are maximum in the solids and decreases on passing from solid toliquids and from liquid to gaseous state. Vander Waal successfully explained theliquefaction of gases on the basis of inter molecular forces. These forces arepurely electrostatic and thus physical in nature.

Hydrogen bonding

Hydrogen bonding comes into existence as a result ofdipole-dipole interactions between the molecule in which hydrogen atom iscovalently bonded to a highly electronegative atom. Therefore, the conditions forthe effective hydrogen bonding are:

1. High electronegativity of the atom bonded to hydrogen atom so that bondis sufficiently polar.
2. Small size of the atom bonded to hydrogen so that it is able to attract thebonding electron pair effectively.

If the atom bonded to hydrogen has low value of electronegativity and/orlarge atomic size, dipole-dipole interactions are not strong enough to allow effectivehydrogen bonding.Only nitrogen, oxygen and fluorine form strong hydrogen bonds becausethey have high value of electronegativity and small atomic size.

Strength of H-bonds

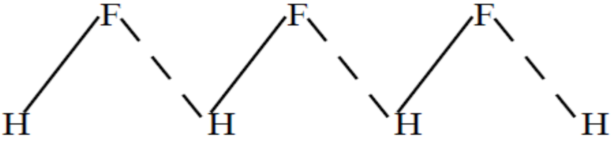
It is a weak bond because it is merely an electrostaticforce and not a chemical bond. Its strength depends upon the electronegativity ofatom to which H atom is covalently bonded. Since electronegativity of F > O >N, the strength of H- bond is in the order H - F ....H > H-O.....H > HN..... H. Hydrogen bonds are much weaker than covalent bonds. The bondstrength of different bonds is in the order : Ionic bond > Covalent bond >Hydrogen bond > dipole-dipole interactions, Vander Waal's (London forces).

Types of Hydrogen bonds

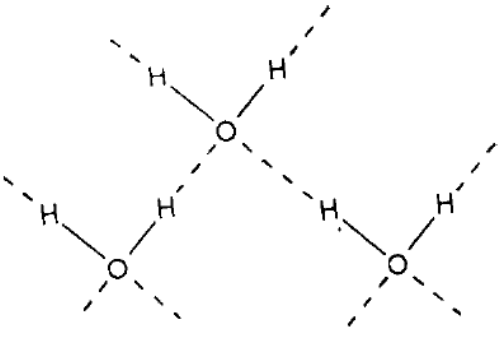
There are two different types of hydrogen bonds as:

i) Intermolecular hydrogen bonding. This type of bond is formed between the two molecules of the same or different compounds. Some examplesof the compounds exhibiting intermolecular hydrogen bonds are:

1. Hydrogen fluoride, $H^{\delta+}$ - $F^{\delta-}$: In the solid state, hydrogen fluoride consistsof long zig-zag chains of molecules associated by hydrogen bonds as shownbelow:

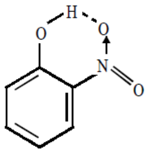


2. Water $H^{\delta+}$- $O^{\delta2-}$ - $H^{\delta+}$: In water molecule, the electronegative oxygen atomforms two polar covalent bonds with two hydrogen atoms. The oxygen atomdue to its higher electronegativity acquires partial negative charge and the twohydrogen atoms acquire partial positive charge. The negatively charged oxygenforms two hydrogen bonds with two positively charged hydrogen atoms of two neighboring molecules. Each oxygen atom is tetrahedrally surrounded by fourhydrogen atoms as shown below:

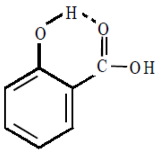


Hydrogen bonding in water results in a hydrogen bridge (H-O-H) networkextending in three dimensions and the associated water molecule may be expressedas $(H_2O)_n$.

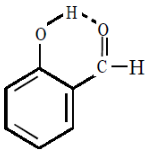
ii) Intramolecular hydrogen bonding. This type of bond is formed between hydrogen atom and N, O or F atom of the same molecule. This type ofhydrogen bonding is commonly called chelation and is more frequently found inorganic compounds. Intramolecular hydrogen bonding is possible when a six orfive membered rings can be formed.



O-Nitrophenol



Salicylic Acid



Salicylaldehyde

Intramolecular hydrogen bonding (chelation) decreases the boiling point ofthe compound and also its solubility in water by restricting the possibility of intermolecularhydrogen bonding.

Importance of H-bonding

1. Life would have been impossible without liquid water which is the result ofintermolecular H-bonding in it.
2. Hydrogen bonding increases the rigidity and strength of wood fibers andthus makes it an article of great utility to meet requirements of housing,furniture, etc.
3. The cotton, silk or synthetic fibers also own their rigidity and tensile strengthto hydrogen bonding.
4. Most of our food materials such as carbohydrates and proteins also consistof hydrogen bonding.
5. Hydrogen bonding also exists in various tissues, organs, skin, blood andbones.

Chapter V Concepts of Organic Chemistry

(Classification and Isomerism)

Catenation - Classification of organic compounds - Functional groups - Nomenclature - Types of organic reactions - Fission of bonds - Electrophiles and nucleophiles - Carbonium ion - Carbanion - Free radicals - Electron displacement in covalent bond.

Isomerism - Geometrical isomerism - Conformations of cyclic compounds -Optical isomerism - Optical activity - Chirality - Compounds containing chiral centers - D-L and R-S notation - Isomerism in benzene.

5.01 Introduction

Initially (before 1828), the name organic chemistry was given for the chemistry of compounds obtained from plants and animals (i.e, from living organisms). The word organic signifies life. Lavoisier (who is considered as the father of chemistry) showed that the compounds obtained from plants are often made of C, H and O and the compounds obtained from animals contain C, H, O, N, S, P, etc. Berzelius proposed vital force theory (a theory of life process) to deal with organic compounds. The vital force theory suffered blow in 1828 when Wohler synthesized the first organic compound urea in the laboratory from an inorganic compound, i.e, from ammonium cyanate (NH_4CNO).

$$2KCNO + (NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_4CNO + K_2SO_4$$

$$Pb(CNO)_2 + 2NH_4OH \xrightarrow{\Delta} 2NH_4CNO + Pb(OH)_2$$

$$NH_4CNO \xrightarrow[\text{Rearrangement}]{\Delta} NH_2CONH_2$$

Later on, a further blow to vital force theory was given by Kolbe (1845) who prepared acetic acid, the first organic compound, in laboratory from its elements.

Nowadays organic chemistry is defined as the chemistry of carbon compounds or the chemistry of hydrocarbons and their derivatives.

Organic compounds obey the same fundamental laws of chemistry as the inorganic compounds. However they are studied as a separate branch of chemistry because of two reasons:

1. The total number of organic compounds known so far exceeds several times the total number of inorganic compounds known.
2. There are marked differences between the structure, composition and behavior of organic and inorganic compounds. The phenomenon of **isomerism** and tendency of **catenation** are unique properties of organic compounds.

5.02 Catenation

1. The tendency of atoms of an element to unite with each other forming a chain of covalent bond is known as catenation.
2. Catenation may give rise to open chain or closed chain compounds.
3. Carbon possesses maximum tendency for catenation i.e. Bond energy (kcal mol^{-1}) for catenation of C is maximum.

C-C,	Si-Si,	N-N,	P-P,	O-O,	S-S
85	54	39	50	35	54

4. Carbon also forms double as well as triple bonds.
5. A large number of compounds of carbon are known due to catenation.
6. The stability or strength of bond decreases as the bond energydecreases. Hence the catenation order among the following is:

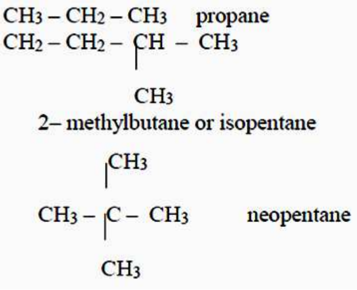
C > Si » S>P>N>O

5.03 Classification of Organic Compounds

Open chain and cyclic compounds

The organic compounds are classified into two main types, namely:

(1) Open - chain or acyclic compounds or aliphatic compounds



The open chain or acyclic compounds are those in which carbon atomsare linked to each other either in linear or branched fashion such that themolecule is having open chain structure. These compounds are also calledaliphatic compounds (Greek word: aliphar meaning fat).Examples are shown left.

(2) Closed chain or cyclic compounds

Organic compounds with closed chain of atoms are called closed chaincompounds or ring compounds.

These compounds are further classified into(a) Homocyclic or carbocyclic compounds and (b) Heterocyclic compounds.

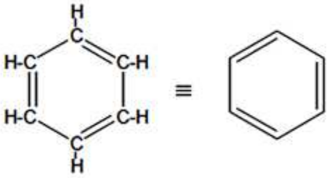
(a) Homocyclic compounds: In these compounds the ring structure is made up of only carbon atoms.These compounds are further classified into:

(i) Aromatic compounds and

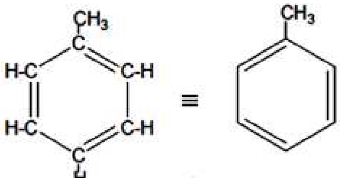
(ii) Alicyclic compounds

(i) **Aromatic compounds (Benzenoid)**: Compounds containing one ormore benzene rings in their structure are classified as aromatic benzenoid compounds. Most of these compounds have pleasant odor (Greek: Aroma - sweet smell).

Examples for Monocyclic compounds

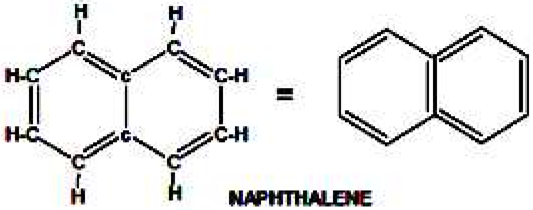


benzene

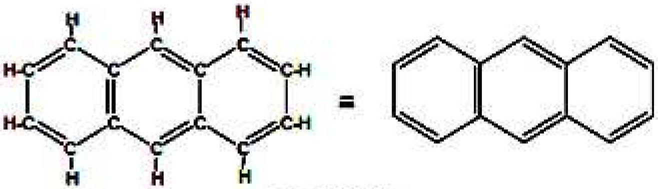


toluene

Examples for Polycyclic compounds

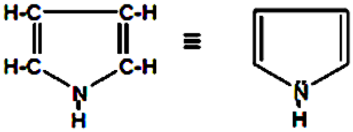


NAPHTHALENE

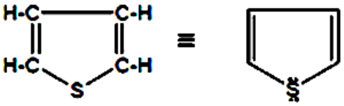


ANTHRACENE

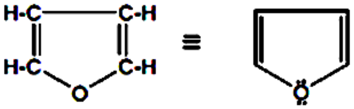
Heterocyclic compounds (Non - benzenoid aromatic): Cyclic compoundsin which the ring atoms are made up of hetero atoms like nitrogen, oxygenand sulphur in addition to carbon atoms are called heterocyclic compounds.



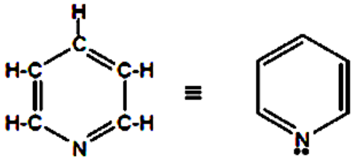
pyrrole



thiophene



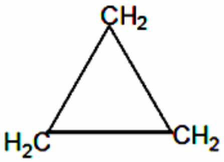
furan



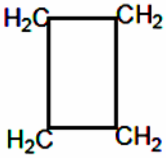
pyridine

The above compounds are aromatic non-benzenoid compounds.

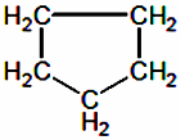
(ii) Alicyclic compounds: Cyclic compounds with ring structure containing only carbon atoms are called alicyclic or carbocycliccompounds. Though these compounds possess a ring structure, theybehave more like aliphatic compounds.



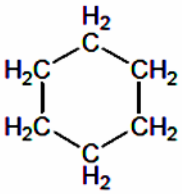
cyclopropane



cyclobutane

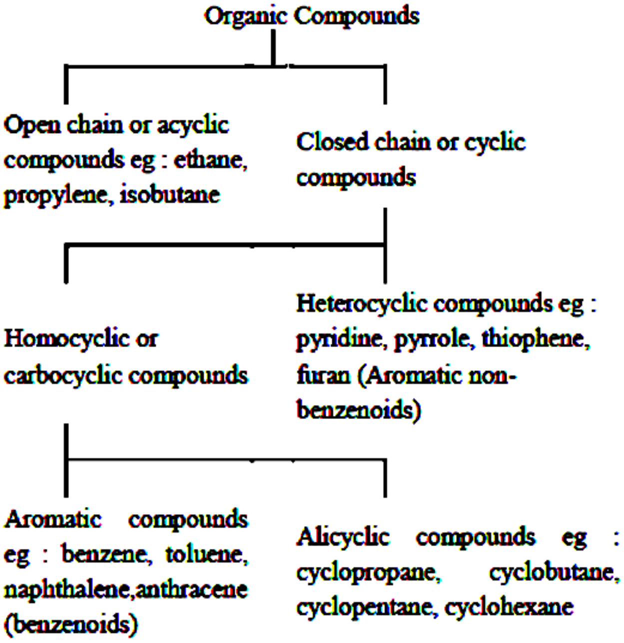


cyclopentane



cyclohexane

The above classification can be schematically represented as follows:



Characteristics of organic compounds

All organic compounds have the following characteristic properties.

(1) Many organic compounds are inflammable.

(2) They are mostly covalent compounds.

(3) They are generally soluble in non - polar solvents like carbontetrachloride, benzene etc.

(4) They have generally low boiling point and melting point.

(5) They exhibit isomerism

Homologous series

A group or class of organic compounds related to each other by a general molecular formula contributes homologous series.

Characteristics of homologous series

Homologous series have the following characteristics:

(1) All members of a series contain same elements and the same functionalgroups.

(2) All the members of a homologous series can be represented by ageneral formula.

Examples

Alkanes C_nH_{2n+2}
Alkenes C_nH_{2n}
Alkynes C_nH_{2n-2}

(3) All the members of a homologous series can be prepared by similarmethods.

(4) All members of a homologous series usually undergo similar chemicalreactions.

(5) Successive members in a series differ by a $-CH_2$ group.

(6) The physical properties of the members of a homologous series vary ina regular way down the series. For example, boiling point, meltingpoint and density of the alkane series vary in a regular way withincreasing number of carbon atoms.

5.04 Functional groups

The chemical properties of all the members of a homologous series arecharacterized by a group called the functional group. It is characteristic of aparticular series.

The following table gives a list of functional groups and names.

Halide	– X
Alcohol	– OH
Ether	– O –
Aldehyde	– CHO
Ketone	–C = O
Carboxylic acid	– COOH
Ester	– COOR
Amide	$– CO – NH_2$
Acid halide	– C – X (X = –Cl, –Br, –I)

Acid anhydride	$-(C=O)_2O-$
Amine	$-NH_2$
Nitro compounds	$-NO_2$

5.05 Nomenclature

IUPAC system of nomenclature (1993)

The international union of pure and applied chemistry (abbreviated as IUPAC) has done a commendable job in framing set rules for namingorganic compounds. Two commonly used systems of nomenclature are (1) Common or Trivial system and (2) IUPAC system.

IUPAC Nomenclature of Aliphatic Compounds

The IUPAC name of a compound essentially consists of three parts.
(a) Root word (b) Suffix (c) Prefix

Root words for alkanes

The root words for the first four members are taken from their trivial orcommon names.

e.g. Meth - for Methane
Eth - for Ethane
Prop - for Propane
But - for Butane

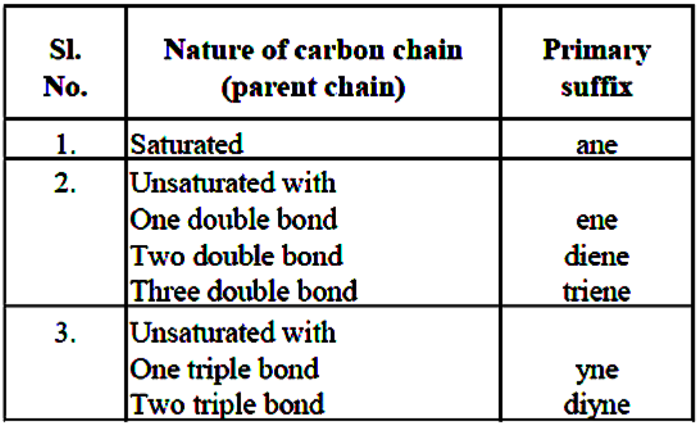
For the higher homologue, root words are derived from the Greek/Latinnumber indicating the total number of carbon atoms.

e.g. Pent - is derived from penta for five
Hex - is derived from hexa for six
Hept - is derived from hepta for seven
Oct - is derived from octa for eight

Suffix

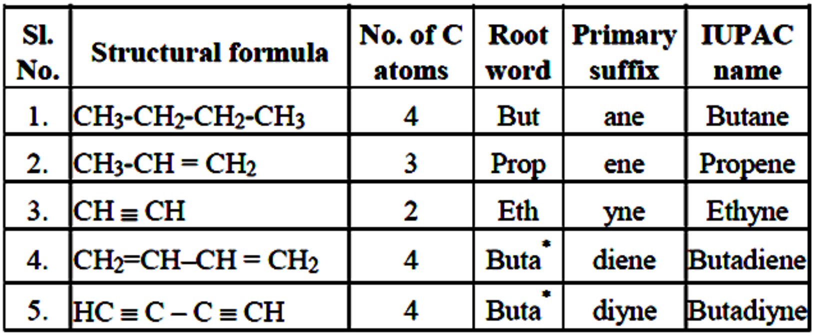
There are two types of suffixes **Primary suffix** and secondary suffix.

Primary suffix



Sl. No.	Nature of carbon chain (parent chain)	Primary suffix
1.	Saturated	ane
2.	Unsaturated with One double bond Two double bond Three double bond	 ene diene triene
3.	Unsaturated with One triple bond Two triple bond	 yne diyne

A primary suffix is added to the Root wordto indicate whether the parent chain is saturated or unsaturated. Some primary suffixes are given below.

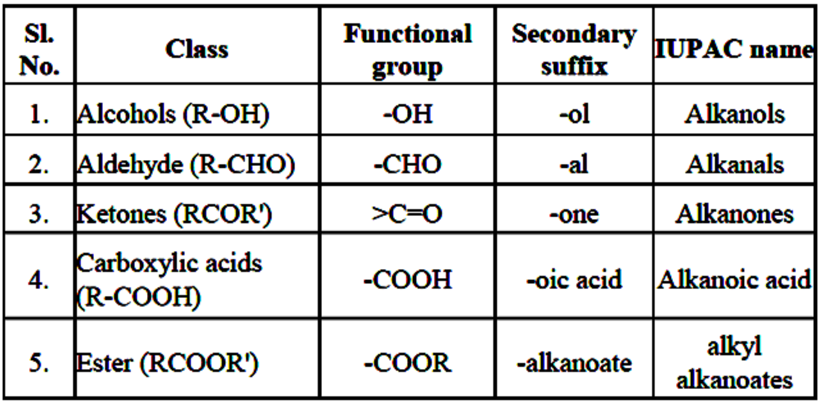


Sl. No.	Structural formula	No. of C atoms	Root word	Primary suffix	IUPAC name
1.	$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$	4	But	ane	Butane
2.	$CH_3\text{-}CH = CH_2$	3	Prop	ene	Propene
3.	$CH \equiv CH$	2	Eth	yne	Ethyne
4.	$CH_2{=}CH{-}CH = CH_2$	4	Buta*	diene	Butadiene
5.	$HC \equiv C - C \equiv CH$	4	Buta*	diyne	Butadiyne

*extra 'a' has been added to the root word since the primary suffix, ie dieneor diyne begins with a consonant (d).

Secondary suffix

Secondary suffix is used to indicate the functional group in the organiccompound secondary suffixes for various functional groups are givenbelow.



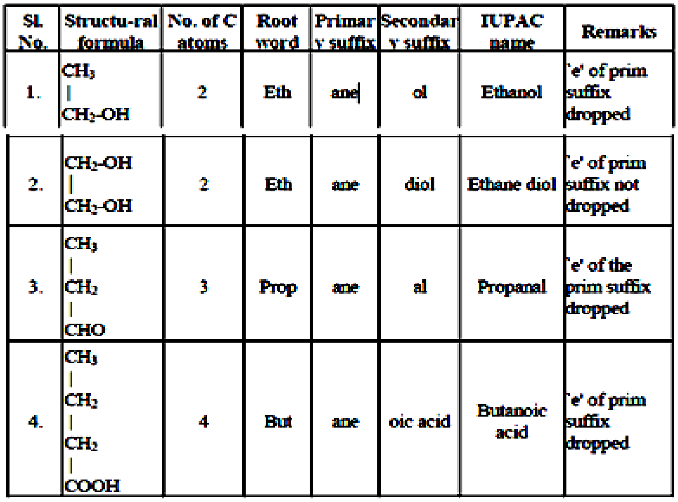
Sl. No.	Class	Functional group	Secondary suffix	IUPAC name
1.	Alcohols (R-OH)	-OH	-ol	Alkanols
2.	Aldehyde (R-CHO)	-CHO	-al	Alkanals
3.	Ketones (RCOR')	>C=O	-one	Alkanones
4.	Carboxylic acids (R-COOH)	-COOH	-oic acid	Alkanoic acid
5.	Ester (RCOOR')	-COOR	-alkanoate	alkyl alkanoates

Secondary suffix is added to the primary suffix; ie written after the primary suffix. While adding the secondary suffix to the primary suffixfollowing rules should be followed.

a) If the secondary suffix begins with a vowel, then the terminal **e** of the primary suffix is dropped before adding the secondary suffix.

b) If the secondary suffix begins with a consonant, then the last(terminal) **e** is retained and the secondary suffix is added after e.

c) If the secondary suffix has some **numerical prefix**, such as, **di, tri etc.**,before it then the terminal **e** of the primary suffix is retained.



Sl. No.	Structu-ral formula	No. of C atoms	Root word	Primary suffix	Secondary suffix	IUPAC name	Remarks
1.	CH_3 | CH_2-OH	2	Eth	ane	ol	Ethanol	'e' of prim suffix dropped
2.	CH_2-OH | CH_2-OH	2	Eth	ane	diol	Ethane diol	'e' of prim suffix not dropped
3.	CH_3 | CH_2 | CHO	3	Prop	ane	al	Propanal	'e' of the prim suffix dropped
4.	CH_3 | CH_2 | CH_2 | COOH	4	But	ane	oic acid	Butanoic acid	'e' of prim suffix dropped

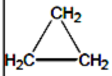
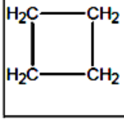
The addition of the secondary suffix to the primary suffix is shown above.

Prefix

Prefix is a part of the name which appears before the root word. There are two types of prefixes - primary prefix and secondary prefix.

Primary prefix

A primary prefix is used to distinguish alicyclic (aliphatic cyclic compounds) from acyclic (open chain) compounds. If the given compound is an alicyclic compound, then a prefix cyclo is used just before the root word. For example,

Structural formula	No. of C atoms	Root word	Primary suffix	Primary prefix	IUPAC name
	3	Prop	ane	Cyclo	Cyclo propane
	4	But	ane	Cyclo	Cyclo butane

Secondary prefix

In the IUPAC system of nomenclature, certain characteristic groups are not considered as functional groups. Such characteristic groups are considered as the substituents. Each such group or substituent is denoted by a secondary prefix. Some typical secondary prefixes are listed below.

Substituent group	Secondary prefix
- F	Fluoro
- Cl	Chloro
- Br	Bromo
- I	Iodo
- CH_3	Methyl
- C_2H_5	Ethyl
CH_3 - CH_2 - CH_2 -	n-propyl
$(CH_3)_2$ CH -	Iso propyl
$(CH_3)_3$ C -	t - Butyl
- NO_2	Nitro
- NH_2	Amino
- NO	Nitroso
$N \equiv N$	Diazo
- OCH_3	Methoxy
- OC_2H_5	Ethoxy

Sl. No.	Structural formula	No. of C atoms	Root word	Suffix		Prefix		IUPAC Name
				Primary	Sec	Pri	Sec	
1.	CH_3-CH_2-Cl	2	Eth	ane	-	-	Chloro	Chloro ethane
2.	CH_3-NO_2	1	Meth	ane	-	-	Nitro	Nitro methane

In the case of open chain compounds, the secondary prefix is added just before the root word in the **alphabetical** order. This is illustrated below.

Saturated hydrocarbons

General formula : C_nH_{2n+2} **Suffix** : ane

Sl. No.	Structural formula	Common Name	IUPAC name
1.	CH_4	Methane	Methane
2.	$H_3C - CH_3$	Ethane	Ethane
3.	$H_3C - CH_2 - CH_3$	Propane	Propane
4.	$H_3C - CH_2 - CH_2 - CH_3$	n-butane	Butane

Alkyl groups

The univalent hydrocarbon unit derived from an alkane by the loss of one hydrogen atom is termed as alkyl group. The alkyl groups are named after their parent alkanes by replacing thesuffix-**ane** by- **yl**.

Continuous straight chain alkyl groups (or, normal alkyl (n-) groups)

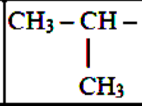
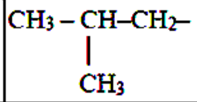
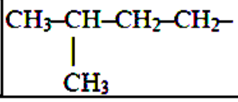
Sl. No.	Alkane		Alkyl group	
	Formula	Name	Formula	Name
1.	CH_4	Methane	CH_3 -	Methyl
2.	$CH_3 - CH_3$	Ethane	$CH_3 - CH_2$ -	Ethyl
3.	$CH_3-CH_2-CH_3$	Propane	$CH_3-CH_2-CH_2$-	Propyl

Branched chain alkyl groups

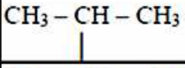
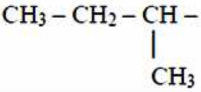
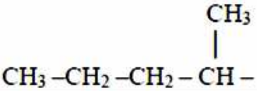
When a hydrogen atom from a secondary or tertiary carbon atom in any carbon chain is removed, a branched chain alkyl group is obtained. The common prefixes used are,

a) iso - b) sec - c) tert - d) neo –

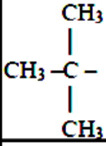
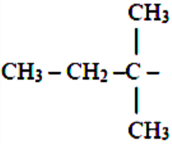
a) **iso –** The alkyl group in which a - CH_3branch is present at the end of the chain is designated as isoalkyl group. In other words, the alkyl group in which the second last carbon atom in the chain is branched to one -CH_3 group is called on isoalkyl group.

Sl.No.	Structure	IUPAC name
1.	 $CH_3-\underset{\substack{\vert \\ CH_3}}{CH}-$	1-methyl ethyl (iso-propyl)
2.	 $CH_3-\underset{\substack{\vert \\ CH_3}}{CH}-CH_2-$	2-methyl propyl (iso-butyl)
3.	 $CH_3-\underset{\substack{\vert \\ CH_3}}{CH}-CH_2-CH_2-$	3-methyl butyl (iso-pentyl)

b) Sec - The prefix sec - before the name of the alkyl group indicates thatthe H-atom was removed from a secondary carbon atom.

Sl.No.	Structure	IUPAC name
1.	 $CH_3-\underset{\vert}{CH}-CH_3$	1 - Methyl ethyl (Sec - propyl)
2.	 $CH_3-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-$	1 - methyl propyl (Sec - butyl)
3.	 $CH_3-CH_2-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-$	1 - methyl butyl (Sec - pentyl)

c) Tert - (or) t - The prefix tert - before the name of the alkyl group indicates that the H- atom has been removed from a tertiary carbon atom.

Sl. No.	Structure	IUPAC name
1.	 $CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-$	1,1 – dimethyl ethyl (tert - butyl)
2.	 $CH_3-CH_2-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-$	1,1 – dimethyl propyl (tert - pentyl)

Alkenes

General formula: C_nH_{2n}**Suffix: ene**

The common name of alkene is obtained by replacing the ending – **ane** from the name of its parent alkane with - **ylene**.The IUPAC name of an alkene is obtained by replacing - **ane** of thealkane by - **ene**.

Structural formula	Common Name	IUPAC name
$CH_2 = CH_2$	Ethylene	Ethene
$CH_3 - CH = CH_2$	Propylene	Propene
$CH_3\text{-}CH_2\text{-} CH= CH_2$ (double bond starts at C_1)	1- Butylene	But-1-ene
$CH_3\text{-}CH = CH\text{-}CH_3$ (double bond starts at C_2)	2- Butylene	But-2-ene

Alkenyl group

The group obtained by removing a hydrogen atom from an alkenemolecule, are called alkenylgroup. The IUPAC name of alkenyl group is obtained by replacing - **e** of thealkene by the suffix - **yl**.

Sl. No.	Structure	Common name	IUPAC name
1.	$CH_2 = CH_2$	vinyl	ethenyl
2.	$CH_2{=}CH\text{-}CH_2\text{-}$	allyl	Prop - 2 - enyl

Alkynes

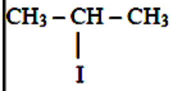
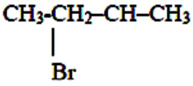
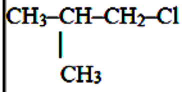
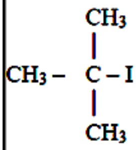
General formula: C_nH_{2n-2} **Suffix**: - yne

The IUPAC name of an alkyne is obtained by replacing the ending - **ane** from the name of the parent alkane with - **yne**.

Sl. No.	Structural formula	Common Name	IUPAC name
1.	$HC \equiv CH$	Acetylene	Ethyne
2.	$CH_3 \text{-}C \equiv CH$	Methyl acetylene	Propyne
3.	$CH_3\text{-}C \equiv C - CH_3$	Dimethyl acetylene	But-2– yne

Alkyl halides

The general formula of alkyl halides is R-X where R stands for alkyl group and "X" stands for halogen (F, Cl, Br, I). They are named by introducing the prefix halo (chloro, bromo, iodo, fluoro) to the name of the parent alkane.

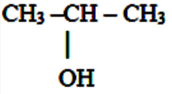
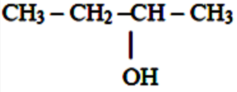
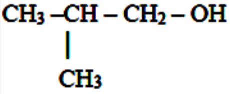
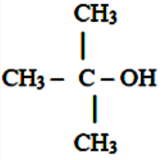
Formula	Common name	IUPAC name
CH_3-Cl	Methyl chloride	Chloromethane
CH_3-CH_2-Br	Ethyl bromide	Bromoethane
$CH_3-CH_2-CH_2-Br$	n-propyl bromide	1-bromopropane
 $CH_3-\underset{I}{\underset{\mid}{CH}}-CH_3$	Iso-propyl iodide	2-iodopropane
$CH_3-CH_2-CH_2-CH_2-Cl$	n-butyl chloride	1-chlorobutane
 $CH_3-CH_2-\underset{Br}{\underset{\mid}{CH}}-CH_3$	Sec-butyl bromide	2-bromobutane
 $CH_3-\underset{CH_3}{\underset{\mid}{CH}}-CH_2-Cl$	Isobutyl chloride	1-chloro-2-methyl propane
 $CH_3-\overset{CH_3}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{C}}}}-I$	ter-butyl iodide	2-iodo-2-methyl propane
$CH_2=CH-Cl$	Vinyl chloride	Chloroethene
$CH_2=CH-CH_2-Cl$	Allyl chloride	3-Chloro-1-propene

Alcohols

The term alcohol is applied to all organic compounds obtained by replacing one or more hydrogen atoms of an open-chain hydrocarbon by hydroxyl groups. The alcohols are further classified into mono-, di-, trihydricalcohols according to the number of hydroxyl groups which theymay contain.In IUPAC nomenclature, the terminal "**e**" of the alkane is replaced by"**ol**".

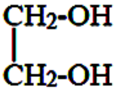
Monohydric alcohols

Alcohols which contain only one hydroxyl group per molecule are called monohydric alcohols.

Formula	Common name	IUPAC name
$CH_3\text{-}OH$	Methyl alcohol	methanol
$CH_3\text{-}CH_2\text{-}OH$	Ethyl alcohol	ethanol
$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$	n-propyl alcohol	1-propanol
 $CH_3-\underset{\underset{OH}{\mid}}{CH}-CH_3$	Isopropyl alcohol	2-propanol
$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$	n-butyl alcohol	1-butanol
 $CH_3-CH_2-\underset{\underset{OH}{\mid}}{CH}-CH_3$	sec-butyl alcohol	2-butanol
 $CH_3-\underset{\underset{CH_3}{\mid}}{CH}-CH_2-OH$	Isobutyl alcohol	2-methyl-1-propanol
 $CH_3-\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-OH$	tert-butyl alcohol	2-methyl-2-propanol
$CH_2{=}CH\text{-}CH_2\text{-}OH$	Allyl alcohol	2-propene-1-ol

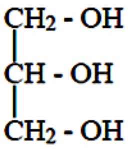
Dihydric alcohols

Alcohols which contain two -OH groups per molecule are called dihydric alcohols.

Structural formula	Common name	IUPAC name
 $\begin{matrix} CH_2\text{-}OH \\ \mid \\ CH_2\text{-}OH \end{matrix}$	Ethylene glycol	1,2-Ethanediol

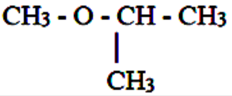
Trihydric alcohols

Alcohols which contain three -OH groups per molecule are called trihydric alcohols.

Structural formula	Common name	IUPAC name
 CH_2-OH $CH-OH$ CH_2-OH	Glycerol	1,2,3-propanetriol

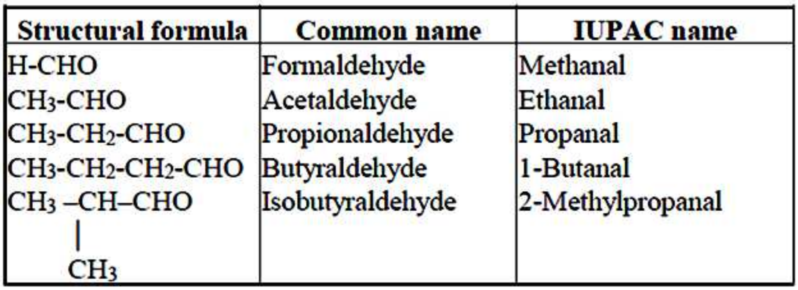
Ethers

An ether is a substance that has two organic groups bonded to the sameoxygen atom, **R-O-R'**. The organic group may be alkyl or aryl. When thegroups attached to the oxygen atom are the same, they are termed as simpleethers. When the groups attached to the oxygen atom are different, they aretermed as mixed ethers.In IUPAC system, ethers are considered to be alkoxy derivatives ofhydrocarbons.

Structural formula	Common name	IUPAC name
Simple ethers		
CH_3-O-CH_3	Dimethyl ether	Methoxymethane
$CH_3-CH_2-O-CH_2-CH_3$	Diethyl ether	Ethoxyethane
Mixed ethers		
$CH_3-O-CH_2-CH_3$	Ethyl methyl ether	Methoxyethane
$CH_3-O-CH_2-CH_2-CH_3$	Methyl n-propyl ether	1-methoxypropane
 $CH_3-O-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$	Isopropyl methyl ether	2-methoxypropane

Aldehydes

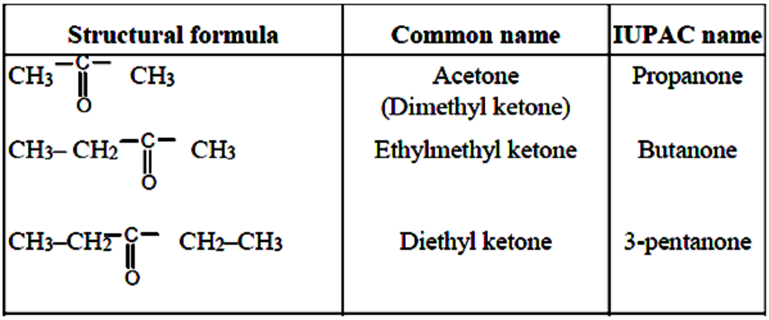
Aldehydes and ketones are two important classes of compoundscontaining the carbonyl group. In aldehydes the group islinked to an alkyl group and a hydrogen or two hydrogens. Aldehydes arerepresented by the general formula R-CHO.IUPAC names of aldehydes are obtained by replacing the terminal "**e**"of alkane with "**al**".



Structural formula	Common name	IUPAC name
H-CHO	Formaldehyde	Methanal
CH_3-CHO	Acetaldehyde	Ethanal
CH_3-CH_2-CHO	Propionaldehyde	Propanal
CH_3-CH_2-CH_2-CHO	Butyraldehyde	1-Butanal
$CH_3-\underset{\substack{\vert \\ CH_3}}{CH}-CHO$	Isobutyraldehyde	2-Methylpropanal

Ketones

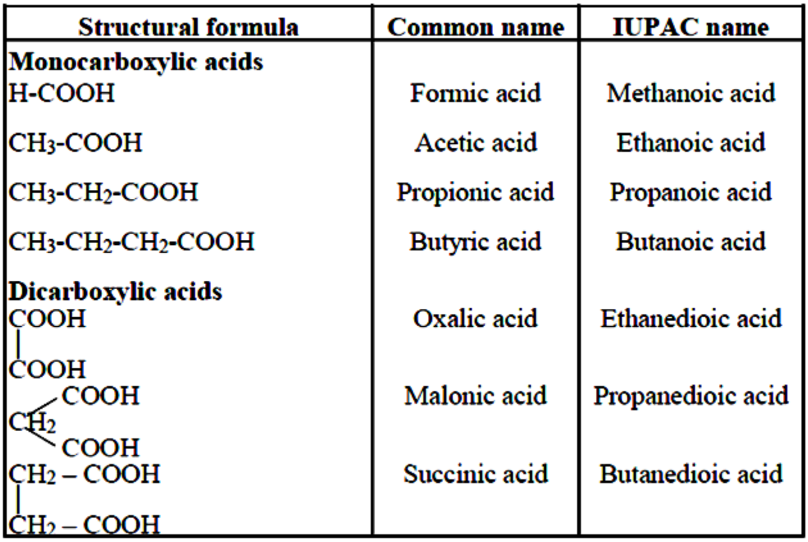
In ketones group is united with 2 alkyl groups. Thesecompounds are represented by the general formula.R – CO – R'. Ketones are named by replacing the terminal "**e**" of the correspondingalkane name with "**one**".



Structural formula	Common name	IUPAC name
$CH_3-\underset{\substack{\Vert \\ O}}{C}-CH_3$	Acetone (Dimethyl ketone)	Propanone
$CH_3-CH_2-\underset{\substack{\Vert \\ O}}{C}-CH_3$	Ethylmethyl ketone	Butanone
$CH_3-CH_2-\underset{\substack{\Vert \\ O}}{C}-CH_2-CH_3$	Diethyl ketone	3-pentanone

Carboxylic acids

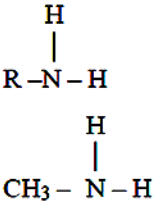
These are represented by the general formula R-COOH. IUPAC name is derived by replacing the terminal "**e**" of the alkane name with "**oic acid**". These compounds are further classified into **mono**- and **di**-carboxylic acids.



Structural formula	Common name	IUPAC name
Monocarboxylic acids		
H-COOH	Formic acid	Methanoic acid
CH_3-COOH	Acetic acid	Ethanoic acid
CH_3-CH_2-COOH	Propionic acid	Propanoic acid
CH_3-CH_2-CH_2-COOH	Butyric acid	Butanoic acid
Dicarboxylic acids		
COOH | COOH	Oxalic acid	Ethanedioic acid
COOH CH_2 COOH	Malonic acid	Propanedioic acid
CH_2 – COOH | CH_2 – COOH	Succinic acid	Butanedioic acid

Amines

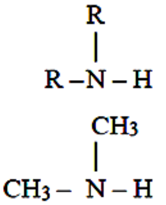
Amines are the derivatives of ammonia in which one or more H – atomshave been replaced by alkyl groups. They are designated as primary,secondary and tertiary amines according as one, two or three hydrogenatoms in ammonia molecule have been replaced by alkyl groups.



$R-NH-H$

CH_3-NH-H

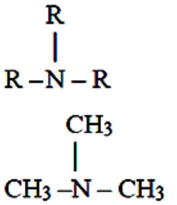
Methylamine
(primary amine)



$R-N(R)-H$

$CH_3-N(CH_3)-H$

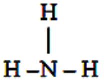
Dimethyl amine
(secondary amine)



$R-N(R)-R$

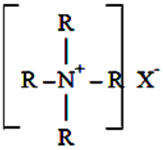
$CH_3-N(CH_3)-CH_3$

Trimethyl amine
(teritary amine)



$H-\overset{\displaystyle H}{\overset{|}{N}}-H$

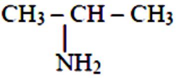
Ammonia

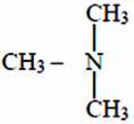
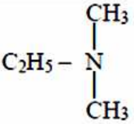


$\left[R-\overset{\displaystyle R}{\overset{|}{\underset{\underset{\displaystyle R}{|}}{N^+}}}-R\right]X^-$

(quarternary salt)

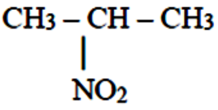
When one alkyl group is attached to N-atom, it is called primary amine,when two alkyl groups are attached to nitrogen atom, then it is calledsecondary amine. When three alkyl groups are attached to nitrogen atom itis called tertiary amine. When four alkyl groups are attached to nitrogenatom it is called quarternary salt.

Structural formula	Common	IUPAC name
Primary Amines		
CH_3-NH_2	Methyl amine	aminomethane
CH_3-CH_2-NH_2	Ethyl amine	aminoethane
CH_3-CH_2-CH_2-NH_2	n-propyl amine	1-aminopropane
 $CH_3-\underset{\underset{\displaystyle NH_2}{\mid}}{CH}-CH_3$	Isopropyl amine	2-aminopropane
Secondary Amines		
CH_3-NH-CH_3	Dimethyl amine	(N-methylamino) methane
CH_3-CH_2-NH-CH_2-CH_3	Diethyl amine	(N-ethylamino) ethane
CH_3-NH-CH_2-CH_3	Ethylmethyl amine	(N-methylamino) ethane

Structural formula	Common name	IUPAC name
Tertiary Amines		
 $CH_3-\overset{\displaystyle CH_3}{\overset{\mid}{\underset{\underset{\displaystyle CH_3}{\mid}}{N}}}$	Trimethyl amine	(N.N - dimethyl amino) methane
 $C_2H_5-\overset{\displaystyle CH_3}{\overset{\mid}{\underset{\underset{\displaystyle CH_3}{\mid}}{N}}}$	Ethyldimethyl amine	(N.N - dimethyl amino) ethane

Nitro compounds

These compounds are represented by the general formula RNO_2.IUPAC names are obtained by adding the prefix "**nitro**" to the alkane.

	Structural formula	Common/IUPAC name
1.	$CH_3 - NO_2$	Nitromethane
2.	$CH_3 - CH_2 - NO_2$	Nitroethane
3.	$CH_3 - CH_2 - CH_2 - NO_2$	1-Nitropropane
4.	 $CH_3 - \underset{\underset{NO_2}{\mid}}{CH} - CH_3$	2-Nitropropane

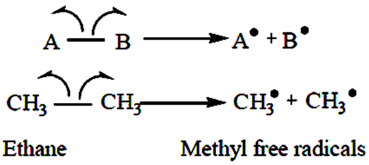
5.05 Fission of bonds

How bond fission occurs?

A covalent bond(σ) pair of electrons. When two atoms are separated from each other, bond fission is said to have taken place. The fission process can take place in twoways.

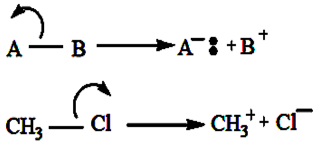
Homolytic fission

A covalent bond between two atomsA and B may be shown as A· · B or A–B. This bond may undergo fission in such a way that each atom retains the electrons of the shared pair. Such species are known as **free radicals** or odd electron molecules.



Heterolytic fission

A covalent bond breaks in such a way that the shared pair of electron stay on any one of the atoms. Breaking of the bond in this manner is known as heterolytic fission or heterolysis.



The atom or group which carries the unshared pair of electrons are represented with a negative sign as A–: is known as anions. The carbonium ion carries the positive charge which lacks a pair of electrons. Heterolysis occurs only when the initially bonded atoms are of different in electronegativities and in that the electron pair becomes attached to the more electronegative atom.

An organic reaction may be represented as:

Reactants + attacking agent → [intermediate] → product

Depending upon the nature of the reaction which the intermediate species undergo, the reactions of the organic compounds are classified as substitution reactions, addition reactions, elimination reactions, polymerization reactions, condensation reaction, hydrolysis, oxidation and reduction reactions.

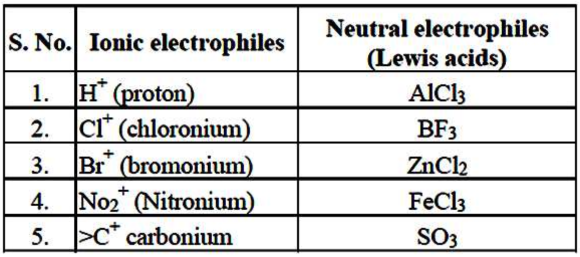
5.06Reagents and Reaction intermediates

Electrophilic reagents

These reagents are electron deficient. This deficiency accounts for theiraffinity for electrons (electro = electron, philic = loving). They are also called cationic reagents and may carry positive charge or have incomplete valence shells. These reagents can therefore, be of two types.

(i) Positive electrophiles (or) Ionic electrophiles
(ii) Neutral electrophiles

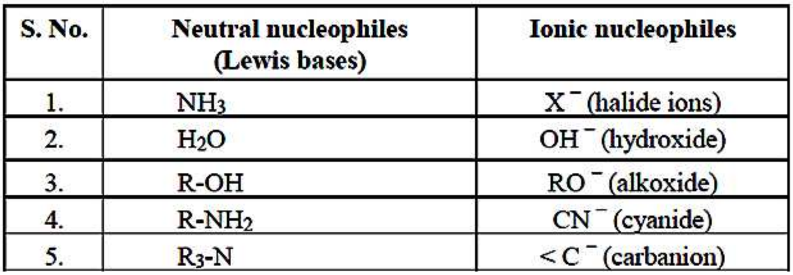
Some common electrophiles are given in the table:



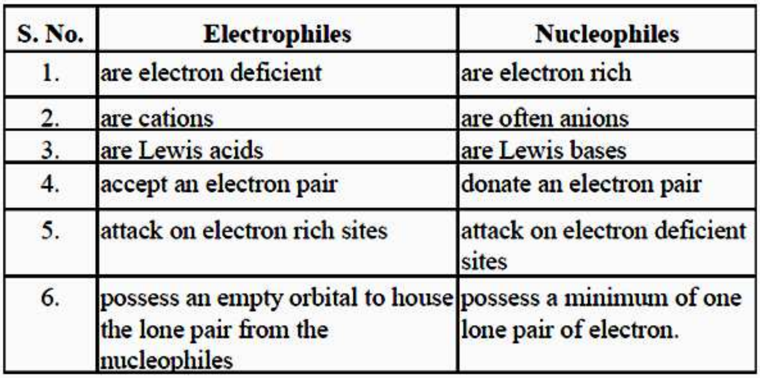
S. No.	Ionic electrophiles	Neutral electrophiles (Lewis acids)
1.	H^+ (proton)	$AlCl_3$
2.	Cl^+ (chloronium)	BF_3
3.	Br^+ (bromonium)	$ZnCl_2$
4.	No_2^+ (Nitronium)	$FeCl_3$
5.	$>C^+$ carbonium	SO_3

Nucleophilic reagents

Nucleophiles or nucleophilic reagents are electron rich substances containing atoms which have at least an unshared pair of electron. Thesereagents are nucleus loving (nucleo = nucleus, philic = loving). Nucleophiles can be (i) negatively charged (or) Ionic (ii) neutral species(Lewis bases). Some of the common nucleophiles are reported in table.



S. No.	Neutral nucleophiles (Lewis bases)	Ionic nucleophiles
1.	NH_3	X^- (halide ions)
2.	H_2O	OH^- (hydroxide)
3.	R-OH	RO^- (alkoxide)
4.	$R-NH_2$	CN^- (cyanide)
5.	R_3-N	$< C^-$ (carbanion)

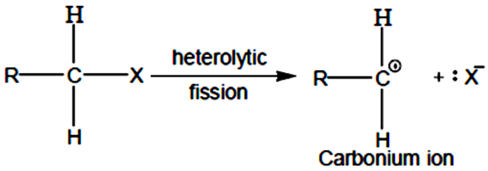


S. No.	Electrophiles	Nucleophiles
1.	are electron deficient	are electron rich
2.	are cations	are often anions
3.	are Lewis acids	are Lewis bases
4.	accept an electron pair	donate an electron pair
5.	attack on electron rich sites	attack on electron deficient sites
6.	possess an empty orbital to house the lone pair from the nucleophiles	possess a minimum of one lone pair of electron.

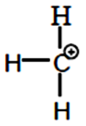
The differences between these reagents are summarized in the above table.

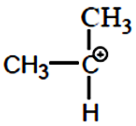
Carbonium ions

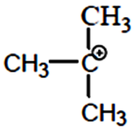
Let us consider the heterolytic fission of the bond C – X present in anorganic molecule. If the atom X has greater electronegativity than the carbon atom, the former takes away the bonding electron pair and becomesnegatively charged while the carbon will lose its electron and thus acquire apositive charge. Such cationic species carrying a positive charge on carbon are known as carbonium ions.For illustration:

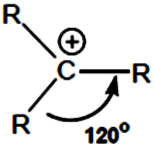


These carbonium ions are called primary, secondary and tertiary depending up on the nature of the carbon atom bearing the charge.


Carbonium ion (primary)


Methyl carbonium ion (secondary)


Trimethyl carbonium ion (tertiary)



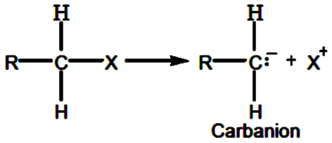
The geometry of alkyl carbonium ion

Since the carbon of the carbonium ion is in sp2 hybridized state, the ionis planar with a vacant p orbital perpendicular to the plane of the three covalent bonds to carbon.

Carbanion

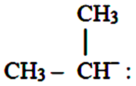
Let us consider the heterolytic fission of the bond C - X present in an organic molecule. If the carbon atom has greater electronegativity than theatom X, the former takes away the bonding electron pair and acquires anegative charge. The resulting carbon anion is known as carbanion.

For illustration



Examples

$CH_3 - CH_2^- :$ methyl carbanion



$CH_3 - CH(CH_3)^- :$ dimethyl carbanion

Free Radicals

Free radicals are species with one or more unpaired electrons obtainedby the homolytic fission of covalent bond. The free radicals themselves are electrically neutral. The free radicals are denoted by putting a dot againstthe atom or group of atoms.

Few examples: $Cl\bullet$, $CH_3\bullet$, $C_6H_5\bullet$

They are classified as short lived free radicals and long lived free radicals on the basis of their life time.

Formation of free radicals

(a) Photochemical fission: When an organic compound is exposed to ultraviolet region it under goes bond fission.

$$Cl\cdot\ \cdot\overline{Cl} \xrightarrow{uv} Cl\cdot + Cl\cdot$$

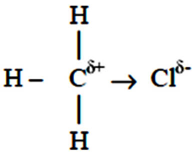
(b) Thermal fission: All organic compounds on heating yield free radicals.

$$(C_2H_5)_4Pb \xrightarrow{\Delta} Pb + 4C_2H_5\cdot$$

Polar Effects

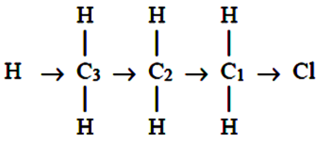
Inductive Effect

If a covalent bond is formed by two atoms differing much inelectronegativity then the bond is said to be polarized. The electron pairshifts towards the more electronegative atom resulting in the origin offractional charges on the atoms. Consider methyl chloride,



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C^{\delta+}}} \rightarrow Cl^{\delta-}$$

In this molecule, chlorine atom is more electronegative than the carbonatom. Due to this, chlorine pulls the electron pair and acquires a smallnegative charge.Let us consider, 1 – chloropropane



$$H \rightarrow \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C_3}} \rightarrow \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C_2}} \rightarrow \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C_1}} \rightarrow Cl$$

As C1 is positively charged, it attracts towards itself the electron pairshared between C1 and C2. This causes C2 to acquire a small positive charge but the charge is smaller than the charge on C1. This type of electron displacement occurring in saturated compounds along a carbon chain istermed, inductive effect.

It is a permanent effect and decreases rapidly as the distance from the electronegative atom increases. It is represented by the arrow head (→) pointing towards the more electronegative atom. This effect operates in the case of σ - electrons only.

For measurements of relative inductive effect, atoms or groups having greater electron affinity than hydrogen are said to have - I effect. Similarly,atoms or groups having lesser electron affinity than hydrogen are said tohave + I effect. Some of the atoms and groups arranged in the increasingorder of inductive effect are given as:

Groups having - I effect [electron - attracting].

$-C_6H_5$, -OH, -I, -Br, -Cl, -F

Groups having + I effect [electron pumping]

CH_3 -, CH_3 - CH_2 - , $(CH_3)_2CH$-, $(CH_3)_3C$ -
(Methyl) (Ethyl) Isopropyl tertiarybutyl

Resonance (Mesomeric) Effect

When several structures may be assumed to contribute to the truestructure of a molecule but none of them can be said to represent ituniquely, then the molecule is referred to as a resonance hybrid and the phenomenon is termed as resonance.It is somewhat abstract, but it can be better understood if we considerthe structure of a simple molecule carbon dioxide.

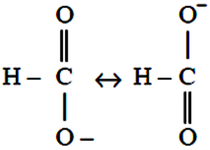
$$O = C = O$$
(I)

The above structure does not account for all observed properties although it can explain many. The C-O bond length in CO_2molecule is1.15 Å where as it is expected to be 1.22 Å on the basis of the abovestructure.Again, the heat of formation of carbon dioxide is 1592 kJ.mol^{-1} whereas on the basis of the above structure it is expected to be approximately 1466 kJ.mol^{-1}. These discrepancies can be explained only if we assume thefollowing resonance hybrid for carbon dioxide.

$$O^{+}\equiv C-O^{-}\leftrightarrow O=C=O\leftrightarrow {}^{-}O-C\equiv O^{+}$$

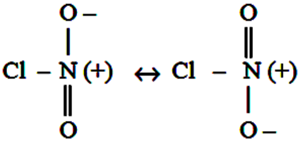
The difference in energy i.e. 126 KJ.mol^{-1}is regarded as resonance energy.Few other examples

1. Formate ion, HCOO–

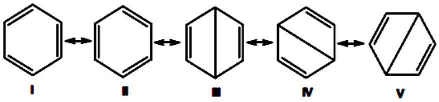


$$H-\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O-}{|}}{C}}}\leftrightarrow H-\overset{\displaystyle O^{-}}{\overset{|}{\underset{\underset{\displaystyle O}{\|}}{C}}}$$

2. Nitryl chloride, NO_2Cl



$$Cl-\overset{\displaystyle O-}{\overset{|}{\underset{\underset{\displaystyle O}{\|}}{N}}}(+)\leftrightarrow Cl-\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O-}{|}}{N}}}(+)$$



5.07Types of organic reactions

Substitution or Displacement reactions

Displacement reaction is one in which an atom or group linked to a carbon atom is removed and in its place another atom or group is attached.The substitution reactions are classified into three types.

a) Nucleophilic substitution reaction (S_N)

When a substitution reaction is brought about by a nucleophile, the reaction is termed as SN (S stands for substitution and N for nucleophile).These reactions are divided into two classes:

(1) S_N1 (substitution, nucleophilic, unimolecular) and

$$\underset{\text{tert-butyl chloride}}{(CH_3)_3\,C\,Cl} + KOH \xrightarrow{\text{aqueous}} (CH_3)_3\,C\,OH + KCl$$

(2) S_N2 (Substitution, nucleophilic, bimolecular)

$$\underset{\text{(Methyl Chloride)}}{CH_3Cl} + KOH \xrightarrow{\text{aqueous}} CH_3OH + KCl$$

b) Electrophilic substitution reaction (SE)

When a substitution reaction involves an attack by an electrophile, the reaction is referred to as SE (S - stands for substitution and E for electrophile).

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \quad \text{(Free radical)}$$

$$\underset{\text{Methane}}{CH_4} + 2Cl\cdot \rightarrow CH_3Cl + HCl$$

c) Free radicals substitution reaction

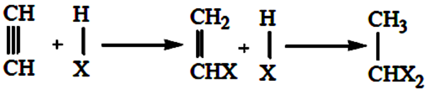
These reactions are initiated by free radicals.

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \quad \text{(Free radical)}$$

$$\underset{\text{Methane}}{CH_4} + 2Cl\cdot \rightarrow CH_3Cl + HCl$$

Addition Reactions

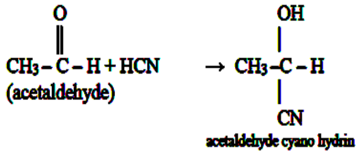
All organic compounds having double or triple bond adopt addition reactions in which two substances unite to form a single compound.



$$\begin{array}{c}CH\\ \|\!|\\ CH\end{array} + \begin{array}{c}H\\ |\\ X\end{array} \longrightarrow \begin{array}{c}CH_2\\ \|\\ CHX\end{array} + \begin{array}{c}H\\ |\\ X\end{array} \longrightarrow \begin{array}{c}CH_3\\ |\\ CHX_2\end{array}$$

Depending on the type of reagent initiating these reactions, addition reactions are classified into three types.

(a) Nucleophilic addition

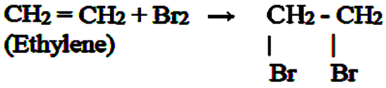


$$CH_3-\overset{\overset{O}{\|}}{C}-H+HCN \rightarrow CH_3-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-H$$

(acetaldehyde)

acetaldehyde cyano hydrin

(b) Electrophilic addition



$$CH_2=CH_2+Br_2 \rightarrow \underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}}$$

(Ethylene)

(c) Free radical addition

$$CH_3-CH=CH_2 \xrightarrow[H_2O]{HBr} CH_3-CH_2-CH_2-Br$$

Elimination reactions

In these reactions, two atoms or groups are removed from a molecule without being substituted by other atoms (or) groups. The reverse of addition reactions are eliminations. These reactions are classified into twotypes.

(a) Unimolecular elimination (E1)

$$(CH_3)_3C\text{-}Br \xrightarrow[KOH]{alcoholic} (CH_3)_2C=CH_2+H_2O+Br^-$$

2-Methyl propene

(b) Bimolecular elimination (E2)

$$CH_3-CH_2-CH_2-Br \xrightarrow[KOH]{alcoholic} CH_3-CH=CH_2+KBr+H_2O$$

Polymerization

The union of two or more molecules to form a large single molecule is called polymerisationand the product is a polymer.

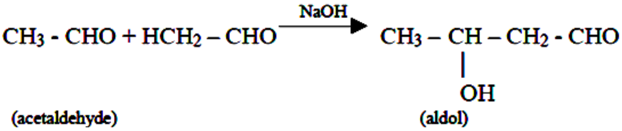
$$\underset{\substack{\text{Ethylene}\\\text{(Monomer)}}}{n\,CH_2=CH_2} \xrightarrow{473K,1000\ atm} \underset{\substack{\text{Polyethene}\\\text{(Polymer)}}}{(-CH_2-CH_2-)_n}$$

Condensation reactions

When two molecules (similar or different) combine to form a single molecule with or without the elimination of simple molecules like H_2O,NH_3, HCl, CO_2, it is called a **condensation** reaction.

Example

Aldol condensation reaction



$$\underset{\text{(acetaldehyde)}}{CH_3-CHO+HCH_2-CHO} \xrightarrow{NaOH} \underset{\text{(aldol)}}{CH_3-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_2-CHO}$$

Hydrolysis

Esters are hydrolyzed by boiling with mineral acids or alkalis.

a) Acid hydrolysis

An ester can be hydrolyzed to give the parent carboxylic acid and alcohol by using mineral acid (H_2SO_4 or HCl) as catalyst.

$$\underset{\text{Ethylacetate}}{CH_3-COOCH_2-CH_3}+H_2O \overset{H^+}{\rightleftharpoons} \underset{\text{acetic acid}}{CH_3-COOH}+\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH}$$

The above reaction is reversible and is exactly opposite of esterification. In order to hydrolyze most of the ester, the equilibrium must be pushed to the right by using large excess of water.

b) Basic hydrolysis

When an ester is treated with an alkali (NaOH or KOH) as catalyst, the hydrolysis yields the parent alcohol and sodium salt of the carboxylic acid.

$$CH_3 - CH_2 - COOC_2H_5 + NaOH \rightarrow CH_3 - CH_2 - COONa + C_2H_5OH$$

Ethyl propionate → Sodium propionate + Ethyl alcohol

Reduction and oxidation reactions

A reaction which proceeds by the addition of hydrogen is termedReductionand the one that involves the addition of oxygen is calledOxidation. For example,

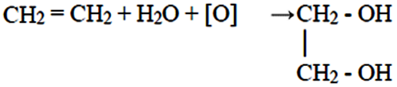
1) Clemmensen Reduction

Ketones can be reduced to their corresponding hydrocarbons by themixture of Zn/Hg and conc. HCl.

$$C_6H_5COCH_3 \xrightarrow[HCl]{Zn/Hg} C_6H_5 - CH_2 - CH_3$$

acetophenone → Ethyl benzene

2)Very mild oxidizing agent such as $KMnO_4$, causes a splitting of the molecule at the double bond.



$$CH_2 = CH_2 + H_2O + [O] \rightarrow \begin{array}{l} CH_2 - OH \\ | \\ CH_2 - OH \end{array}$$

Ethylene → Ethylene glycol

Isomerism

The molecular formula of an organic compound represents only the number of different atoms present in a molecule. But the molecular formuladoes not tell about the arrangement of atoms. A given molecular formulamay lead to more than one arrangement of atoms such that there are manycompounds which may have same molecular formula but with differentphysical and chemical properties. This phenomenon in which the samemolecular formula may exhibit different structural arrangement is calledisomerism. Compounds that have the same molecular formula but different structural formulae are called isomers (from the Greek word isos + meros,"made of the same parts").

There are two types of isomerism, namely,

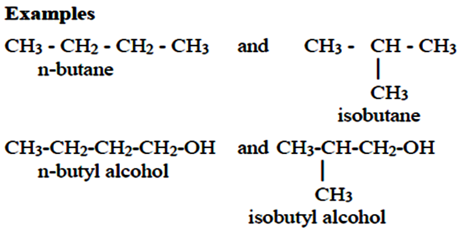
1. Structural isomerism and
2. Stereoisomerism

Structural isomerism

When two or more compounds possess the same molecular formula but different structural formulae, they are said to exhibit structural isomerism.Structural isomerism is divided into.

1. Chain isomerism or Nuclear isomerism

Chain isomers are compounds that have the same molecular formula but have different carbon skeletons.



Examples

$CH_3-CH_2-CH_2-CH_3$ and $CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_3$

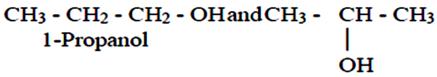
n-butane isobutane

$CH_3-CH_2-CH_2-CH_2-OH$ and $CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-OH$

n-butyl alcohol isobutyl alcohol

2. Position Isomerism

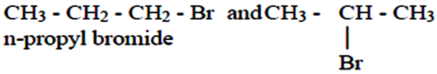
Position isomers are compounds that have the same formula, carbon skeleton and functional groups but have the functional groups located at different positions along the carbon skeleton.



$$CH_3-CH_2-CH_2-OH \text{ and } CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

1-Propanol

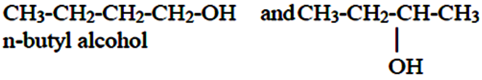
2-Propanol



$$CH_3-CH_2-CH_2-Br \text{ and } CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

n-propyl bromide

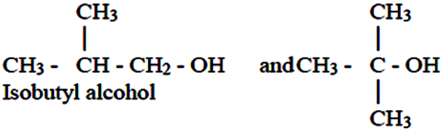
Isopropyl bromide



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH \text{ and } CH_3\text{-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_3$$

n-butyl alcohol

Sec - butyl alcohol



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-OH \text{ and } CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-OH$$

Isobutyl alcohol

ter - butyl alcohol

$CH_3-CH_2-CH=CH_2$ 1-Butene

$CH_3-CH=CH-CH_3$ 2-Butene

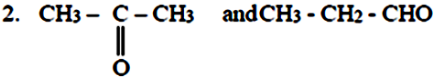
Functional isomerism

Functional isomers are compounds that have the same molecular formula but have different functional groups.

Examples

1. CH_3-CH_2-OH and CH_3-O-CH_3

   Ethyl alcohol — Dimethyl ether

2. 

   $$CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 \text{ and } CH_3-CH_2-CHO$$

   Acetone — Propionaldehyde

3. CH_3-CH_2-COOH and $CH_3-COO-CH_3$

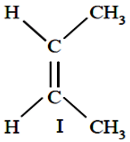
   Propionic acid — Methyl acetate

Stereoisomerism

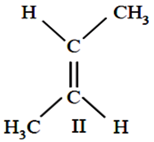
Stereoisomerism arises out of the differencein the arrangement of atoms in the molecule, with reference to each other in space.Stereoisomers (have the same structure) differ in the way the atoms areoriented in space. They have the same structure and hence do not differmuch in properties.There are **two types** of Stereoisomerism. They are (i) Geometricalisomerism and (ii) Optical isomerism.

(i) Geometrical Isomerism:

Isomerism that arises out of difference in the spatial arrangement of atoms or groups about the doubly bonded carbon atoms is called Geometricalisomerism. These isomers are not mirror images of each other. Rotationabout C=C is not possible at normal conditions and hence the isomers areisolable.If different atoms or groups are bonded to the 'C=C' bond in a molecule,more than one spatial arrangement is possible. For example, 2-butene existsin two isomeric forms.

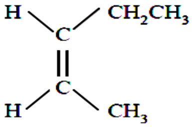


Cis isomer

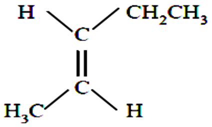


Trans isomer

The isomer in which similar groupslie on the same side is called 'cis isomer' (I). The other in which similar groups lie in opposite direction iscalled 'Trans isomer' (II). This isomerism is called 'Cis-Trans' isomerism.The two groups attached to the carbon atoms need not be same, it may be different also. e.g., 2-pentene



Cis



Trans

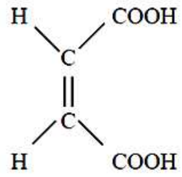
This isomerism arises out of the hindrance to rotation about the C=C bond in such molecules.The cis-trans isomers do not differ much in chemical properties. They differ in physical properties like boiling point, melting point, crystal structure, solubility and refractive index. Highly substituted olefin is more stable than less substituted olefin. Among substituted olefins, trans olefin is more stable than cis olefin.

In the cis isomer because similar groups are very near each other, Van der Waals repulsion and steric hindrance make the molecule much unstable. In the trans isomer, similar groups are diagonally opposite to each other. Hence there is no such steric interaction. Generally trans isomer is more stable than cis isomer. Hence reactivity of cis isomer may be little higher than the trans isomer. The energy of the cis isomer is greater than that of trans isomer.

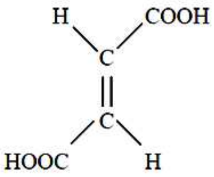
Though at room temperature, cis and trans isomers are stable and are not inter-convertible, on heating to a certain temperature, trans isomer can be converted to cis isomer and vice-versa. ‘Breaking of carbon-carbon p-bond and its reformation is responsible for the inter-conversion’.

$$\text{Trans isomer} \overset{\Delta}{\rightleftharpoons} \text{Cis isomer}$$

Consider unsaturated dicarboxylic acid - Maleic acid and Fumaric acid. These are geometrical isomers.

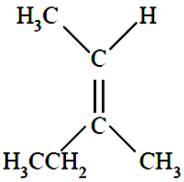


Cis
[Maleic acid]



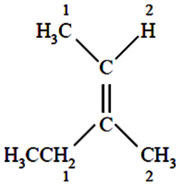
Trans
[Fumaric acid]

‘Cis-trans’ system of nomenclature may not be suitable for many substituted olefins.For example,

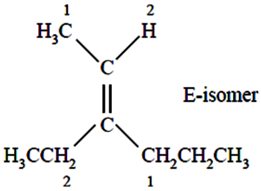


A newer system based on the priority of groups is the Cahn-Ingold-Prelog convention. This system is called the (E-Z) system, applies to alkene diastereomers of all type. If the two groups of higher priority are on the same side of the double bond, the alkene is designated ‘Z’ (from the German word Zusammen-meaning together). If the two groups of high priority are on opposite sides of the double bond, the alkene is designated ‘E’ (from the German, entgegen, meaning opposite).

The priorities follow the order of decreasing atomic number of the atom directly bonded to the carbon. For some compounds the priority is shown by numbers as:



Z-isomer

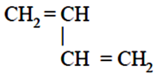


E-isomer

Dipole moment studies is one of the best methods of identifying cis-trans isomers. Generally cis isomers have larger dipolemoment than trans isomers. Often DPM of trans isomer is zero. e.g., Trans 2-butene and Trans 2,3-dibromo-2-butene.

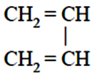
1,3Butadiene **$CH_2= CH – CH = CH_2$**

This molecule can exist in two forms.



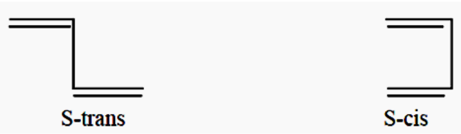
I

and

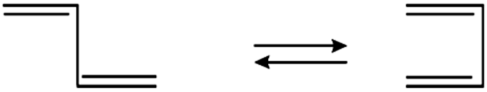


II

Though these two forms do not differ very much in their energy and stability, the (I) form, which is similar to ‘trans’ is more stable than (II) form which is similar to ‘cis’. These two forms do not arise out of the hindrance to rotation about C=C, instead the restricted rotation about C–C. In order to indicate that, this cis-trans isomerism is due to restricted rotation about C–C bond, they are named as,



These are easily inter-convertible and exist in equilibrium.

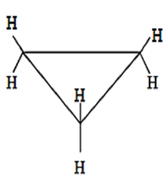


S-trans form is also called 'transoid form'. S-cis form is also called 'cisoid form'. The energy of S-trans form is 3 Kcals less than the S cis form. These two forms differ in chemical reactivity. Very often they give different products in reactions.

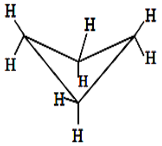
Conformation in cyclic systems:

The different forms that arise out of the rotation about C–C single bond are called conformers. Free rotation about C–C single bond is not always possible. Very often the rotation is restricted depending upon the nature and the size of atoms or groups bonded to each carbon atom. The different conformers differ in energy though not appreciably. Restriction to free rotation about C–C single bond is much pronounced in cyclic systems. In these cases, the restriction to rotation is so appreciable as to make the different forms isolable or identifiable.

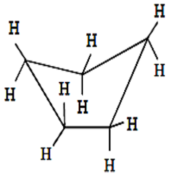
Thus cyclopropane is flat, cyclobutane can form butterfly shape while cyclopentane can form an open-envelope shape.



Cyclopropane
[Planar conformation]



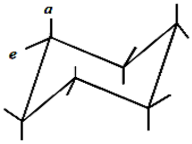
Cyclo butane
[non planar conformation]



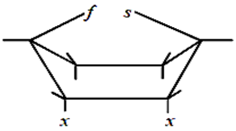
Cyclo pentane
[non planar conformation]

Cyclohexane:

As early as 1890, Sachse suggested that cyclohexane ring exists in two non-planar forms (i.e.,) boat and chair conformations. The energy difference between these two forms was found to be only 6.5 K.cal/mole by Pitzer. The energy difference is small enough for inter-conversion to take place. Both the boat form and chair form are free of angle strain called Baeyer's strain (i.e., the valence bond angle is 109°28'].



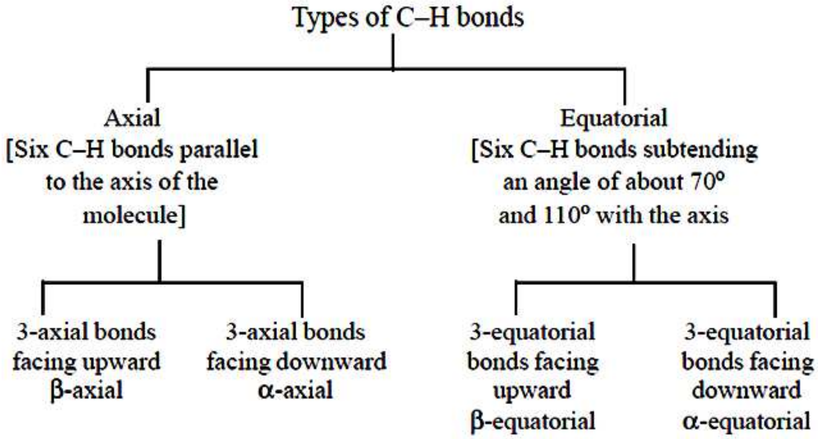
Chair conformation
a = axial, *e* = equatorial



Boat conformation
f = flagpole, *s* = bowspirit,
x-*x* = pair of eclipsing hydrogen atoms

Chair conformation:

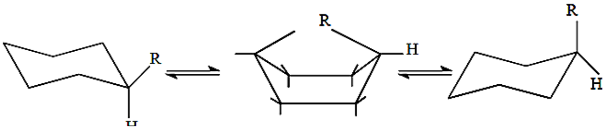
There are two types of C–H bonds.



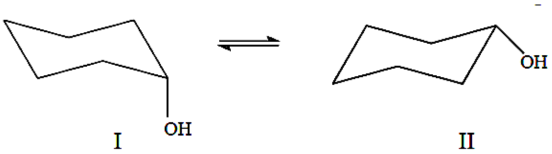
Every pair of carbon atoms (Two carbon atoms directly bonded to each other) in chair form exists in skew form.

Boat conformation

This form has two pairs of carbon atoms with eclipsing bonds. This eclipsing interaction destabilizes boat form. Though the chair form is stable, it is sufficiently flexible to turn itself upside down called ring flipping so that all bonds which are axial originally become equatorial and vice versa.

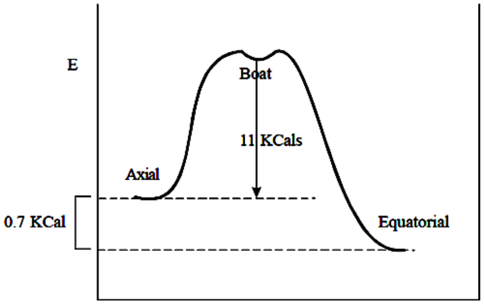


There exists an equilibrium between these two chair forms with boat form as intermediate. A mono substituted cyclohexane like cyclohexanol exists in the two chair forms. These two forms are inter-convertible and exist in equilibrium.



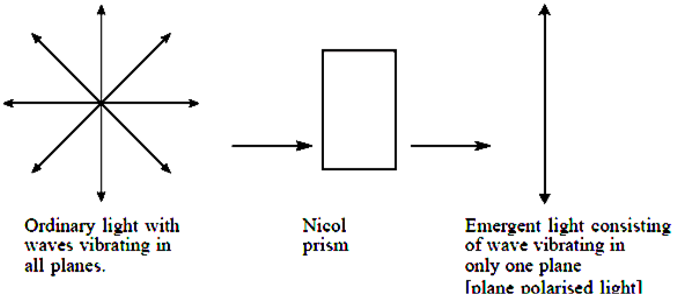
In one form (I) the –OH group is axially oriented. In the other form (II) the –OH group is equatorially oriented. The energy of the axial conformer is little higher than that of the equatorial conformer. Because the axial substituent experiences steric interaction with the axial H-atoms present at the third carbon atoms. This decreases the stability of the axial conformer. This is called 1:3-diaxial interaction. This interaction is absent in the equatorial conformer. Hence equatorial cyclohexanol is present to an extent of about 90% in the equilibrium mixture. The axial isomer is present only to 10%.

Energy level diagram for axial and equatorial alcohols

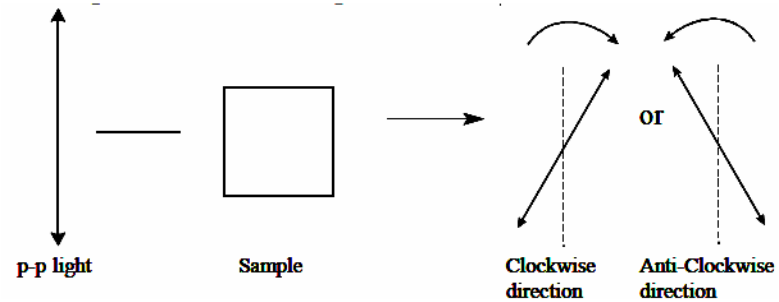


Optical activity and optical isomerism:

Light is propagated in the form of waves. Ordinary monochromatic light is supposed to consist of waves vibrating in all planes. If such a light is passed through a Nicol prism, the emergent light is found to consist of waves vibrating in only one plane. Such a light is called plane polarized light.



When the plane polarized light is passed through certain substances or solutions (such as lactic acid), the emergent light is found to be vibrating in a different plane. This is called optical rotation.



Such substances are called optically active substances. This property of such substances is called 'Optical activity'. If the rotation is towards the right side [clockwise] it is called dextrorotation and the substance is said to be dextrorotatory. Dextrorotation is indicated by the symbol (+) or'd'. If the rotation is towards the left side [Anticlockwise] it is called laevorotation and the substance is said to be laevo rotatory. Laevorotation is indicated by the symbol (–) or '*l*'.

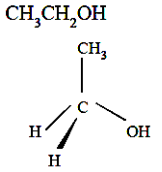
Conditions of optical activity:

Not all substances are optically active. For example substances like$CHCl_3$, CH_3CH_2OH, $CH_3CH_2CH{=}CH_2$, $CH_3CH_2COCH_3$ are not opticallyactive. On the other hand substances like CHIBrCl, $CH_3CHBr–CH{=}CH_2$,$CH_3CH(OH)COCH_3$, CH_3CHDOH are found to be optically active.

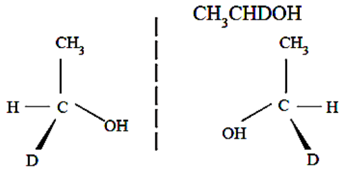
When the structures of the compounds which are optically inactive andoptically active, are compared, one thing is clear. All the optically activecompounds, mentioned above have atleast one carbon atom that is bondedto four different atoms or groups.

A carbon atom attached to four different atoms or groups is called"asymmetric carbon atom".Pasteur suggested that optical activity arises from molecular dissymmetrywhich is supported by Vant-Hoff and LeBel. According to them, a carbonatom has its four valencies directed towards the four corners of a regulartetrahedron. In this situation a molecule with an 'asymmetric carbon atom'becomes asymmetric.It so happens that an asymmetric molecule is not superimposable on itsmirror image. That means an optically active molecule has more than [atleasttwo] one configuration. [configuration refer to three dimensional arrangementof atoms in a molecule] that is, an optically active molecule exhibits isomerismwhich is called optical isomerism.

Consider ethanol and deuterated ethanol:



(ethanol-symmetric molecule)



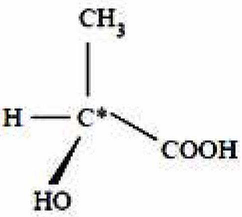
(deuterated ethanol- asymmetric and non-superimposable)

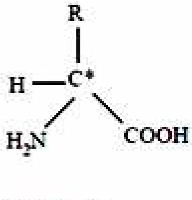
The isomers-called optical isomers have configurations which are non-superimposable.

Hence the criteria for a molecule to be asymmetric (hence optically active) is that its configuration is non-superimposable on its mirror image. Such molecules are also called 'chiral' molecules.

'Chirality' is'the essential and the sufficient' condition for a molecule to be optically active.

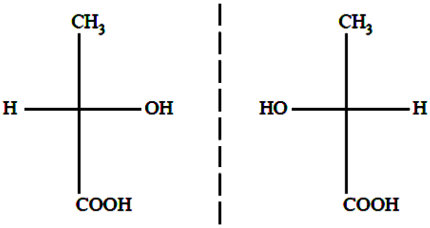
Chirality means handedness or non-superimposability. Right hand and left hand, Right leg shoe and left leg shoe are examples of objects having handedness or the property of chirality and non superimposability. The molecules which are optically inactive are ‘achiral’. Simple optically active molecules like lactic acid, are said to have “chiral carbon” or “chiral center”. Example,





α-amino acid

The carbon with “astreik” is called the chiral carbon. All the a-amino acids (except glycine) have chiral centers (chiral carbon) and are optically active.



d,l pair of lactic acid

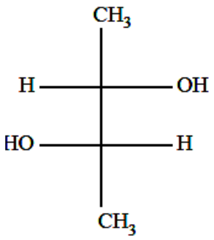
Optical isomers:

Chiral molecules can have two different configurations. Each configuration stands for one optical isomer. Thus dextrorotatory isomer hasconfiguration which is the mirror image of the laevorotatory isomer. Suchoptical isomers which differ only in the sign of (or direction of) optical rotationare called “enantiomers”.

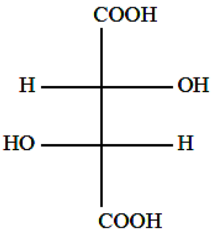
When equal amounts of d-isomer and l-isomer are mixed one gets a “racemic mixture” and this process is called racemization. A racemic mixturebecomes optically inactive. Because,in this mixture rotation towardsclockwise direction by the dextro isomers is compensated by the rotationtowards the anticlockwise direction by the laevo isomers. The opticalinactivity of a racemic mixture is said to be due to ‘external compensation’.Any how an optically inactive racemic form can be separated into two activeforms. This process of separation is called “resolution of the racemicmixture”.

A molecule with more than one chiral carbon

A molecule can have more than one chiral centers. Correspondingly thenumber of isomers is increased. In general for a molecule with *n*-differentchiral centers, 2*n*-isomers are possible. A molecule can have more than oneidentical asymmetric carbon atoms. (e.g.,) butane -2,3-diol and tartaric acid.



Diol

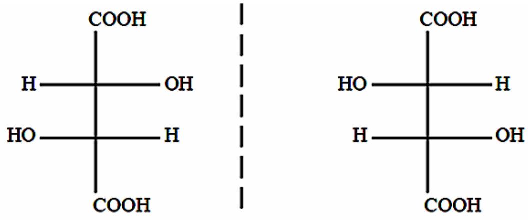


Tartaric acid

In such cases the number of optical isomers is not 22 = 4, it is less than 4(i.e.,) 3.

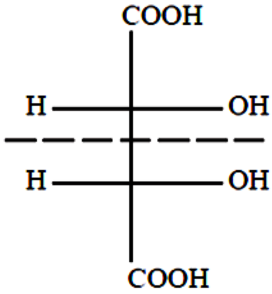
Isomerism in Tartaric acid:

Tartaric acid is dihydroxydioic acid, having two identical chiral carbonatoms.



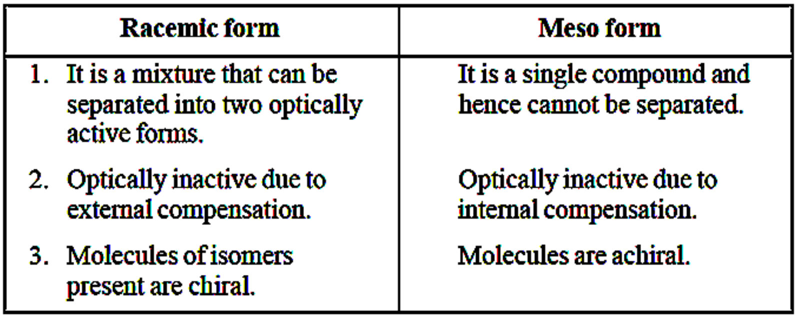
(*d*, *l* pair of tartaric acid)

The enantiomers of tartaric acid, have the same magnitude but differentsign of optical rotation. They have object-mirror image relationship.In the *d*-isomer, each of the two asymmetric carbon atoms rotate theplane of the polarized light towards right leading to overall dextro rotation.In the same way in the *l* - isomer, the overall rotation is laevo.There is another optical isomer for tartaric acid in which one asymmetriccarbon atom is dextrorotatory and the other laevorotatory- both rotating tothe same extent in opposite directions. The net result is, that this isomerbecomes optically inactive and is called the "Meso" isomer.



Though the Meso isomer has two asymmetric carbon atoms the configuration of one carbon is the mirror image of the other, the net resultbeing the molecule as a whole becomes symmetric. This molecule is said tohave a symmetric plane, which divides the molecule into two equal halves.The molecule becomes "achiral". It has configuration which is superimposableon its mirror image.

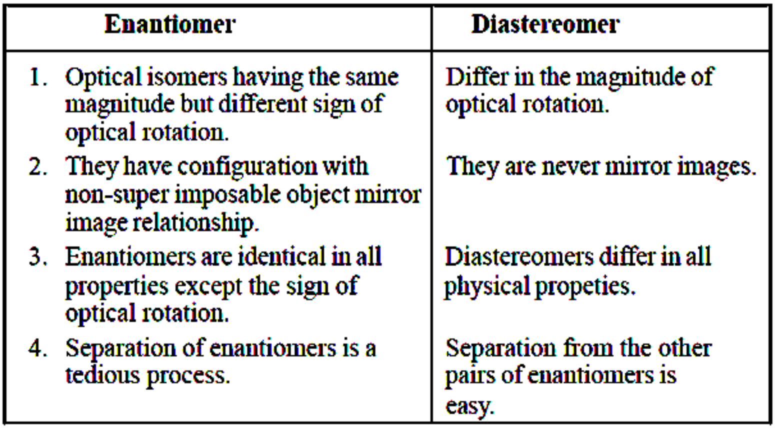
The optical inactivity of the 'Meso' isomer is due to the internal compensation. It is due to the inherent symmetry in the molecule. Mesoformcannot be separated into optically active enantiomeric pairs. This form is asingle substance and not a mixture.



Racemic form	Meso form
1. It is a mixture that can be separated into two optically active forms.	It is a single compound and hence cannot be separated.
2. Optically inactive due to external compensation.	Optically inactive due to internal compensation.
3. Molecules of isomers present are chiral.	Molecules are achiral.

When equal amounts of *d*-tartaric acid and *l*-tartaric acid are mixed, weget racemic tartaric acid which is an optically inactive mixture.

This can beseparated into two optically active forms.*d*- and *l*-isomers have the same magnitude but different sign of opticalrotation, hence they are called enantiomers.

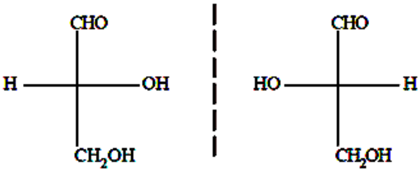


Enantiomer	Diastereomer
1. Optical isomers having the same magnitude but different sign of optical rotation.	Differ in the magnitude of optical rotation.
2. They have configuration with non-super imposable object mirror image relationship.	They are never mirror images.
3. Enantiomers are identical in all properties except the sign of optical rotation.	Diastereomers differ in all physical propeties.
4. Separation of enantiomers is a tedious process.	Separation from the other pairs of enantiomers is easy.

The Meso tartaric acid differs inthe magnitude of optical rotation from the *d*- or *l*- isomer. Hence Mesoformis said to be a "diastereomer' of the active form.

Representation of configurations of the molecule:

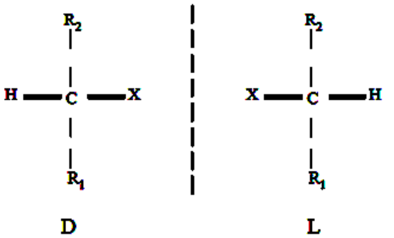
In order to indicate the exact spatial arrangement of atoms or groups ina molecule having asymmetric carbon atom, Fischer proposed DL-systemof nomenclature. Glyceraldehyde was taken as the standard. The dextroisomer and laevo isomer of glyceraldehyde are designated as D and L asfollows. These are Fischer's projection formulae.



Sign of rotation : *d* or (+) glyceraldehyde *l* or (–) glyceraldehyde

Designation of configuration : D L

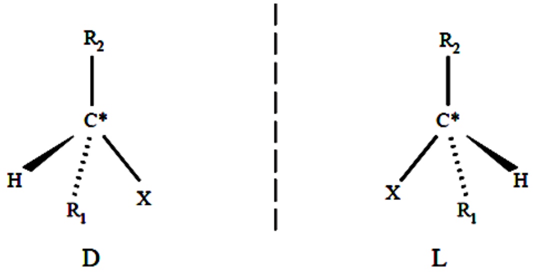
In general more oxidised group is shown at the top and the reducedgroup at the bottom. The chiral molecule is viewed in such a way that H, Xlieabove the plane of the paper and R1, R2-lie below the plane of the paper.The D, L-configurations are shown as:



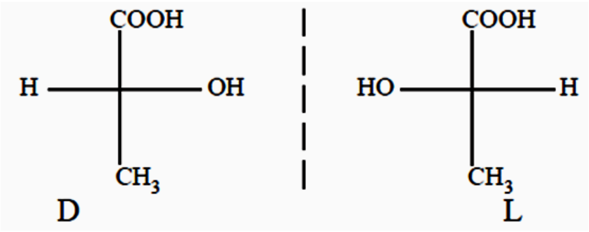
R_2 = Oxidised group - COOH, CHO, CO...
R_1 = Reduced group CH_3, CH_2OH ...
X = a heteroatom or a group with hetero atom
(i.e.,) Cl, Br, I, –OH, $–NH_2$, etc.,

(In the projection formula, the broken lines indicate the bonds that are going below and thick lines, the bonds coming above the plane of the paper)

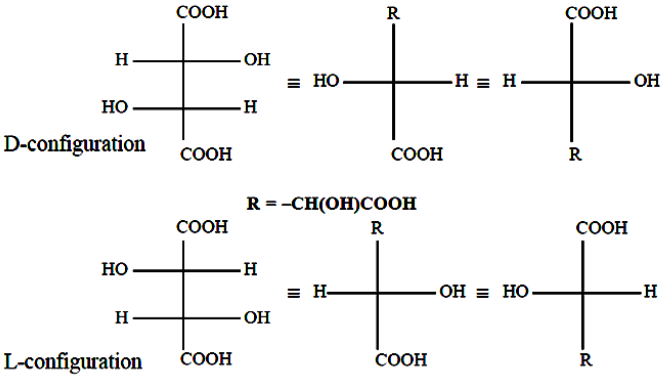
The above projection formulae can be understood from the followingdiagram.



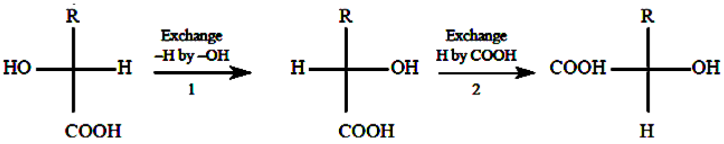
Thus D and L lactic acids are:



and tartaric acid - (R-stands for the remaining half portion of the molecule)



This system of designating configuration is of limited applicability.In Fischer's projection formula any two exchanges of groups attachedto the asymmetric carbon atom, are allowed, then the configuration is notchanged.i.e.,



I II

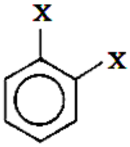
Though I and II appears to be different but both represent the same configuration. Both are identical.

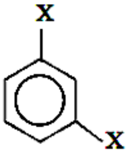
Disubstituted benzene:

When any two hydrogen atoms of the benzene ring are replaced by anyother atoms or groups disubstituted benzene is obtained.

(e.g.,) $C_6H_4Cl_2$, $C_6H_4(OH)_2$, $CH_3C_6H_4Br$, $HOC_6H_2NO_2$

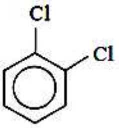
The disubstituted benzenes can exist in three isomeric forms.



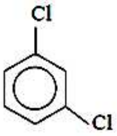


X = Any substitutent

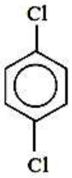
These are three distinct forms differing in many properties though theyhave the same formula. Hence they are said to exhibit isomerism. In thesethree structures the isomers differ in the relative position of the substitutents.Hence they are called position isomers. When the substituents are in adjacent positions in the benzene ring, it iscalled ortho isomer.When the two substituents are exactly opposite to each other, it is apara isomer.When the angle between two substituents is 120°. It is a meta isomer.Example,



Ortho dichloro benzene



Meta dichloro benzene

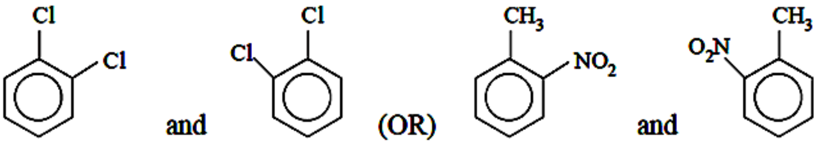


Para-dichloro benzene

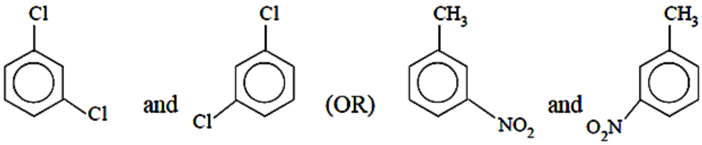
Isomers can also be named using the number of the carbon atom thus:

Ortho isomer is	1,2-dichloro benzene
Meta isomer is	1,3-dichloro benzene
Para isomer is	1,4-dichloro benzene

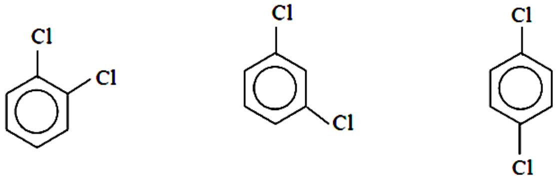
It should be remembered that there are two ortho and two meta and only one para position to the substituent already present in a molecule ofbenzene.



These two are identical and are not isomers. Similarly the following tworepresent one and the same compound and are not non-superimposable mirrorimages.



Ortho, meta and para isomers differ mainly in physical properties like melting point, refractive index, solubility. Their behavior under an appliedelectric field differs widely. This behavior is measured by a quantity called'Dipole moment'.



angle $\theta = 60^\circ$ $\theta = 120^\circ$ $\theta = 180^\circ$

For di-substituted benzenes the magnitude of DPM depends on the angle between the two substituents. For example, for dichloro benzene Their DPM, is in the order.

Ortho isomer > Meta isomer > Para isomer

Note: For para dichloro benzene DPM = 0

Hence dipole moment measurement is the best method of distinguishingthe three isomers of disubstituted benzenes.