Black body: An ideal body, which emits and absorbs all frequencies of electro magnetic radiation.

Quantum: The smallest quantity of energy that can be emitted or absorbed in the form of electro magnetic radiation. Quantum is just an energy packet and it has no mass.

Planck's Quantum Theory:

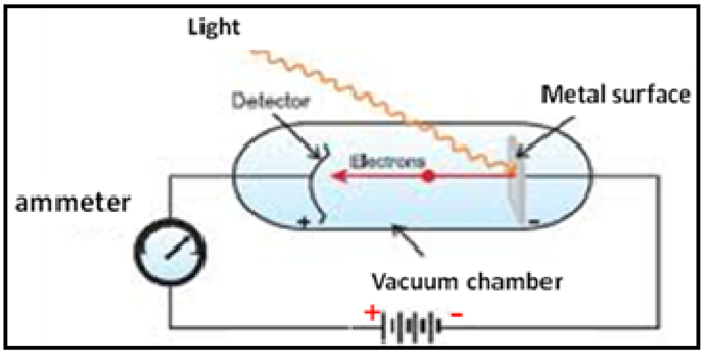
Planck's quantum theory explains the black body radiation. It supports particle nature of electro magnetic radiation.

Features of Planck's Quantum Theory:

1) The emissions of radiation are due to vibrations of charged particles (electrons) in the body.
2) The emission of radiant energy is not continuous. It happens in the form of small discrete packets of energy called 'Quanta'.
3) The energy of quantum is given by $E = h\vartheta$
   Where, h = Planck's constant = 6.625×10^{-27} erg sec.
   ϑ = frequency of radiation
4) Moreover, $E = n(hv)$, n= 1,2,3,………..thus, energy is quantized.
   i.e. the energy emitted or absorbed by a black body, is an integral multiple of 'quanta'.
5) 'Quantums' will propagate in the form of waves.
6) The frequency distribution of the emitted radiations from a black body depends only on its temperature.

Photoelectric effect:

It is phenomenon in which electrons are ejected from the clean surface of certain metals (alkali metals, Ex: K, Rb, Cs), when the metals are exposed to a light.



The results observed in this experiment were:

1) The electrons are ejected from the clean metal surface as soon as the beam of light strikes the surface.
2) The number of electrons ejected is proportional to the intensity or brightness of light.
3) For each metal, there is a characteristic minimum frequency, v_o (also known as threshold frequency) below which photoelectric effect is not observed. At a frequency $v > v_o$ the ejected electrons comes out with certain kinetic energy. The kinetic energies of these electrons increase of frequency of the light used.

BOHR'S ATOMIC MODEL:

To overcome the objections of Rutherford's model and to explain the hydrogen spectrum, Bohr proposed a quantum mechanical model of the atom.

Postulates:

i) The atom has a nucleus where all the protons and neutrons are present. The size of the nucleus is very small. It is present at the centre of the atom.

ii) Negatively charged electrons are revolving around the nucleus in the same way as the planets are revolving around the sun.

iii) The path of electron is circular. The force of attraction between the nucleus and the electron is equal to centrifugal force of the moving electron.

iv) Out of infinite number of possible circular orbits around the nucleus, the electron can revolve only on those orbits whose angular momentum is an integral multiple of $h/2\Pi$,
i.e., $mvr = nh/2\Pi$.
Where m = mass of electron, v = velocity of electron, r = raidus of the orbit
n = 1, 2, 3,….. number of the orbit
therefore angular momentum can have values such as $1h/2\Pi$, $2h/2\Pi$, $3h/2\Pi$., ….etc. but cannot have a fractional value. Thus, angular momentum is quantized. The specified or circular orbits are called **stationary orbits**.

v) By the time, the electron remains in any of the stationary orbits, it dose not lose energy. Such a state is called is called ground or normal state.

vi) Each stationary orbit is associated with a definite amount of energy. These orbits are also called energy levels and are number as 1, 2, 3, 4,…. or K, L, M, N, from nucleus outwards. i.e., $E_1 < E_2 < E_3 < E_4$……….

$$(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3)\ldots..$$

vii) The emission or absorption of energy in the form of radiation can only occur when an electron jumps from one stationary orbit to another.

$$\Delta E = E_{high} - E_{low} = h\vartheta$$

Energy is absorbed when the electron jumps from inner to outer orbit (excited state) and is emitted when it moves from outer to an inner orbit.

Limitations of Bohr's theory:

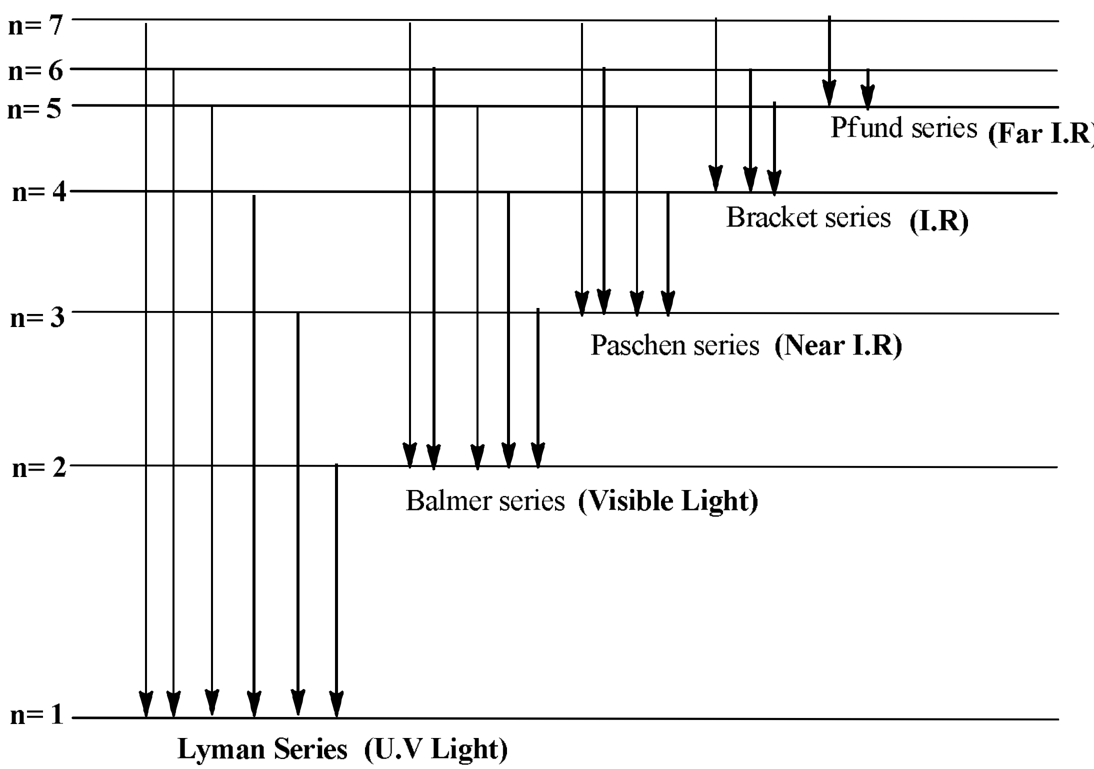
i) It does not explain the spectra of multi-electron atoms.
ii) Bohr's theory does not explain the fine spectra of even hydrogen atom.
iii) It does not explain the splitting of spectral lines in presence of magnetic field (Zeeman effect) and electric field (stark effect).
iv) Bohr's theory is not in agreement with Heisenberg's uncertainty principle.

Hydrogen spectrum – Bohr's Explanation:

1) When electric discharge is passed through gaseous hydrogen, the electrons in various hydrogen atoms absorbs various amounts of energies.
2) Then they enter into higher energy orbits.
3) In higher orbits, the energy is more but stability is less.
4) So, the excited electrons falls back to lower orbits.
5) This happens in one step or in multiple steps.
6) Energy released during this process and it appears in the form of spectral lines of hydrogen spectrum.
7) The transmission of energy of electrons from any higher orbit to
   i) n = 1 produces spectral lines in the UV region. This is named as **Lyman Series**.
   ii) n = 2 produces spectral lines in the visible region. This is named as **Balmer Series**.
   iii) n = 3, 4, 5 produces spectral lines in the IR region. These are named as **Paschen, Brackett** and **pfund Series** respectively.

   Formula to find wavenumber ($\bar{\upsilon}$) and wavelength (λ) of spectral lines:

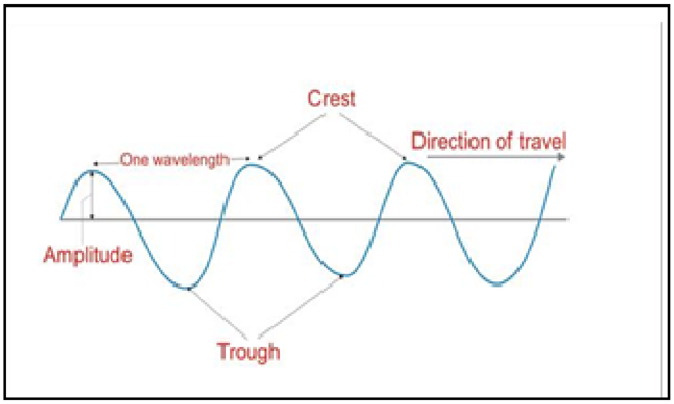
   $\bar{\upsilon} = 1/\lambda = R_H [1/n_1^2 - 1/n_2^2]$



Energy level diagram of Hydrogen spectrum

Electromangnetic radiation:

An electromagnetic radiation is generated by oscillations of a charged body in a magnetic field or a magnet in an electrical field. These radiations or waves have electrical and magnetic fields associated with them and travel at right angle to these fields.



1) **Wavelength:** The distance between two nearest crests or nearest troughs is called the wavelength. It is denoted by λ.
   Units: cm, nm, Å, µm.
   1 Å = 10^{-8} cm = 10^{-10} m
   1 µm = 10^{-4} cm = 10^{-6} m
   1 nm = 10^{-7} cm = 10^{-9} m
   1 cm = 10^{8} Å = 10^{4} µm = 10^{7} nm
2) **Frequency:** It is defined as the number of waves which pass through a point in one second. It is denoted by the ϑ. It is expressed in Hz.
   $$\vartheta = c/\lambda$$
3) **Velocity:** It is defined as the distance covered in one second by the wave. It is denoted by c. It is expressed in cm/sec.
   $$c = \vartheta\lambda$$
4) **Wave number:** This is the reciprocal of wavelength, *i.e.* the number of wave length per cm. It is denoted by $\bar{\upsilon}$. It is expressed in cm^{-1} or m^{-1}.
   $$\bar{\upsilon} = 1/\lambda$$
5) **Amplitude:** It is defined as the height of the crest or depth of the trough of a wave. It is denoted by a. it determines the intensity of radiation.
6) **Time Period:** time taken by the wave for one complete cycle or vibration is called time period. It is denoted by *T*. Units: sec/cycle
   $$T = 1/v$$

Dual nature of matter:

de Broglie proposed that micro particles like electrons exhibit both particle and wave like properties. Thus, electron should also have momentum as well as wave length.

i) According to Planck's quantum theory of radiation, the energy of photon is given by
$E = h\vartheta \Longrightarrow E = h\, c/\lambda$ …………..(1)

ii) According to Einstein's mass-energy equivalence equation, $E = mc^2$ ………(2)
From (1) & (2), $h\, c/\lambda = mc^2$
$\Longrightarrow h/\lambda = mc$
$\Longrightarrow \lambda = h/mc = h/p$ ……….(3) [since $mc = p$ = momentum

de Broglie hypothesized that, equation (3) applicable to photons, can be extended to all micro particles like electrons, moving with high speeds.

Hence (3), the velocity of photon (c) can be replaced by the velocity of microparticle (v).

Therefore equation (3) be re-written as $\lambda = h/p = h/v$ ……….(4)

This equation (4) is called de Broglie equation.

Here λ = particle wave length

Thus, the micro particle electron posses wave length λ, given by the above expression. Hence, electron is associated with wave nature.

Significance or importance: Equation (4) should hold true for all the moving material bodies.

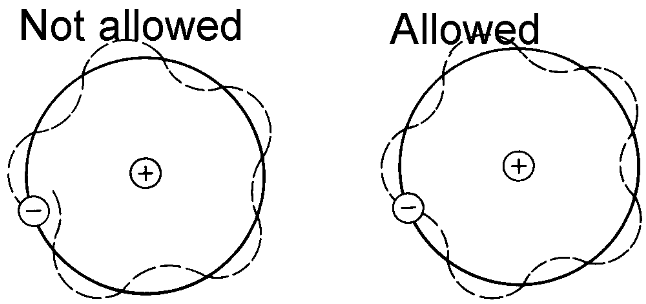
In (4) 'm' is in the denominator. For macroscopic bodies like planets, the value of m is very large. Hence λ becomes very small, so that it is neglected.

But, microscopic particles like electrons posses very low masses. Hence, the value of λ is very significant.

Further, for an electron moving around the nucleus in circular path, two different types of waves of different wave lengths are possible.

One is due to constructive interference (when $n\, \lambda = 2\pi r$) and the other is due to destructive interference ($n\lambda \neq 2\pi r$).

If the circumference of the electron orbit is an integral multiple of λ, the electron waves are said to be 'in-phase'. Otherwise, they are 'out of phase'.



If the electron wave is in ‘in – phase’, then $n\lambda = 2\pi r \Longrightarrow \lambda = 2\pi r/n$………(5)

From eq (4) & (5) we get, $h/mv = 2\pi r/n \Longrightarrow mvr = nh/2\pi$……..(6)

Eq (6) is nothing but the relation of Bohr’s quantization of angular momentum.

Thus,de Broglie’s theory and Bohr’s theory are in well agreement with each other, in the quantization of angular momentum.

Heisenberg uncertainty principle:

It is impossible to measure simultaneously the exact position and the momentum of a body as small as an electron. Mathematically represented as

$$\mathbf{\Delta x \cdot \Delta p \geq h/4\pi}$$

Where Δx = uncertainty of measurement of position

Δp = uncertainty of measurement of momentum

h = Planck's constant = 6.625×10^{-27} erg-sec

We know that momentum p = mv,

Therefore $\Delta p = \Delta mv$ and Heisenberg uncertainty principle mathematically can be written as

$$\mathbf{\Delta x \cdot \Delta mv \geq h/4\pi}$$

or

$$\mathbf{\Delta x \cdot \Delta v \geq h/4\pi m}$$

For an electron of mass m = 9.10×10^{-28} g, the product of uncertainty is

$$\begin{aligned}\mathbf{\Delta x \cdot \Delta v} &\geq \mathbf{h/4\pi m}\\ &\geq \mathbf{6.625 \times 10^{-27}/4\pi m}\\ &\geq \mathbf{6.625 \times 10^{-27}/4\,(3.14)\,9.10 \times 10^{-28}}\\ &\geq \mathbf{0.56\ erg\ sec/g}\end{aligned}$$

$\Delta x \cdot \Delta v$ = uncertainty in product

When $\Delta x = 0$, $\Delta v = \infty$ and $\Delta x = \infty$, $\Delta v = 0$.

In case of bigger particles, the value of uncertainty product is negligible. If the position is known accurately *i.e.*, Δx is very small, Δv becomes large and vice-versa. Thus, uncertainty principle is important only in the case of smaller moving particles like electrons.

Quantum Numbers:

In order to locate a particular electron in an atom, quantum numbers are required. These are

1) **Principl Quantum Number (n) :** it is given by Bohr.
   It represents the **name, size** and **energy of the shell** to which the electron belongs. The value of n is 1 to ∞. i.e., n = 1, 2, 3, 4, ………. ∞

n =	1	2	3	4	5	6
Shell =	K	L	M	N	O	P

   i) Higher the value of 'n', greater is the distance of the shell from nucleus.
   $r_1 < r_2 < r_3 < r_4 < r_5 <$…………
   ii) Higher the value of 'n', greater is the magnitude of energy.
   $E_1 < E_2 < E_3 < E_4 < E_5 <$…………
   Energy separations between two shells decreases on moving away from nucleus.
   $(E_2 - E_1) > (E_3 - E_2) > (E_4 – E_3) > (E_4 – E_3)$ ….
   iii) Maximum number of electrons in a shell = $2n^2$.
   iv) Angular momentum can be calculated by using principal quantum number

   $$mvr = nh/2\pi$$

2) **Azimuthal Quantum Number (l):** it is given by Sommerfeld. It is also called as angular quantum number, subsidiary quantum number or secondary quantum number.
   value of l is l = 0, 1, 2, 3, 4, ………. (n-1)
   it describes the spatial distribution of electron cloud and angular momentum. It gives the name of the subshell associated with the main shell.

l = 0	s-subshell
l = 1	p-subshell
l = 2	d-subshell
l = 3	f-subshell

   Orbital angular momentum of an electron is calculated by using $\mu_l = \sqrt{l(l+1)}\ h/2\pi$

   The magnitude of magnetic moment $\mu_L = \sqrt{l(l+1)}$ B.M.

   $$1 \text{ B.M.} = eh/4\pi mc = 9.273 \text{ X } 10^{-14} \text{ J}$$

   Maximum electrons present in a subshell = 2(2l+1)

s-subshell	2 electrons
p-subshell	6 electrons
g-subshell	10 electrons

3. Magnetic Quantum Number (m): it is given by Linde. It explains about **Zeeman effect**. It describes the orientation of electron cloud.

value of m is, m = -l, 0, +l i.e., total (2l+1) values.

l = 0, m = 0	s-subshell	l = 1, m = -1, 0, +1	p-subshell
l = 2, m= -2, -1, 0, 1, +2	d-subshell;	l = 3, m= -3, -2, -1, 0, +1, +2, +3	f-subshell

4. Spin Quantum Number (s): it is given by Gold Schmidt. It represents the direction of electron around its own axis.

For clockwise spin, s = +1/2 (↑)

For anticlockwise spin, s = -1/2 (↓)

Spin electron produces angular momentum is $\mu_s = \sqrt{s(s+1)}\ h/2\pi$

Spin magnetic moment $\mu_s = \sqrt{s(s+1)}\ eh/2\pi mc$

Each orbital accommodate two electrons with opposite spin or paired.

Pauli’s exclusion principle:

“No two electrons in an atom can have same values of all the four quantum numbers”

Ex: nitrogen (N) and its atomic number is 7.

Electronic configuration	$1s^2$	$2s^2$	$2p^3$		
			$2p_x^1$	$2p_y^1$	$2p_z^1$
n	1	2	2	2	2
l	0	0	1	1	1
m	0	0	-1	0	+1
s	+1/2 -1/2	+1/2 -1/2	+1/2 -1/2	+1/2 -1/2	+1/2 -1/2

Aufbau principle:

The subshell with minimum energy is filled up first and when this obtains maximum quota of electrons, then the next subshell of higher energy starts filling.

The sequence of various subshell is filled as 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s

The subshell with lowest (n+l) value is filled up first. When two or more subshells have same (n+l) values, the subshell with lowest value of n is filled up first.

Ex: [write Pottasium (K) electronic configuration here]

Hund’s rule of maximum multipilicity:

electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electrons with parallel spins.

Ex: [write C, N, O, F electronic configuration here]

Atomic number

- **Protons present in atom are called Atomic number. It is denoted by 'Z'. All atoms of an element have the same atomic number Z. In fact, elements are defined by the number of protons they possess.**
- **For hydrogen, Z = 1, because in hydrogen atom, only one proton is present in the nucleus.**
- **Similarly, for carbon, Z = 6. Therefore, the atomic number is defined as the total number of protons present in the nucleus of an atom.**

Electronic configuration

- **Distribution of electrons in to different shells, sub shells and orbitals of an atom is called electronic configuration.**
- **The electronic configuration of any orbital can be represented as : nl^X**
- **Where n: represents principle quantum number,**
  l: Orbital or sub shell,
  x: number of electrons present in the orbital..
- **For example: $4p^1$ means p sub shell of 4^{th} main shell contains one electron.**

Electronic configuration of some elements are given below,

Name	Atomic Number	Electron Configuration
Period 1		
Hydrogen	1	$1s^1$
Helium	2	$1s^2$
Period 2		
Lithium	3	$1s^2\ 2s^1$
Beryllium	4	$1s^2\ 2s^2$
Boron	5	$1s^2\ 2s^2 2p^1$
Carbon	6	$1s^2\ 2s^2 2p^2$
Nitrogen	7	$1s^2\ 2s^2 2p^3$
Oxygen	8	$1s^2\ 2s^2 2p^4$
Fluorine	9	$1s^2\ 2s^2 2p^5$
Neon	10	$1s^2\ 2s^2 2p^6$
Period 3		
Sodium	11	$1s^2\ 2s^2 2p^6 3s^1$

Magnesium	**12**	**$1s^2\ 2s^2 2p^6 3s^2$**
Aluminum	**13**	**$1s^2\ 2s^2 2p^6 3s^2 3p^1$**
Silicon	**14**	**$1s^2\ 2s^2 2p^6 3s^2 3p^2$**
Phosphorus	**15**	**$1s^2\ 2s^2 2p^6 3s^2 3p^3$**
Sulfur	**16**	**$1s^2\ 2s^2 2p^6 3s^2 3p^4$**
Chlorine	**17**	**$1s^2\ 2s^2 2p^6 3s^2 3p^5$**
Argon	**18**	**$1s^2\ 2s^2 2p^6 3s^2 3p^6$**
Period 4		
Potassium	**19**	**$1s^2\ 2s^2 2p^6 3s^2 3p^6 4s^1$**
Calcium	**20**	**$1s^2\ 2s^2 2p^6 3s^2 3p^6 4s^2$**

Unit-II

Periodic Classification of elements

Construction of long form of periodic table:

Modern periodic table: 'the physical and chemical properties of elements are the periodic functions of their atomic numbers'.

Long form of periodic table: In this table all the elements are arranged in the increasing order of atomic numbers. It is a graphical representation of Aufbau's principle.

Construction: The table is divided into 7 horizontal rows called periods and 18 vertical columns called groups. Also, the table is divided into 4 blocks.

Periods: periods represents principle quantum number of the outer shell. Each period starts with an alkali metal and ends with a noble gas element.

1) The 1^{st} period contains only 2 elements H and He. Hence it is called shortest period.
2) The 2^{nd} period contains 8 elements from Li to Ne. It is called short period.
3) The 3^{rd} period contains 8 elements from Na to Ar. It is also called short period.
4) The 4^{th} period contains 18 elements from K to Kr. It is called long period.
5) The 5^{th} period contains 18 elements from Rb to Xe. It is also called long period.
6) The 6^{th} period contains 32 elements from Cs to Rn. It is called the longest period.
7) The 7^{th} period is an incomplete period. It starts from Fr.
8) The 14 Lanthanides and 14 actinides are placed at the bottom of the table.
9) Each period starts with an alkali metal and ends with an inert gas element.
10) Most of the physical and chemical properties of elements change gradually in periods.

Groups:

1) All the 18 groups are numbered 1 to 18 according to IUPAC format. The previous format: IA (1), IIA (2), IIIB to VIIB (3 to 7), VIII (8, 9, 10), IB (11), IIB (12), IIIA to VIIA (13 to 17) and 0 gropup (18).
2) Zero group elements are placed at the extreme right side of the table. They are called noble gas or inert gas elements. They have stable octet configuration.
3) All the elements in a group have same valency. Hence, all the elements in a group show similar properties.

Blocks:

Based on the entry of the differentiating electron in to subshell of main shell, all the elements are divided into 4 blocks. They are s-block, p-block, d-block and f-block.

Essay on s, p, d and f block elements: Basing on the entry of differentiating electron into sub-shells of main shells, all the elements are classified into 4 blocks. They are s-block, p-block, d-block and f-block.

1. **s-block elements:**
   1) The elements in which differentiating electrons enter into ns-subshell are called s-block elements.
   2) Their general electronic configuration is ns^{1-2}.
   3) s-block elements are arranged in 2 groups. They are group 1(1A), group 2 (IIA).
   4) First group (1A) elements are called Alkali metals. Second group (IIA) elements are called Alkaline earth metals.
   5) s-block is placed on the left side of the periodic table.
2. **p-block elements:**
   1. The elements in which differentiating electrons enter into np-subshell are called p-block elements.
   2. Their general electronic configuration is $ns^2\ np^{1\ to\ 6}$.
   3. p-block elements are arranged in 6 groups. They are from group 13(IIIA) to group 18.
   4. p-block elements are starts with 13^{th} group and ends with 18^{th} group.
      i) 13^{th} group or IIIA group is called Boran family.
      ii) 14^{th} group or IVA group is called Carbon family.
      iii) 15^{th} group or VA group is called Nitrogen family.
      iv) 16^{th} group or VIA group is called Chalcogen family.
      v) 17^{th} group or VIIA group is called Halogen family.
      vi) 18^{th} group or 0 group is called Noble gas family.
   5. p-block is placed on the right side of the periodic table.
3. **d-block elements:**
   1) The elements in which differentiating electrons enter into (n-1)d-subshell are called d-block elements.
   2) Their general electronic configuration is $(n-1)d^{1\ to\ 10}\ ns^{1\ or\ 2}$.
   3) d-block elements are arranged in 10 groups. They are from group 3(IIIB) to group 12 (IIB).
   4) d-block elements are further classified into 4 transition series. They are 3d, 4d, 5d and 6d- series.
   5) d-block is placed at the middle of the periodic table.
4. **f-block elements:**

1) The elements in which differentiating electrons enter into (n-2)f-subshell are called f-block elements.
2) Their general electronic configuration is $(n-2)f^{1 \text{ to } 14}$ $(n-1)d^{0 \text{ or } 1}$ ns^{2}.
3) f-block elements are arranged in 14 columns.
4) f-block elements are further classified into 2 series. They are 4f- series known as Lanthanide series. 5f- series known as Actinide series.
5) f-block is placed separately at the bottom of the periodic table.

Periodic property: In the period table, some properties of elements change gradually with a change in their electronic configurations. Such properties are called periodic properties.

1) **Atomic radius:** The distance between centre of the atomic nucleus and the electronic cloud of the outer most energy level is called atomic radius.
   - **a)** In a group, from top to bottom the atomic radius increases. This is because of the differentiating electron enters into the next orbit. Hence atomic radius increases.
   - **b)** In a period, from left to right the atomic radius decreases. This is because of the differentiating electron remains in the same orbit. Hence atomic radius decreases.

2) **Electron affinity (EA):** The amount of energy released when an electron is added to neutral isolated gaseous atom is called electron affinity (EA) or electron gain enthalpy.
   - a) In a group, from top to bottom, electron affinity decreases. This is because in a group atomic size increases. Hence the effective nuclear attraction on outer electrons decreases. Therefore, electron affinity decreases from top to bottom in a group.
   - b) In a period, from left to right the electron affinity increases. This is because in a period atomic size decreases. Hence the effective nuclear attraction on outer electrons increases. Therefore, electron affinity increases from left to right in a period.

3) **Ionisation potential(IP):** The minimum energy required to remove an electron from the outer most valence shell from an isolated, neutral, gaseous atom is called ionization energy (IE) or ionization potential (IP) or first ionization enthalphy (IE_1).
   - a) In a group, from top to bottom, the ionization potential value decreases. This is because in a group atomic size increases. Hence the effective nuclear attraction on outer electrons decreases. Therefore, ionization potential value decreases from top to bottom in a group.
   - b) In a period, from left to right the ionization potential value increases. This is because in a period atomic size decreases. Hence the effective nuclear attraction on outer electrons increases. Therefore, ionization potential value increases from left to right in a period.

4) **Electronegativity(EN):** The tendency of an atom in a molecule to attract the shared pair of electrons towards itself is known as electronegativity(EN).
   a) In a group, from top to bottom, the electronegativity(EN) value decreases. This is because in a group atomic size increases. Hence the effective nuclear attraction on outer electrons decreases. Therefore, electronegativity(EN) value decreases from top to bottom in a group.
   b) In a period, from left to right the electronegativity(EN) value increases. This is because in a period atomic size decreases. Hence the effective nuclear attraction on outer electrons increases. Therefore, electronegativity(EN) value increases from left to right in a period.

Factors effecting on ionization enthalpy (IE):

i) **Atomic raidus: W**hen atomic raidus increases, the nuclear force of attraction on the valence electrons decreases. So, I.E value also decreases.

ii) **Nuclear charge: W**hen the nuclear charge increases, the nuclear force of attraction on the valence electrons increases. So, I.E value also increases.

iii) **Screening effect:** The electrons present in the 'inner orbits' decrease the nuclear attraction between nucleus and the outer electrons. This is known as screening effect. When the number of inner shells increases, the attraction of nucleus on the outer electrons decreases. So, the I.E value also decreases.

iv) **Penetrating effect:** In a given shell, the penetrating power of the valence electrons decreases in the order of s > p > d > f. So, 'ns' electrons are more tightly held by the nucleus. So, the the I.E value decreases in the same order.

v) **Completely filled or half-filled sub-shells:** Atoms with completely filled or half-filled sub-shell are more stable than the others. Such elements have slightly higher I.E values than expected.

Metallic-non metallic nature:

The metallic nature of an element depends upon the IE. The elements with low IE are metallic nature. The smaller the IE of an element, the greater will be its tendency to lose electrons and thus greater will be its metallic character.

Variation of metallic and non-metallic charcter:

IE decreases down the group and increases from left to right in a period.

The most reactive metals are on the left side of the periodic table. Whereas the least reactive metals are on middle of the periodic table.

In a group as we move from top to bottom metallic character increases and non-metallic character decreases.

Ex: VA group: N, P are non-metals; As, Sb are metalloids; Bi-metal.

In a period as we move from left to right non-metallic character increases and metallic character decreases.

Ex: 3rd group: Na, Mg and Al are metals; Si, P, S, Cl are non metals.

Reducing and oxidizing characters and nature of oxides:

Reducing agents	**Oxidizing agents**
Electropositive elements can lose electrons easily and hence, can act as good reducing agents.	Elements which gain electrons easily acts as good oxidizing agents.
Metals are good reducing agents. Down the group, this reducing character increases.	Non metals are good oxidizing agents. Down the group, decreases oxidizing nature.
From left to right in a period, decreases reducing character.	From left to right in a period, increases oxidising character.
Li is the strongest reducing agent due to high hydration energy of Li^+ ion.	F is the strongest oxidizing agent due to its highest E.N.

Variation of acidic and basic character:

Metals are characterized by basic character and non-metals are characterized by acidic character.

Basic character increases and acidic character decreases down the group.

Ex: N-N_2O_3 and P-P_2O_3 are acidic

As-As_2O_3 and Sb-Sb_2O_3 are amphoteric

Bi-Bi_2O_3 is basic

From left to right in a period, the basic character decreases and acidic character increases.

Ex: Na and Mg-Basic

Al-Amphoteric

Si, P, S, Cl-acidic

Valency and oxidation state:

Valence of an element is the number of H-atoms (or) double the number of O-atoms that can combine with one atom of that element.

Ex: CH_4: Valency of carbon = 1 X 4 = 4

SO_2: Valency of sulphur = 2 X 2 = 4

Exhibition of more than one valency by one element is known as variable valency.

Ex: $FeCl_2$-valency of Fe = 2

$FeCl_3$-valency of Fe = 3

Oxidation state:

The possible charge with which an atom appears in a compound is called oxidation state.

s-block elements, oxidation state is equal to its group number for alkali metals '+1', for alkaline earth metals '+2'.

p-block elements show multi valency.

III group elements can show '+3' oxidation state. Stable oxidation state of Tl is '+1', it is due to inert pair effect.

IVA group elements can show '+4' oxidation state. Stable oxidation state of Pb is '+2'and '+4', it is due to inert pair effect.

VA group elements can show '+5' oxidation state. +3 is more stable than +5 for Bi due to inert pair effect.

VIA group elements oxidation state is '-2'.

VIIA group elements oxidation state is '-1'.

The common oxidation state of d-block elements is '+2'. All the transition elements show variable valency. Highest oxidation state shown by the elements Ru and Os is '+8'.

The common oxidation state of f-block elements is '+3'. Maximum oxidation state of an element never excess its group number.

Diagonal relationship:

The first few elements of period 2 resemble those placed diagonally across them, in period. More generally the element of a group is different from the rest in that group and resembles with an element of the next group in the period.

Group	1	2	13	14	15	16	17
	IA	IIA	IIIA	IVA	VA	VIA	VIIA
Period 2	Li	Be	B	C	N	O	F
Period 3	Na	Mg	Al	Si	P	S	Cl

The relationship is called a diagonal relationship. The pairs of electrons Li, Mg, Be, Al are called diagonal pairs. This relationship however does not exist in the latter half of the period.

Unit-III

Chemical Bonding

Kossel – Lewis approach:

Kossel- Lewis approach gave a logical explanation to the formation two types of chemical bonds.

According to them, atoms combine to acquire nearest inert gas configuration by transferring or sharing of valence electrons.

Kossel's approach: A chemical bond can be formed by the transfer of valence electrons from one atom to another.

Kossel proposed that the highly electronegative elements like halogens, gain electrons and convert into anions. The highly electropositive alkali metals lose electrons and convert into positive ions.

During their conversion into ions, they get the noble gas octet configuration. Now the positive and negative ions unite together by electrostatic attraction between them. Thus, Kossel proposed the ionic bond formation.

Lewis approach: A chemical bond can be formed by the mutual sharing of valence electrons.

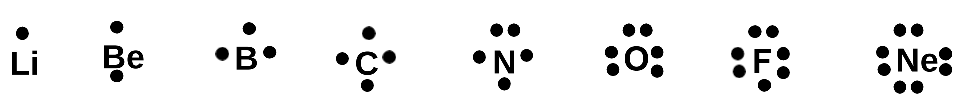
Lewis considered the atom as a positively charged 'Kernel' (Kernel consists of inner electrons and nucleus). Lewis assumed that the outer shell can accommodate a maximum of 8 electrons which occupy the eight corners of a cube surrounding the Kernel. He assumed that noble gases are stable due to this type of arrangement. The atoms which do not have this type of arrangementachieve the stable octet, by sharing of electrons to form chemical bonds.

Thus, Lewis approaches the covalent bond formation and Kossel proposed ionic bond formation.

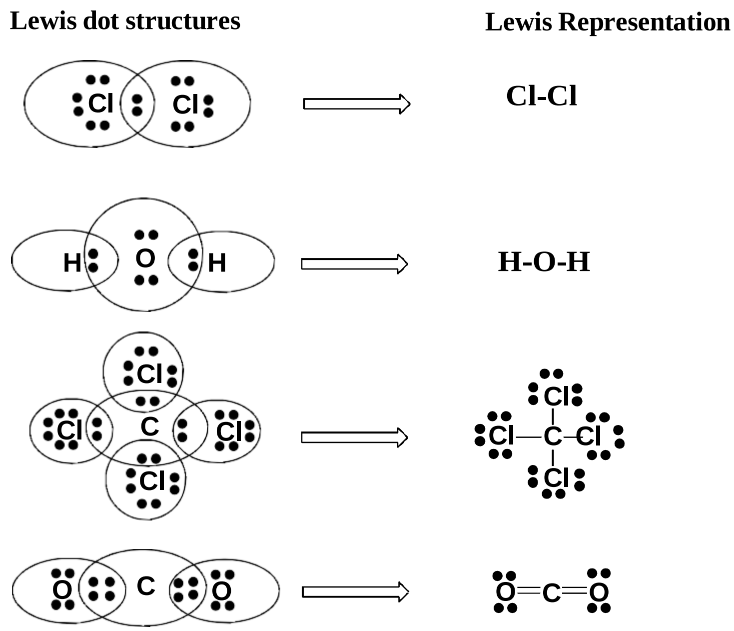
Lewis symbols:

Lewis introduced simple notations to represent valence electrons in an atom. These notations are called Lewis symbols.

Ex:



Lewis dot structures:



Draw the Lewis dot structures for below given molecules:

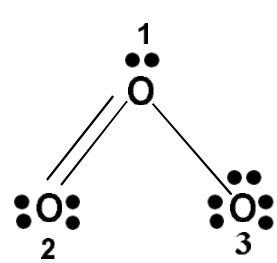
i) Ethylene (C_2H_4) ii) Ethyne (C_2H_2) iii) N_2 iv) O_2 v) H_2

vi) NH_3 vii) HNO_3 viii) CO_3^{2-} ix) O_3

Formal Charge:

$$\text{Formal charge on an atom in a Lewis structure} = \left[\text{total number of valence electrons in the free atom}\right] - \left[\text{total number of non-bonding (lone pair) electrons}\right] - \left(\frac{1}{2}\right)\left[\text{total number of bonding (shared) electrons}\right]$$

Ex: Ozone (O_3):



Formal charge on oxygen atom marked as 1 = $6 - 2 - \frac{1}{2}(6) = +1$

Formal charge on oxygen atom marked as 2 = $6 - 4 - \frac{1}{2}(4) = 0$

Formal charge on oxygen atom marked as 3 = $6 - 6 - \frac{1}{2}(2) = -1$

Octet rule:

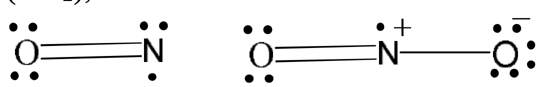
Atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as octet rule.

Significance:

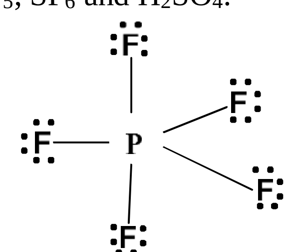
1) It is the basis of electronic theory of valency.
2) It explains the chemical inactivity of zero group elements.
3) It is useful for understanding the structure of most of organic compounds.

Limitations of the octet rule:

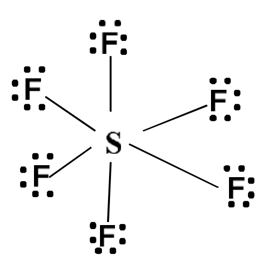
1) **The incomplete octet of the central atom:**
   In some compounds, the number of electrons surrounding the central is less than eight. This is especially the case with elements having less than four valence electrons.
   Ex: LiCl, BeH_2, BCl_3, BF_3.
   Li : Cl   H : Be : H
   Li, Be and B have 1, 2 and 3 valence electrons.
2) **Odd-electron molecules**
   In molecules with an odd number of electrons like nitric oxide (NO), nitrogen dioxide (NO_2), the octet rule is not satisfied for all the atoms.



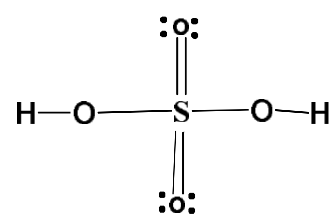
3) **Expanded octet:**
   In some compounds, the number of electrons surrounding the central is more than eight. This is termed as the expanded octet.
   Ex: PF_5; SF_6 and H_2SO_4.



10 electrons arround the P atom



12 electrons arround the S atom



12 electrons arround the S atom

Other drawbacks of octet theory:

- Octet rule is based upon the chemical inertness of noble gases. However, some noble gases (Ex: Xe and Kr) also combine with oxygen fluorine toform a number of compoundslike XeF_2, KrF_2, $XeOF_2$ etc.
- This theory does not account for the shape of molecules.

- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

VSEPR Theory (Valence Shell Electron Pair Repulsion Theory):

This theory was proposed to explain the deviations in the bond angles of some molecules.

Postulates

1) The shape of molecule is determined by the repulsion between all the electron pairs present in the valence shell of central atom.
2) A lone pair of electrons occupies more space around the central atom than bond pair. Because lone pair is attracted to only one nucleus, but the bond pair is attracted by two nuclei.
   Here repulsion between lone pairs is greater than bond pairs.
3) If the central atom contains only bond pairs then the shape of the molecule and bond angles will be according to the expected values.
4) If the central atom contains lone pairs, along with the bond pairs, then the shape of the molecule gets deviated from the expected values. This is due to repulsive forces between various electron pairs. The order of repulsion between various electron pairs:
   (lone pair – lone pair) > (lone pair – bond pair) > (bond pair – bond pair)
5) The order of repulsion between various bonds: Triple bond > Double bond > Single bond
   Ex: i) In $BeCl_2$ molecule there are two Be-Cl bonds.
   The two bond pairs are arranged in the opposite directions.
   The repulsive force between two bond pairs is negligible.
   Therefore, the bond angle is 180^o.
   ii) In H_2O molecule, 'O' has two lone pairs. Here the expected bond angle is 109^o28^1.
   But it is reduced to $104^o30^,$ due to the repulsion between two LP-LP and LP-BP.
   iii) In CH_4 molecule, all the four electron pairs are 'bond pairs' only. Hence the shape of the molecule is tetrahedral with bond angle 109^o28^1.

Valence Bond (VB) Theory:

This theory explains the shapes of covalent molecules as well as the directions of the bonds in them.

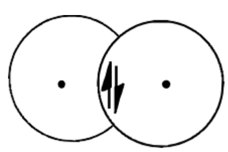
Postulates of VB Theory:

1) A covalent bond is formed by the overlapping of half-filled atomic orbital of one atom with half-filled atomic orbital of another atom.
2) The electrons involved in overlapping must have opposite spin.

3) Except the bond pair of electrons, the remaining electrons do not loose their identity. Such electrons are called non-bonding electrons or lone-pair electrons.
4) Greater the extent of overlap, greater is the strength of covalent bond.
5) The direction of covalent bond lies in the direction of maximum overlapping side.
6) All atomic orbitals, except s-orbital, are directional. So the bonds formed due to their overlap are also directional. This determines the shape of the molecule.
7) A covalent bond formed by the axial overlap of atomic orbitals is called a sigma bond. Thus, inter nuclear axial (head-on) overlappings of s-s, s-p, p-p orbitals leads to the formation of σ bonds.
8) A covalent bond formed by the lateral or sidewise overlap of atomic orbitals called a π bond.
9) A sigma bond is always stronger than a π bond. This is because, during the formation of a sigma bond, the orbitals overlap along the inter nuclear axis hence the standard pair of electrons is concentrated just in between the nuclei. Where as in π bond formation the orbitals overlap laterally. The electron cloud is present, above and below the inter nuclear axis. Hence a sigma bond is always stronger than a π bond.
10) Formation of a π bond is possible only after the formation of a σ bond.
11) In the case of a double bond, there will be one σ bond and one π bond.
    In the case of a triple bond, there will be one σ bond and two π bonds.

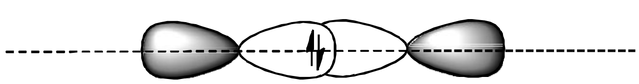
Examples:

1) **Formation of H_2 molecule:** Each hydrogen atom has one electron in 1s orbital. The 1s orbitals of 2 hydrogen atoms overlap axially to form a sigma bond between two H atoms.



H——H

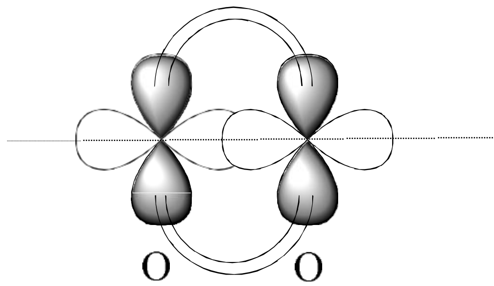
2) **Formation of F_2 molecule:** fluorine has one half filled $2P_z$ orbital. The $2P_z$ orbitals of two fluorine atoms overlap axially to form a sigma bond between two F atoms.



F——F

3) **Formation of O_2 molecule:**
The electronic configuration of oxygen is $1s^2\ 2s^2\ 2P_x^2\ 2P_y^1\ 2\ P_z^1$.
Oxygen has two half filled p orbitals. The $2P_y$ orbital of one atom overlap axially with $2P_y$ orbital of another O atom to form a sigma bond. The $2P_z$ orbitals of two oxygen

atoms overlap laterally to form a π bond. Thus a double bond with one strong σ bond and one weak π bond, is formed.



$O=O$

Hybridisation: The intermixing of atomic orbitals to form new hybrid orbitals is known as hybridization. The number of hybrid orbitals formed is equal to number of atomic orbitals mixed. There are different types of hybridizations involving s, p and d orbitals. They are sp, sp^2, sp^3, sp^3d; sp^3d^2 hybridisations.

1) **sp hybridization:** The inter mixing of one s-orbital and one p-orbital of the outer most shell of an atom is called sp hybridisation.
   In this process, we get two sp hybrid orbitals. The bond angle 180° and its shape is linear. Ex: $BeCl_2$, CO_2, C_2H_2.
   Formation of $BeCl_2$:
   i) In $BeCl_2$, the central atom is Be.
   ii) The electronic configuration of Be in the ground state is $1s^2\ 2s^2$.
   iii) The electronic configuration of Be in the excited state is $1s^2\ 2s^1\ 2p_x^1\ 2p_y^0\ 2p_z^0$.
   iv) In the excited state, the central Be atom undergoes sp hybridisation and forms two sp hybrid orbitals.
   v) The two sp-orbitals of Be overlap with p-orbitals of two Cl atoms and they form two σ bonds.
   vi) The bond angle is 180° and shape of the $BeCl_2$ is Linear.

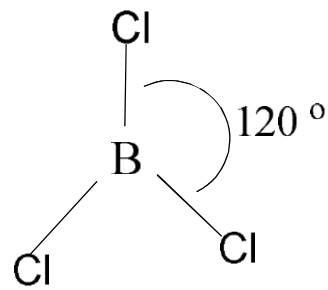
   Cl—Be—Cl

2) **Sp^2 hybridisation:** The inter mixing of one s-orbital and two p-orbitals of the outer most shell of an atom is called sp^2 hybridisation.
   In this process, we get three sp^2 hybrid orbitals. The bond angle is 120° and shape is Trigonal planar. Ex: BCl_3, BF_3, C_2H_4.
   Formation of BCl_3:
   i) In BCl3, the central atom is B.
   ii) The electronic configuration (E.C) of B in the ground state $1s^2\ 2s^2\ 2p^1$.
   iii) The E.C of B in the excited state is $1s^2\ 2s^1\ 2p^1\ 2p_y^1 2p_z^0$.

iv) In the excited state, the central B atom undergoes sp^2 hybridisation and forms three sp^2 hybrid orbitals, each having single electron.

v) The three sp^2 orbitals of B overlap with half filled p_z orbitals of three Cl atoms in a head–on position and they form three σ bonds.

vi) The bond angle is 120° and shape of the BCl_3 molecule is trigonal planar.



3) **Sp^3 hybridisation:** The inter mixing of one s-orbital and three p-orbitals of the outer most shell of an atom is called sp^3 hybridisation.

Here, we get four sp^3 hybrid orbitals. The bond angle is $109\ 28^1$ and shape is Tetrahedral.

Ex: CH_4, H_2O.

Formation of CH_4:

i) In CH_4, the central atom is Carbon (C).

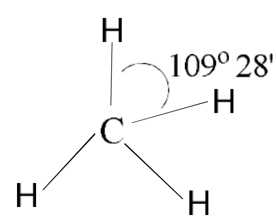
ii) The electronic configuration of C in the ground state is $1s^2\ 2s^2\ 2p^2$.

iii) The electronic configuration of C in the excited state is $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$.

iv) In the excited state, the central C atom undergoes sp^3 hybridisation and forms four sp^3 hybrid orbitals, each having single electron.

v) The four sp^3 orbitals of C overlap with half filled s-orbitals of four H atoms in a head-on position and they form four σ bonds.

vi) The bond angle is $109^{o}\ 28^1$ and shape of the CH_4 molecule is Tetrahedral.



4) **Sp^3d hybridisation:** The inter mixing of one s-orbital, three p-orbitals and one d-orbital of the outer most shell of an atom is called sp^3d hybridisation.

Here, we get five sp^3d hybrid orbitals.

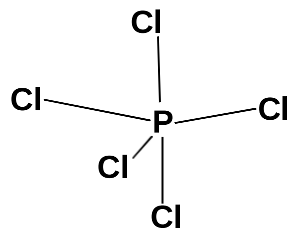
Ex: **PCl_5**. shape is Trigonal bipyramidal.

Formation of PCl_5:

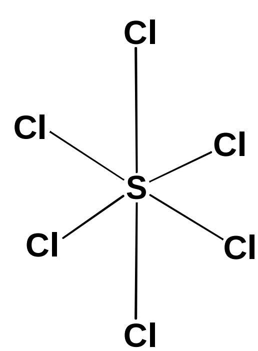
i) In PCl_5, the central atom is phosphorous (P).

ii) The electronic configuration of P in the ground state is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$.

iii) The electronic configuration of P in the excited state is $1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^1$.
iv) In the excited state, the central P atom undergoes sp^3d hybridisation and forms five sp^3d hybrid orbitals, each having single electron.
v) The five sp^3d orbitals of P overlap with half filled s-orbitals of five Cl atoms and they form five σ bonds.
vi) The shape of the PCl_5 molecule is Trigonal bipyramidal.



5) **Sp^3d^2 hybridisation:** The inter mixing of one s-orbital, three p-orbitals and two d-orbital of the outer most shell of an atom is called sp^3d^2 hybridisation.
Here, we get six sp^3d^2 hybrid orbitals.
Ex: **SF_6**. Shape is Octahedral.
Formation of SF_6:
i) In SF_6, the central atom is sulphur (S).
ii) The electronic configuration of S in the ground state is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$.
iii) The electronic configuration of S in the excited state is $1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^2$.
iv) In the excited state, the central S atom undergoes sp^3d^2 hybridisation and forms six sp^3d^2 hybrid orbitals, each having single electron.
v) The six sp^3d orbitals of S overlap with half filled s-orbitals of six F atoms and they form six σ bonds.
vi) The shape of the SF_6 molecule is Octahedral.



Molecular Orbital (MO) Theory:

MO Theory was proposed by Hund and Mulliken. It is explained by LCAO (Liner Combination of Atomic Orbitals) method.

Salient Features of MO Theory:

1) The molecular orbitals are formed when the atomic orbitals of nearly equal energies combined linearly.
2) Only such atomic orbitals which are of symmetry with respect to the inter nuclear axis combine to form molecular orbitals.
3) The total number of molecular orbitals formed is equal to the total number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is called bonding molecular orbital while the other is called anti-bonding molecular orbital.
4) Molecular orbital having lesser energy than atomic orbitals are called bonding molecular orbitals and they are represented by σ and π.
5) Molecular orbitals having higher energy than atomic orbitals are called anti-bonding molecular orbitals and they are represented by σ^* and π^*.
6) The order of energies of bonding, anti-bonding and non-bonding orbitals:
   Bonding orbitals < Non-bonding orbitals < Anti-bonding orbitals.
7) A molecular orbital is polycentric whereas an atomic orbital is monocentric.
8) The shapes of the molecular orbitals depend on the shapes of atomic orbitals.
9) Filling up of electrons in the molecular orbitals is done according to Hund's rule, Paulis exclusion principle and Aufbau principle.
10) MO Theory successfully explained the magnetic nature of molecules.
11) MO Theory is useful to calculate the bond order (number of bonds between atoms) of molecules.

Hydrogen bond:

The week electrostatic force of attraction between hydrogen atom of one molecule and most electronegative atom of another molecule (or) same molecule is called hydrogen bond.

Condition for formation of hydrogen bond:

1) The size of electronegative atom should be small.

2) The electronegativity of the atom to which hydrogen is attached should be high.

Strength of hydrogen bond:

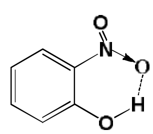
The strength of hydrogen bond is between 5-10K Cal/mol. It is, thus weaker than a covalent bond and stronger than Vander waals force of attraction.

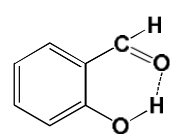
Types of Hydrogen bonds:

1) Inter molecular Hydrogen bond
2) Intra molecular Hydrogen bond

1) **Inter molecular Hydrogen bond :**
   Hydrogen bond formed between two different molecules is called inter molecular hydrogen bond.
   Ex: The bonds presents in NH_3, H_2O, HF.

   H-F····H-F····H-F····H-F
2) **Intra molecular Hydrogen bond:**
   A hydrogen bond formed within the same molecule is called intra molecular hydrogen bond.
   Ex: the bonds present in Orthoitrophenol, Orthohydroxy benzaldehyde.





Questions

1) Define hybridization? Explain the types of hybridisation involving s and p orbitals with one example each.
2) Give an account VSEPR theory and its applications.
3) Give an account VB theory and its applications.
4) Explain the structure and hybridization of a) $BeCl_2$; b) BCl_3 ; c) BF_3 ; d) Methane e) PCl_5 ; f) SF_6.
5) Explain the hybridization of a) Ethane; b) Ethene and c) Ethyne.
6) Write the salient features of MO Theory.
7) Give the MO Energy diagram of a) H_2; b) C_2; c) N_2; d) O_2; e) O_2^+; f) O_2^-; g) O_2^{2-} molecules. Calculate the respective bond order. Write the magnetic nature of N_2 and O_2 molecules.
8) What is Hydrogen bond? Explain different types of hydrogen bonds with examples.
9) Write the differences between σ and π bonds

Gaseous State

Ideal gas equation:

The ideal gas equation is derived from Boyles law, Charles law, Avogadro's law.

Let V = volume, P = Pressure, T = Absolute temperature and n = no of moles of an ideal gas.

1) **Boyle's law (Pressure – Volume relationship)**: "At constant temperature, the volume of a given mass of gas is inversely proportional to its pressure".

Thus, $V \propto 1/p$ (at constant T, n) ----------------- (1)

$\Longrightarrow$ $V = K (1/p)$

$\Longrightarrow$ $pV = K$ = constant

$\Longrightarrow$ $p_1V_1 = P_2V_2 = K$ = constant

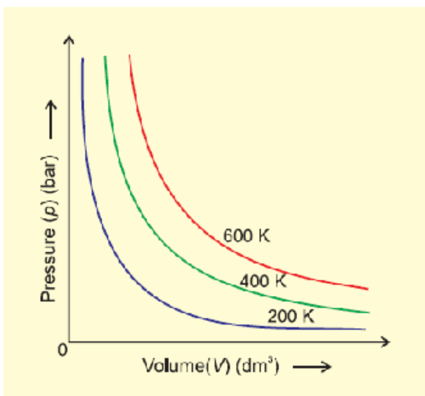


Fig. 5.5(a) *Graph of pressure, p vs. Volume, V of a gas at different temperatures.*

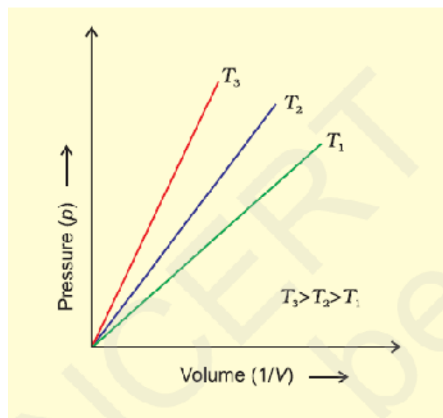


Fig. 5.5 (b) *Graph of pressure of a gas, p vs.* $\frac{1}{V}$

2) **Charles law (Volume - Temperature relationship):** "At constant pressure, the volume of a given mass of gas is directly proportional to its absolute temperature".

Thus, $V \propto T$ (at constant n, p) -----------------(2)

$V = K T$

$\Longrightarrow$ $V/T = K$ = constant

$\Longrightarrow$ $V_1/T_1 = V_2/T_2 = K$ = constant

$\Longrightarrow$ $V_1/V_2 = T_2/T_1 = K$ = constant

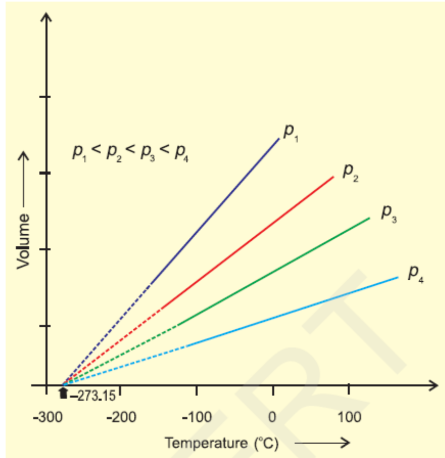


Fig. 5.6 *Volume vs Temperature (°C) graph*

3) **Avogadro's law (Volume – Amount relationship): "**At constant temperature and pressure, the volume of a gas is directly proportional to the number of moles**".**

Thus, V α n (at constant p, T) -----------------(3)

V = K n

We know that, n = m/M (since, m = mass of gass and M = molecular weight of gas)

$\Rightarrow$ V = K m/M = constant

$\Rightarrow$ M = K m/V = K = constant

$\Rightarrow$ M = K d

Combining the equations (1), (2) and (3),

$\Rightarrow$ We get, V α 1/p .T. n

$\Rightarrow$ V = R. 1/p .T. n

$\Rightarrow$ pV = nRT

The above equation is called **'ideal gas equation' or 'equation of state'**.

In the ideal gas equation, R is called gas constant and it is independent of the amount of gas.

Value of gas constant R: the value of gas constant 'R' is same for all gases. So it is called as 'Universal Gas constant'.

The value of gas constant depends on units of pressure and volume.

Ex: R = 0.0821 lit. atm. mole^{-1}.K^{-1}.

= 8.314 X 10^{7} ergs. mol^{-1} K^{-1}

= 8.314 J. mol^{-1} K^{-1}

= 1.987 cal mol^{-1} K^{-1}

Gay Lussac's law (Pressure – Temperature relationship): "At constant volume, the pressure of a mass of gas is directly proportional to its absolute temperature**".**

Thus, p α T (at constant V, n) -----------------(3)

p = K T

p/T = K = Constant

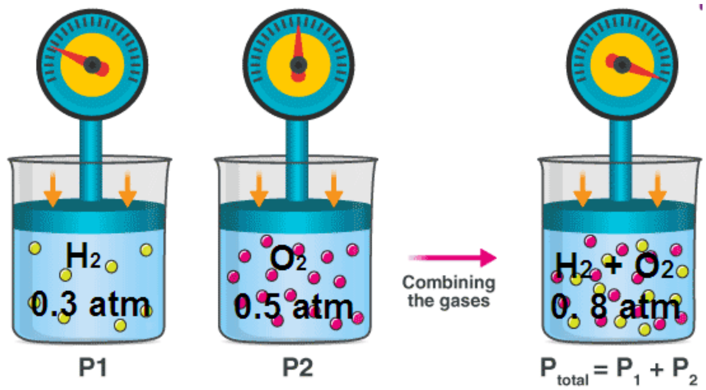
Dalton's law of partial pressure:

"At constant temperature, the total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of all the components gases".

Therefore, total pressure, $P_{total} = p_1 + p_2 + p_3 + \dots\dots\dots + p_n$.

Explanation:

Let 3 vessels of equal volumes are taken and attached with 'manometers'. Let n_1 moles of hydrogen and n_2 moles of oxygen are taken in the first and second vessels respectively. Let the pressure exerted by hydrogen and oxygen be 0.3 atm and 0.5 atm. respectively. These two gases are send into third vessel of same volume. Then the total pressure of the gaseous mixture is found to be 0.8 atm. That means the total pressure exerted by the gaseous mixture is equal to the sum of individual pressures of the gases.



Relation between partial pressure and mole fraction:

The number of moles of the three gases are n_1, n_2 and n_3.

From the Ideal gas equation, we have

Partial pressure of the first gas $p_1 = n_1RT/V$--------------(1)

Partial pressure of the second gas $p_2 = n_2RT/V$----------(2)

Partial pressure of the third gas $p_3 = n_3RT/V$-------------(3)

From the Dalton's law of Partial pressures, total pressure of the mixture is

$P_{total} = p_1+p_2+p_3 = n_1RT/V + n_2RT/V + n_3RT/V$

$= (n_1+n_2+n_3)\ RT/V = n\ RT/V$--------(4)

Here n = total number of moles of mixture

From (1) and (4) we get $p_1/p = n_1RT/V/nRT/V = n_1/n = X_1$

Here X_1 = mole fraction of first gas.

Therefore, $p_1 = X_1\ p$

Similarly we get $p_2 = X_2\ p$ and $p_3 = X_3p$

Conclusion: partial pressure of a gas in the gaseous mixture is equal to the product of its mole fraction and total pressure of mixture.

Postulates of kinetic molecular theory of gases:

1) Every gas contains large number of tiny particles called molecules.
2) The gas molecules move randomly in all directions with high velocities.
3) There will be no attractive or repulsive forces among gas molecules.
4) There will be no effect of gravitational force on the movement of gas molecules.
5) The total volume of gas molecules is negligible when compared to the entire volume of the container.
6) Pressure of gas is due to collisions of the gas molecules on the walls of the container.
7) All collisions are perfectly elastic.
   On the basis of above assumptions, the kinetic gas equation is $PV = 1/3\ mnC^2$
8) The average kinetic energy of a gas is directly proportional to the absolute temperature. Thus, KE α T.

   From this equation we deduce various gas laws mathematically,
   The average kinetic energy of a gas molecule is given by $KE = ½\ mC^2$
   Where m = mass of the molecule and C= velocity
   The quantity C^2 is called mean square velocity; it is the average of the squares of the speeds of all the molecules:

   $C^2 = C_1^2 + C_2^2 + C_3^2 + C_4^2 + \ldots\ldots\ldots + C_n^2/n$
   Where, n = number of molecules and C_1, C_2, C_3………… are velocities of first, second and third…………gas molecules
   From above,

$$KE\ \alpha\ T$$
$$½\ mC^2\ \alpha\ T$$
$$½\ mC^2 = kT$$

Where k = proportionality constant and T = Absolute temperature

1) Boyle's law:
   According kinetic gas equation,
   $PV = 1/3\ mnC^2$
   $PV = 2/2(1/3\ mnC^2)$
   The kinetic energy of 'n' molecules of the gas = $½\ mnC^2$
   We know that, $½\ mnC^2 = kT$
   Therefore, $PV = 2/3\ kT$
   At constant temperature (T), PV = Constant, this is Boyle's law.
2) Charles law:
   $PV = 2/3\ kT$
   $V = 2/3\ kT/P$
   At constant pressure, V = constant X T or V α T, (because n, P are constants). This is Charles law.

Deviations from ideal behavior:

It is identified that real gases deviation from gas laws are more at high pressures and low temperatures.

van der Waals suggested that these deviations are due to the following two wrong assumptions in the kinetic theory of gases.

i) Actual volume of the gas molecules is negligible as compared to the total volume of the container.

ii) Intermolecular attractions are absent in gases.

van der Waals pointed out that in the case of real gases, molecules do have a volume and also exert intermolecular attractions particularly when the pressure is high and temperature is low.

He made two corrections. a) Volume correction; b) Pressure correction

a) Volume correction:

van der Waals assumed that molecules of a real gases are rigid spherical particles which possess a definite volume. Thus, the volume of a real gas, i.e., volume available for compression or movement is, therefore, actual volume minus the volume occupied by gas molecules. If b is the effective volume of the molecules per mol of the gas, the ideal volume for the gas equation is (V-b) and not V, i.e.,

Corrected volume 'V_i' = V- b for one mole of the gas

For n mole of the gas, 'V_i' = V- nb.

b is termed the excluded volume which is constant and characteristic for each gas.

b) Pressure correction:

A molecule in the interior of the gas is attracted by other molecules on all sides. These forces, thus, are not effective, as equal and opposite forces cancel each other. However, a gas molecule which is just going to collide the wall of the container experiences an inward pull due to unbalanced attractive forces. Therefore, it collides the wall with less momentum and the observed pressure will be less than the ideal pressure.

$P_{ideal} = P_{obs} + P^1$

Where, p^1 is the pressure correction.

Pressure correction depends upon two factors.

i) The attractive force exerted on a single molecule about to collide the wall is proportional to the number of molecules per unit volume in the bulk of the gas.

ii) The number of molecules striking the wall which is also proportional to the number of molecules per unit volume of the gas.

The above two factors are proportional to the density of the gas. Therefore, the attractive force is proportional to the square of the density of the gas.

P^1 α total attractive force

α d^2

α $1/V^2$

$P^1 = a/V^2$

Where a is the constant depending upon the nature of the gas and V is the volume of the one mole of the gas.

Hence, corrected pressure, $P_{ideal} = P_{obs} + a/V^2$

Therefore, the gas equation PV = RT can be written as

$$\left[P + \frac{a}{V^2}\right](V - b) = RT$$

This equation is known as van der Walls equation for one mole of gas.

Similarly, for van der Walls gas equation for n moles of gas is,

$$\left[\mathbf{P} + \frac{\mathbf{n^2 a}}{\mathbf{V^2}}\right](\mathbf{V - nb}) = \mathbf{nRT}$$

The constants ‘a’ and ‘b’ are called van der Walls constants and they are characteristic of each gas.

Types of Molecular velocities:

R.M.S. velocity (C):

It is the square root of mean of squares of velocities of the molecules present in the gas. It is represented by 'C'. RMS velocity of gas molecules is the square root value of the ratio of the sum of the squares of velocities of all the molecules to the total number of molecules.

$$C = \sqrt{\frac{C_1^2 + C_2^2 + C_3^2 + \dots\dots\dots\dots + C_n^2}{n}}$$

$$C_{RMS} = \sqrt{\frac{3\,RT}{M}}$$

In the expression, if the value of R used is 8.314×10^7 erg mol^{-1} K^{-1}, the units of 'C' will be in cm s^{-1} and if the value of R used is 8.314 joule mol^{-1} K^{-1}, the units of 'C' will be in ms^{-1} and M is in kg mol

$$\boxed{\begin{aligned} C_{RMS} &= \sqrt{\frac{3\,RT}{M}} \\ &= \sqrt{\frac{3\,PV}{M}} = \sqrt{\frac{3\,P}{d}} \end{aligned}}$$

Since, $\frac{V}{M} = \frac{\text{Gram molar volume}}{\text{Gram molecular mass}} = \frac{1}{(\text{density})}$

$$\therefore \quad C_{RMS} = \sqrt{\frac{3\,p}{d}}$$

Average velocity($\bar{C}$):

Average velocity of gas molecules is the ratio of the sum of the velocities of gas molecules to the total number of molecules. It is the average of the velocities of the molecules in a gas.

$$\bar{C} = [\frac{C_1 + C_2 + C_3 + \ldots + C_n}{n}]$$

Where $C_1, C_2, C_3 \ldots\ldots C_n$ are the individual velocities of molecules. The average velocity $(\bar{C})$ is calculated as follows.

$$\bar{C} = \sqrt{\frac{8\,RT}{\pi M}} = \sqrt{\frac{8\,PV}{\pi M}} = \sqrt{\frac{8\,P}{\pi d}}$$

Also average velocity $\bar{C} = 0.9213 \times$ RMS velocity.

Most probable velocity (C_P):

It is the velocity possessed by the maximum number of molecules present in the gas. It is represented by 'C_p" and calculated as follows

$$C_p = \sqrt{\frac{2\,RT}{M}} = \sqrt{\frac{2\,PV}{M}} = \sqrt{\frac{2\,P}{d}}$$

Most probable velocity $C_p = 0.923 \times$ RMS velocity.

Ratio of the molecular velocities:

The ratio of the three types of molecular velocities can be calculated from the relation

$$C_p : \bar{C} : C = \sqrt{\frac{2\ RT}{M}} : \sqrt{\frac{8\ RT}{\pi M}} : \sqrt{\frac{3\ RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$= \sqrt{2} : \sqrt{\frac{8 \times 7}{22}} : \sqrt{3} = 1.000 : 1.128 : 1.224$$

$$\boxed{C_p : \bar{C} : C_{RMS} = 1 : 1.128 : 1.224}$$

Stoichiometry

Concept of Equivalent Weight

Stoichiometry is the branch of chemistry and chemical engineering that deals with the quantities of substances that enter into, and are produced by, chemical reactions. Stoichiometry provides the quantitative relationship between reactants and products in a chemical reaction. Stoichiometry calculations can predict how elements and components diluted in a standard solution react in experimental conditions. Stoichiometry is founded on the law of conservation of mass: the mass of the reactants equals the mass of the products. For example, when methane unites with oxygen in complete combustion, 16g of methane require 64g of oxygen. At the same time 44g of carbon dioxide and 36g of water are formed as reaction products.Every chemical reaction has its characteristic proportions. The method of obtaining these from chemical formulas, equations, atomic weights and molecular weights, and determination of what and how much is used and produced in chemical processes, is the major concern of **Stoichiometry.** Stoichiometry is simply the math behind chemistry. Given enough information, one can use stoichiometry to calculate masses, moles, and percents within a chemical equation

We discussed atomic masses and molecular masses and mole concept in our earlier classes. Now let us know about the concept of equivalent weight.

Concept of equivalent weight:

The concept of equivalent weight is more important. The accurate atomic weight of an element is ascertained from the equivalent weight. Calculations involving chemical transformation are made on the basis of equivalent weights. The term equivalent weight is a misnomer. It is neither a mass, nor a weight but a mere number.

The numerical magnitude of the equivalent weight of a substance is not necessarily being a fixed value. It may be a variable factor.

Example:

The equivalent weight of $KMnO_4$ in acid medium is equal to $\left[\frac{Mol.Wt}{5}\right]$. But in neutral or alkaline medium, the equivalent weight may be $\left[\frac{\text{Mol.Wt}}{3}\right]$. It also depends on whether one needs to calculate the equivalent weight of an element or an acid or base or an oxidant or a reductant. The definition, in each case, of an equivalent weight is different as can be seen from the following discussions.

In general the equivalent weight of an element is defined as “a number which denotes the number of parts by weight of the element required to combine with or displace 8 parts by weight of oxygen, 1.008 parts by weight of hydrogen or 35.5 parts by weight of chlorine.

There is a simple relationship between the atomic weight of an element and its equivalent weight.It can be understood from the following discussion. Suppose one atom of an element 'A' combines with 'n' atoms of hydrogen. The hydride formed has the formula AH_n. We know the atomic weight of hydrogen is 1.008. Let the atomic weight of the element 'A' be x. According to the above formula, an atom of 'A', weighing x, combines with nx1.008 parts by weight of hydrogen to form the hydride. Then by definition, the equivalent weight of 'A' is (x/n).

Where x = mass of an atom of A.

$$\frac{\text{Atomic weight of A}}{\text{Equivalent weigh of A}} = \frac{x}{(x/n)} = n.$$

This is the valency of the element 'A'. Similarly it can be deduced for any element.

$$\frac{\text{Atomic weight of the element}}{\text{Equivalent of the element}} = \text{Valency of the element.}$$

The valency of an element may vary, though the atomic weight of the element is constant. Hence, the same element may possess more than one equivalent weight.

Example:

Equivalent weight of iron in ferrous compounds $= \frac{\text{At.wt of Fe}}{\text{valency}} = \frac{55.84}{2} = 27.92$

Whereas its equivalent weight in ferric compounds is $\frac{55.84}{3} = 18.613$

Radicals too possess equivalent weights. A radical behaves like an element. Hence, the equivalent weight of a radical is equal to its molecular weight divided by its valency.

Example:

Sulphate radical (SO_4^{2-})has an equivalent weight $= \frac{\text{mass of the radical}}{\text{valency}} = \frac{96}{2} = 48$

The equivalent weight of an element or radical expressed in grams is called gram equivalent weight. Thus gram equivalent weight of oxygen is 8 g. The gram equivalent weight of carbonate radical is$\frac{60}{2}$ g = 30 g.

Calculation of equivalent weights of substances:

The equivalent weights can be calculated not only for elements but for compounds also. The compounds may be considered as acids, bases, salts, oxidants or reductants for the present calculations. Let us now see how the equivalent weights of these substances are calculated from their molecular weights.

1. Equivalent weights of acids:

"The number of hydrogen (H) atoms, in a molecule of the acid, which can be displaced by metal ions is known as basicity of the acid". If displacement of a hydrogen atom takes place, it is equal to displacement of 1.008 parts by weight of hydrogen. Then the number of hydrogen atoms that get displaced from a molecular weight of acids is equal to the number of equivalents per molecular weight of the acid. Then one can say

$$\text{Equivalent weight of an acid} = \frac{\text{Mol. Wt. or Formula Wt of acid}}{\text{Basicity of the acid}}$$

The equivalent weights of some common acids are presented in the following table.

S.No	Name of the acid	Mol. Formula of acid	No. of displaceable hydrogens 'n'	Equivalent weight calculated = [Mol.Wt/n]	Equivalent weight
1	Hydrochloric acid	HCl	1	$\left[\frac{\text{Mol. Wt. of HCl}}{1}\right]$	$\left[\frac{35.5 + 1.008}{1}\right] = 36.58$
2	Nitric acid	HNO_3	1	$\left[\frac{\text{Mol. Wt. of } HNO_3}{1}\right]$	$\left[\frac{1.008 + 14 + 48.0}{1}\right] = 63.008$
3	Sulphuric acid	H_2SO_4	2	$\left[\frac{\text{Mol. Wt. of } H_2SO_4}{2}\right]$	$\left[\frac{2.016 + 32 + 64}{2}\right] = \left[\frac{98.016}{2}\right] = 49.008$
4	Phosphoric acid	H_3PO_4	3	$\left[\frac{\text{Mol. Wt. of } H_3PO_4}{3}\right]$	$\left[\frac{3 + 30 + 64}{3}\right] = \left[\frac{97.0}{3}\right] = 32.33$
5	Phosphorous acid	H_3PO_3	2	$\left[\frac{\text{Mol. Wt. of } H_3PO_3}{2}\right]$	$\left[\frac{3 + 30 + 48}{2}\right] = \left[\frac{81.0}{2}\right] = 40.50$

Fig. Some common acids – their equivalent weights

Even though there are three hydrogen atoms in H_3PO_3. Only two of them can be displaced by metal ions. Hence, the basicity of H_3PO_3 is 2.

2. Equivalent weights of bases:

In chemistry generally one sees Arrhenius acids.And frequently bases of this type contain hydroxyl groups.

Example: NaOH, KOH, $Ba(OH)_2$ etc.

"The number of hydroxyl groups present in a molecule of the Arrhenius base" is known as its acidity of the base. Each OH group unites with one equivalent weight of hydrogen (i.e. one hydrogenion) that means the weight of one OH group is the same as its equivalent weight. From this we know that the number of parts by weight of a base containing the weight of one OH group is equivalent weight of the base. If there are 'n' OH groups in one molecule of a base, then the equivalent weight of the base can be written as follows;

$$\text{Equivalent weight of a base} = \frac{\text{Mol. Wt. or Formula Wt. of a base}}{\text{'acidity' or 'n'}}$$

In the table given below, the equivalent weights of some common bases are calculated. The equivalent weights of other bases can be also calculated in the same way.

S.No	Name of the base	Mol. Formula of base	No. of displaceable base 'n'	Equivalent weight calculated = [Mol.Wt of base/n]	Equivalent weight
1	Sodium hydroxide	NaOH	1	$\left[\frac{\text{Mol. Wt. of NaOH}}{1}\right]$	$\left[\frac{23+16+1}{1}\right] = 40.0$
2	Potassium hydroxide	KOH	1	$\left[\frac{\text{Mol. Wt. of KOH}}{1}\right]$	$\left[\frac{39+16+1}{1}\right] = 56.0$
3	Calcium hydroxide	$Ca(OH)_2$	2	$\left[\frac{\text{Mol. Wt. of } Ca(OH)_2}{2}\right]$	$\left[\frac{40+2\,(16+1)}{2}\right] = \left[\frac{74}{2}\right] = 37$
4	Barium hydroxide	$Ba(OH)_2$	2	$\left[\frac{\text{Mol. Wt. of } Ba(OH)_2}{2}\right]$	$\left[\frac{137+\ 2\,(16+1)}{2}\right] = \left[\frac{171}{2}\right] = 85.5$

Fig. Calculation of the equivalent weights of some common bases

3. Equivalent weights of oxidizing and reducing agents:

The basis of determining the equivalent weights of oxidants and reductants is the reactions in which they participate. In Red–Ox reactions electrons are transferred from the reductant to the oxidant. In a stoichiometric equation if the number of electrons (n) transferred from one mole of reductant or to one mole of oxidant, then $\left\{\frac{\text{Mol.Wt.of reductant}}{\text{n}}\right\}$ or $\left\{\frac{\text{Mol.Wt.of oxidant}}{\text{n}}\right\}$ value is the equivalent weight of the respective reagent.

Example – 1: $FeSO_4$ is a reducing agent. If it gets oxidized to $Fe_2(SO_4)_3$, the reaction can be written as $[O] + 2\,H^+ + 2\,Fe^{2+}(SO_4^{2-}) + SO_4^{2-} \rightarrow 2\,Fe^{3+} + 3\,SO_4^{2-} + H_2O$

$$\text{i.e.}\quad Fe^{2+} \rightarrow Fe^{3+} + e^-$$

That means one mole of ferrous ion loses one mole of electrons. Therefore

$$\text{The equivalent weight of ferrous ion} = \frac{\text{Wt. of ferrous ion in the reaction}}{\text{no. of electrons involved in the reaction}}$$

$$= \frac{\text{weight of ferrous ion}}{1} = \frac{55.84}{1}$$

Example–2:

Oxalate ion ($C_2O_4^{2-}$)is another reductant, when it gets oxidized the reaction is written as

$$C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2\,e^-$$

That is one mole of oxalate ion loses two moles of electrons. Hence, the equivalent weight of $C_2O_4^{2-}$ ion $= \left\{\frac{\text{formula weight of } C_2O_4^{2-}}{\text{no.of electrons involved in the reaction}}\right\}$

$$= \left\{\frac{\text{formula weight of } C_2O_4^{2-}}{2}\right\} = \frac{88}{2} = 44.0$$

Instead of the equivalent weight of$C_2O_4^{2-}$, if one requires the equivalent weight of ($Na_2C_2O_4.2H_2O$) sodium oxalate dihydrate, then one has the relation.

$$\text{equivalent weight of } Na_2C_2O_4.2H_2O = \left\{\frac{\text{Mol. wt. } Na_2C_2O_4.2H_2O}{2}\right\}$$

(Since a molecule of $Na_2C_2O_4.2H_2O$ contains one $C_2O_4^{2-}$ ion)

$$= \frac{\{2\,(23) + 2\,(12) + 4\,(16) + 2\,(18)\}}{2}$$

$$= \frac{170}{2} = 85.0$$

Example – 3:

In acid medium $KMnO_4$ is a strong oxidizing agent. Then the half reaction it undergoes can be represented as

$$KMnO_4 + 8\,H^+ + 5\,e^- \rightarrow K^+ + Mn^{2+} + 4\,H_2O$$

i.e., one mole of $KMnO_4$ reacts with five electrons. Hence, the equivalent weight of $KMnO_4$.

$$= \left\{\frac{\text{formula weight of } KMnO_4}{\text{no. of electrons involved in the reaction per mole of } KMnO_4}\right\}$$

$$= \left\{\frac{\text{Mol. wt. of } KMnO_4}{5}\right\}$$

$$= \frac{(39.102 + 54.938 + 64.0)}{5}$$

$$= \frac{158.04}{5} = 31.608$$

$$\text{or, the equivalent weight of } MnO_4^- \text{ can be written as}$$

$$\frac{(\text{formula weight of } MnO_4^-)}{5} = \frac{(54.938 + 64.0)}{5}$$

$$= \frac{118.938}{5} = 23.7876$$

Example – 4:

$KMnO_4$functions as an oxidizing agent in neutral as well as basic solutions. Then, the half reaction, in alkaline condition, is represented as

$$KMnO_4 + 2\ H_2O + 3e^- \rightarrow K^+ + 4\ OH^- + MnO_2$$

$$\text{The equivalent weight of } KMnO_4$$

$$= \frac{\text{formula Wt. of } KMnO_4}{\text{no. of electrons involved in the reaction per mole of } KMnO_4}$$

$$= \frac{\text{Mol. Wt. of } KMnO_4}{3} = \frac{158.04}{3} = 52.68$$

In the same manner, the reaction in strongly alkaline medium is

$$2\ KMnO_4 + 2\ K^+ + 2\ OH^- \rightarrow 2\ K_2MnO_4 + H_2O$$

(or)

$$MnO_4^- + e^- \rightarrow MnO_4^{-2}$$

$$\text{Then the equivalent weight of } KMnO_4 = \left\{\frac{Mol.Wt.of\ KMnO_4}{1}\right\} = 158.04$$

(Since one electron participates in the reaction)

On observation of the above examples 2 and 3, it immediately comes to mind, that the equivalent weight of $KMnO_4$ changes with the reaction. In the same manner, one can say that the equivalent weight of substances also change with the chemical reaction. Another common oxidizing agent is potassium dichromate ($K_2Cr_2O_7$). Its equivalent weight in acid medium is $1/6^{th}$ of its molecular weight.

$$= \left\{\frac{2\,(39.102) + 2\,(52) + 7\,(16)}{6}\right\} = \frac{294.204}{6} = 49.034$$

4. Equivalent weights of salts:

Salts are neutral substances. We know that they consist of cations and anions. For them to be neutral the overall positive charge on the cations must be equal to the overall negative charge on the anions present in the molecule. If the salt is not an oxidant or a reductant, then its equivalent weight is

$$= \frac{\text{Mol. Wt. of the salt}}{(\text{overall no. of positive charges on all cations in the salt molecule})}$$

$$= \frac{\text{Mol. Wt. of the salt}}{(\text{overall no. of negative charges on all anions in the salt molecule})}$$

Example – 1:

The equivalent weight of NaCl

$$= \frac{\text{Mol. Wt . of NaCl}}{(\text{no. of positive charges on all cations } (\text{Na}^{+} \text{ ion}) \text{ in the salt molecule})}$$

$$= \frac{\text{Mol. Wt. of NaCl}}{(\text{overall no. of negative charges on all anions in the salt molecule})}$$

$$= \frac{58.50}{1} = 58.5$$

Example – 2:

The equivalent weight of Na_2CO_3

$$= \frac{\text{Mol. Wt . of } Na_2CO_3}{(\text{overall no. of positive charges on all } Na^{+} \text{ in the salt molecule})}$$

$$= \frac{\text{Mol. Wt . of } Na_2CO_3}{(\text{overall no. of negative charges on all } CO_3^{2-} \text{in the salt molecule})}$$

$$= \left\{\frac{2\,(23) + 12 + 3\,(16)}{2}\right\} = \frac{106}{2} = 53.0$$

Self-Check Questions:

1. Molecular formula is AH_n. Equivalent weight of ‘A’ is

a. $\left(\frac{a}{n}\right)$
b. $\left(\frac{x}{n}\right)$
c. $\left[\frac{x}{a/n}\right]$
d. (xn)

Solution: b)

2. Valency for an element
   a. $\frac{\text{atomic weight of the element}}{\text{equivalent weight of the element}}$
   b. $\frac{\text{equivalent weight of the element}}{\text{atomic weight of the element}}$
   c. $\frac{\text{atomic weight of the element}}{\text{molecular weight of the element}}$
   d. both a) and b)

Solution:a)

3. equivalent weight of iron in ferrous compound is
   a. 27.82
   b. 18.61
   c. 30
   d. 48

Solution: a)

4. Equivalent weight of a base =
   a. $\frac{\text{molecular weight of the base}}{\text{basicity of the acid}}$
   b. $\frac{\text{molecular weight of the base}}{\text{acidity of the base}}$
   c. molecular weight of the base
   d. $\frac{\text{molecular weight of the base}}{\text{acidity of the acid}}$

Solution: b)

5. Equivalent weight of an oxidant =
   a. $\frac{\text{molecular weight of the oxidant}}{\text{no.of electrons tranferred}}$
   b. $\frac{\text{molecular weight of the oxidant}}{\text{overall positive charges of all cations in the salt}}$
   c. $\frac{\text{atomic weight}}{\text{valency}}$
   d. All of these

Solution: a)

Example set:

1. Calculate the equivalent weight of HNO_3?

Solution:

No. of displaceable hydrogens in HNO_3= basicity =1.

Equivalent weight of $HNO_3 = \frac{\text{molecular weight of } HNO_3}{\text{basicity of } HNO_3}$

Molecular weight of HNO_3 = [atomic weight of H + atomic weight of N + 3 (atomic weight of O)].

= [1 + 14 + 3 (16)]

= 15 + 48] = 63

Therefore equivalent weight of HNO_3 = 63/1 = 63.

2. Calculate the equivalent weight of $Ba(OH)_2$.

Solution:

No. of displaceable (OH) groups Acidity of$Ba(OH)_2$ is 2.

Molecular weight of $Ba(OH)_2$ = [atomic weight of Ba + 2 (atomic weight of O) + 2(atomic weight of H)]

= [137 + 2 (16 + 1)]

= 171

Therefore equivalent weight of $Ba(OH)_2$ = 171/2 = 85.5

3. Calculate the equivalent weight of phosphorous acid

Solution:

Formula of phosphorous acid = H_3PO_3.

Molecular weight of H_3PO_3 = [3 (1) + 31 + 3 (16)] = 82

No. of replaceable hydrogens (basicity) in H_3PO_3 is '2', not '3' because one hydrogen atom is directly attached to P in the structure of H_3PO_3. So it is difficult to remove the 3rd hydrogen. Hence its basicity is '2'.

Therefore equivalent weight of H_3PO_3 = 82/2= 41

Stoichiometry

Percentage Composition of Compounds

Percent Composition:

The molecular formula of a compound tells us the number of atoms of each element in a given compound. We can calculate theoretically, from the molecular formula, what percent of the total mass of the compound is contributed by each element. Then by comparing it with the percent composition obtained experimentally, we could determine the purity of the sample.

The **percentage composition by mass** is the percent by mass of each element in a compound. We can calculate percentage composition by volume also but here we are dealing with percentage by mass only. Percentage composition is obtained by dividing the mass of each element in 1 mole of the compound by the molar mass of the compound and then multiplying with 100. If n denotes the number of moles of atoms of the element in 1 mole of the compound, the percentage composition of an element in a compound is mathematically expressed as

$$\text{Percentage composition of an element} = \frac{\text{n} \times \text{molar mass of an atom of the element}}{\text{molar mass of compound}} \times 100$$

For example, in 1 mole of hydrogen peroxide (H_2O_2) there are 2 moles of H atoms and 2 moles of O atoms. The molar masses of H_2O_2, H, and O are 34.02 g, 1.008 g, and 16.00 g, respectively. Therefore, the percentage composition of H_2O_2 is given by:

$$\%\,\text{H} = \frac{2 \times 1.008\ \text{g}}{34.02\ \text{g}} \times 100 = 5.93\%$$

$$\%\,\text{O} = \frac{2 \times 16.00\ \text{g}}{34.02\ \text{g}} \times 100 = 94.07\%$$

Another method of calculating percentage composition is as follows.

Let ‘w’ g of the organic substance give ‘x’ g of the silver halide

$$\therefore \text{ percentage of Halogen} = \frac{\text{At Wt of halogen}}{\text{M Wt of silver halide}} \times \frac{100\ \text{x}}{\text{w}}$$

Example 1: Calculate the percent by mass (weight) of sodium (Na) and chlorine (Cl) in sodium chloride (NaCl).

The relative molecular mass (Molecular weight): M.wt = 22.99 + 35.45 = 58.44

1. Calculate the total mass of Na present:
   1 Na is present in the formula, mass = 22.99
2. Calculate the percent by mass (weight) of Na in NaCl:
   %Na = (mass Na ÷ M.wt) x 100 = (22.99 ÷ 58.44) x 100 = **39.34%**
3. Calculate the total mass of Cl present:
   1 Cl is present in the formula, mass = 35.45
4. Calculate the percent by mass (weight) of Cl in NaCl:
   %Cl = (mass Cl ÷ M.wt) x 100 = (35.45 ÷ 58.44) x 100 = **60.66%**

The answers above are probably correct if %Na + %Cl = 100, that is, 39.34 + 60.66 = 100.

Example 2. Calculate the percent by mass (weight) of each element present in sodium sulphate (Na_2SO_4).

1. Calculate the relative molecular mass (M.wt):
   M.wt = (2 x 22.99) + 32.06 + (4 x 16.00) = 142.04
2. Calculate the total mass of Na present:
   2 Na atoms are present in the formula, mass = 2 x 22.99 = 45.98
3. Calculate the percent by mass (weight) of Na in Na_2SO_4:
   %Na = (mass Na ÷ M.wt) x 100 = (45.98 ÷ 142.04) x 100 = **32.37%**
4. Calculate the total mass of S present in Na_2SO_4:
   1 S atom is present in the formula, mass = 32.06
5. Calculate the percent by mass (weight) of S present:
   %S = (mass S ÷ M.wt) x 100 = (32.06 ÷ 142.04) x 100 = **22.57%**
6. Calculate the total mass of O present in Na_2SO_4:
   4 O atoms are present in the formula, mass = 4 x 16.00 = 64.00
7. Calculate the percent by mass (weight) of O atom in Na_2SO_4:
   %O = (mass O ÷ M.wt) x 100 = (64.00 ÷ 142.04) x 100 = **45.06%**

The answers above are correct if %Na+ %S + %O = 100, that is, 32.37 + 22.57 + 45.06 = 100

Example 3:0.2175 g of the substance gave0.5825 g of Barium sulphate. Calculate the percentage of sulphur in the substance. (Mol. Wt of $BaSO_4$ =233, At.wt of S = 32)

Solution: We know, $BaSO_4 \equiv$ S

(137 + 32 + 64) 32

233 g of $BaSO_4$ contain 32 g of sulphur

$$0.5825 \text{ g of } BaSO_4 \text{ contain } \frac{32}{233} \times 0.5825 \text{ g of sulphur}$$

This is the weight of sulphur present in 0.2175 g of the substance.

$$\text{Hence, percentage of S} = \frac{32 \times 0.5825}{233} \times \frac{100}{0.2157} = 36.78$$

SAQs:

1. The percentage compositionin a compound is,
   a. Percentage by mass of each element
   b. Percentage by mass of few elements
   c. Mass of each element in the compound.
   d. Both a) and b)

Solution: a)

2. From percentage composition, we could determine the ______ of the sample
   a. Atomicity of an element
   b. Purity
   c. Quantity containing 100 g.
   d. Chemical nature.

Solution: b)

3. What is the percentage of the various elements in Sodium Carbonate [Na_2CO_3]? (Given Atomic Weights: C = 12 ; O = 16 ; Na = 23)

Solution: The first step is to calculate the Molecular Weight (or the Formula Weight) of the chemical compound by adding the atomic weights of the atoms (elements) that constitute the compound.

Molecular weight of Na_2CO_3
= (2 x Atomic weight of Na) + Atomic weight of C + (3 x Atomic weight of O)
= (2 x 23) + 12 + (3 x 16)
= 46 + 12 + 48 = 106

Now, 106 grams of Sodium Carbonate [Na_2CO_3] contain 46 grams of Sodium [Na], 12 grams of Carbon [C], and 48 grams of Oxygen [O].

So,
Percentage of Sodium [Na] in Sodium Carbonate [Na_2CO_3] = 46/106 x 100 = 43.40%.
Percentage of Carbon [C] in Sodium Carbonate [Na_2CO_3] = 12/106 x 100 = 11.32%.
Percentage of Oxygen [O]in Sodium Carbonate [Na_2CO_3] = 48/106 x 100 = 45.28%.

LAQs:

1. Phosphoric acid (H_3PO_4) is a colorless, syrupy liquid used in detergents, fertilizers, toothpastes and in carbonated beverages for a characteristic flavor. Calculate the percent composition by mass of H, P, and O in this compound.
   (P = 30.97 g mol^{-1}; H = 1.00g mol^{-1}; O = 16.0 g mol^{-1})

Solution: The molar mass of H_3PO_4 is 97.99 g. The percent by mass of each of the elements in H_3PO_4 is calculated as follows:

$$\% H = \frac{3 \times 1.008\ g}{97.99\ g} \times 100 = 3.086\%$$

$$\% \mathrm{P} = \frac{30.97\ \mathrm{g}}{97.99\ \mathrm{g}} \times 100 = 31.61\%$$

$$\% \mathrm{O} = \frac{4 \times 16.00\ \mathrm{g}}{97.99\ \mathrm{g}} \times 100 = 65.31\%$$

The procedure used in the example above can be reversed. Given the percent composition by mass of a compound, we can determine the empirical formula of the compound. Because we are dealing with percentages and the sum of all the percentages is 100, it is convenient to assume that we started with 100 g of a compound.

2. 0.395 g of an organic compound gave 0.582 of $BaSO_4$. Find the percentage of sulphur in the compound.

Solution: We know, $BaSO_4 \equiv S$

233 32

i.e. 233 g of $BaSO_4$ contains 32 g of sulphur.

$$\therefore\ 0.582\ \mathrm{g\ of\ BaSO_4\ contains}\ \frac{32}{233} \times 0.582\ \mathrm{g\ of\ sulphur.}$$

This is the weight of sulphur present in 0.395 g of the substance.

$$\mathrm{Hence, the\ percentage\ of\ S} = \frac{32}{233} \times 0.582 \times \frac{100}{0.395} = 20.24\ \%$$

Stoichiometry

Module 5.3: Concept of Empirical and Molecular formulae of compounds

Empirical Formula:

We can determine the empirical formula of a compound if we know it's percent composition. This enables us to identify compounds experimentally. The procedure is as follows.

The empirical formula of a compound gives the simplest ratio of the number of atoms of different elements present in one molecule of the compound. It does not give the actual number of atoms of different elements present in one moleculeof the compound.

"Empirical formula of a compound is the simplest formula showing the relative number of atoms of different elements present in one molecule of the compound".

Example:

1. Empirical formula of ethene (ethylene)is CH_2. The ratio of atoms of carbonto hydrogen in ethene is 1 : 2, which is the simplest ratio.

   Molecular formula of ethene is C_2H_4. This formula gives the actual number of carbon and hydrogen atoms present tin one molecule of the compound.

There are many compounds that can have the empirical formula CH_2. These include:

- C_2H_4 (ethene or ethylene) molecular mass=28.0g/mol and n=2
- C_3H_6 (propene or propylene) molecular mass=42.0g/mol and n=3
- C_3H_6 (cyclopropane) molecular mass=42.0g/mol and n=3
- C_4H_8 (butene or butylene) molecular mass=56.0g/mol and n=4
- C_4H_8 (cyclobutane) molecular mass=56.0g/mol and n=4

2. Empirical formula of acetic acid: CH_2O

   Molecular formula of acetic acid: $C_2H_4O_2$.

The empirical formula of a compound can be calculated by using the following steps:

1. Detect elements present in the compound
2. Find out experimentally, the percentage composition by weightof each element present in the compound
3. Divide the percentage of each element by its atomic weight to get the relative number of atoms of each element.

4. Divide each number obtained for the respective elements in step (3) by the smallest number among those numbers so as to get the simplest ratio.
5. If any number obtained in step (4) is not a whole number then multiply all the numbers by a suitable integer to get whole number ratio. This ratio will be the simplest ratio of the atoms of different elements present in the compound. Empirical formula of the compound can be written with the help of this ratio.

Example:

A carbon compound on analysis gave the following percentage composition, carbon 14.5 %, hydrogen 1.8 %, chlorine 64.46 %, oxygen 19.24 %. Calculate the empirical formula of the compound.

(Atomic masses: C = 12; H = 1.0; Cl = 35.5; O=16)

Solution:

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
C = 14.5	$\frac{14.5}{12} = 1.21$	$\frac{1.21}{1.20} = 1$
H = 1.8	$\frac{1.8}{1} = 1.8$	$\frac{1.8}{1.2} = 1.5$
Cl = 64.46	$\frac{64.46}{35.5} = 1.81$	$\frac{1.81}{1.2} = 1.5$
O = 19.24	$\frac{19.24}{16} = 1.2$	$\frac{1.2}{1.2} = 1$

Multiplication by a suitable integer,we get whole number ratio.

C	H	Cl	O
(1×2)	(1.5×2)	(1.5×2)	(1×2)
2	3	3	2

The simplest ratio of the atoms of different elements in the compound is:

C : H : Cl : O = 2 : 3 : 3 : 2

Therefore the empirical formula of the compound is $C_2H_3Cl_3O_2$.

Chemical analysis tells us the number of grams of each element present in a given amount of compound. Next, we can calculate the percentage composition of the given compound. Then, we find the empirical formula of the compound.

The same results can be obtained by following a different approach.

As a specific example, let us consider the compound ethanol. When ethanol is burned in an apparatus with an adequate input of oxygen through an inlet pipe, carbon dioxide (CO_2) and water (H_2O) are given off, and they are absorbed in CO_2 and H_2O absorbers, respectively. Because neither carbon nor hydrogen was in the inlet gas, we can conclude that both carbon (C) and hydrogen (H) were present in ethanol and that oxygen (O) may also be present. (Molecular oxygen was added in the combustion process, but some of the oxygen may also have come from the original ethanol sample.)

The masses of CO_2 and of H_2O produced can be determined by measuring the increase in mass of the CO_2 and H_2O absorbers, respectively.

Suppose that in one experiment the combustion of 11.5 g of ethanol produced 22.0 g CO_2 and 13.5 g of H_2O. We can calculate the mass of carbon and hydrogen in the original 11.5 g sample of ethanol as follows:

$$\text{mass of C} = 22.0\ \mathrm{g\ CO_2} \times \frac{1\ \mathrm{mol\ CO_2}}{44.01\ \mathrm{g\ CO_2}} \times \frac{1\ \mathrm{mol\ C}}{1\ \mathrm{mol\ CO_2}} \times \frac{12.01\ \mathrm{g\ C}}{1\ \mathrm{mol\ C}} = 6.00\ \mathrm{g\ C}$$

$$\text{mass of H} = 13.5\ \mathrm{g\ H_2O} \times \frac{1\ \mathrm{mol\ H_2O}}{18.02\ \mathrm{g\ H_2O}} \times \frac{2\ \mathrm{mol\ H}}{1\ \mathrm{mol\ H_2O}} \times \frac{1.008\ \mathrm{g\ H}}{1\ \mathrm{mol\ H}} = 1.51\ \mathrm{g\ H}$$

Thus 11.5 g of ethanol contains 6.00 g of carbon and 1.51 g of hydrogen. The remainder must be oxygen, whose mass is

Mass of O = [mass of sample – (mass of C + mass of H)]

= [11.5 g – (6.00 g + 1.51 g)] = 4.0

The number of moles of each element present in 11.5 g of ethanol is

$$\text{Moles of C} = 6.00\ \mathrm{g\ C} \times \frac{1\ \mathrm{mol\ C}}{12.01\ \mathrm{C}} = 0.500\ \mathrm{mol\ C}$$

$$\text{Moles of H} = 1.51\ \mathrm{g\ H} \times \frac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g\ H}} = 1.50\ \mathrm{mol\ H}$$

$$\text{Moles of O} = 4.0\ \mathrm{g\ O} \times \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g\ H}} = 0.25\ \mathrm{mol\ O}$$

The formula of ethanol can be written,therefore, as $C_{0.50}H_{1.5}O_{0.25}$. Because the number of atoms must be an integer, we divide the subscripts by 0.25, the smallest of the subscripts, and obtain the empirical formula C_2H_6O.

Chemists often want to know the actual mass of an element in a certain mass of a compound. For example, in the mining industry, this information will tell the scientists about the quality of the ore.

The word "empirical" literally means "based only on observation and measurement." The empirical formula of ethanol is determined from analysis of the compound in terms of its constituent elements. No knowledge of how the atoms are linked together in the compound is required.

Molecular Formula:

The formula calculated from percent composition by mass is always the empirical formula because the subscripts in the formula are always reduced to the smallest whole numbers. To calculate the actual, molecular formula we must know the approximate molar mass of the compound in addition to its empirical formula. Knowing that the molar mass of a compound must be an integral multiple of the molar mass of its empirical formula, we can use the molar mass to find the molecular formula.

Calculation of molecular formula:

"Molecular formula represents the actual number of atoms of different elements present in one molecule of the compound".

For certain compounds the molecular formula and the empirical formula may be one and the same.

The molecular formula of a compound may be same as empirical formula or a whole number multiple of it. Thus,

The molecular formula = $(\text{empirical formula})_n$

Where n is an integer 1, 2, 3, …….etc.

Example:

Ethene – $(CH)_2 = C_2H_4$

Acetic acid – $(CH_2O)_2 = C_2H_4O_2$

Glucose – $(CH_2O)_6 = C_6H_{12}O_6$.

Since molecular formula = $(\text{Empirical formula})_{\mathbf{n}}$

Molecular weight = Empirical formula weight × n

$$\text{i.e.n} = \frac{\text{molecular weight}}{\text{empirical formula weight}}$$

If the vapour density of the substance is known, its molecular weight can be calculated by using the equation.

$$2 \times \text{vapour density} = \text{molecular weight.}$$

Example:

A sample of a compound contains 1.52 g of nitrogen (N) and 3.47 g of oxygen (O). The molar mass of this compound is 90 g. Determine the molecular formula and the accurate molar mass of the compound.

Solution:

Let 'n' represent the number of moles of each element. We write

$$n_N = 1.52 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 0.108 \text{ mol N}$$

$$n_O = 3.47 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.217 \text{ mol O}$$

Thus, we arrive at the formula $N_{0.108}O_{0.217}$, which gives the identity and the ratios of atoms present. However, chemical formulas are written with whole numbers. By dividing the subscripts by the smaller subscript (0.108), we obtain NO_2 as the empirical formula.

The molecular formula might be the same as the empirical formula or some integral multiple of it. This integral relationship is determined by comparing the molar mass to the molar mass of the empirical formula. The molar mass of the empirical formula NO_2 is (46.01)

Empirical molar mass = 14.01 g + 2(16.00 g) = 46.01

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{90 \text{ g}}{46.01 \text{ g}} \approx 2$$

The molar mass is twice the empirical molar mass. This means that there are two NO_2 units in each molecule of the compound, and the molecular formula is $(NO_2)_2$ or N_2O_4.

The actual molar mass of the compound is two times the empirical formula mass, that is, 2(46.01 g) or 92.02 g.

SAQs:

1. Empirical formula of cyclo propane is
   a. CH_3
   b. CH_2
   c. C_2H_4
   d. CH

Solution:b)

2. Ratio of atoms presentin $CHCl_3$molecule is;
   a. 1: 1: 2
   b. 1: 2: 3
   c. 1: 1: 3
   d. 1: 1: 1

Solution: c)

3. Molecular formula = ________
   a. (Empirical formula) / n
   b. $(\text{empirical formula})_n$
   c. $(\text{Empirical formula})_{2n}$
   d. (Empirical formula) / 2n

Solution: b)

4. Molecular weight = ________
   a. n (empirical formula weight)
   b. 2 (vapour density)
   c. n(vapour density)
   d. Both a) and b)

Solution: d)

LAQs:

1. Chemical analysis of a carbon compound gave the following percentage composition by weight of the elements present, carbon = 10.06%, hydrogen = 0.81%, Chlorine = 89.10%, Calculate the empirical formula of the compound.
   (Atomic masses: C = 12; H = 1.0; Cl = 35.5)

Solution:

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
C = 10.06	$\frac{10.06}{12} = 0.84$	$\frac{0.84}{0.84} = 1$
H = 0.84	$\frac{0.84}{1} = 0.84$	$\frac{0.84}{0.84} = 1$
Cl = 89.10	$\frac{89.10}{35.5} = 2.51$	$\frac{2.51}{0.84} = 3$

Ratio of the atoms present in the molecule C : H : Cl = 1 : 1 : 3

Therefore the empirical formula of the compound$C_1H_1Cl_3$or $CHCl_3$.

2. Calculate the empirical formula of a compound having percentage composition: potassium (K) = 26.57, chromium (Cr) = 35.36; oxygen (O) = 38.07. (Given the atomic weights of K, Cr and O as 39; 52 and 16 respectively.)

Solution:

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
K = 26.57	$\frac{26.57}{39} = 0.68$	$\frac{0.68}{0.68} = 1$
Cr = 35.36	$\frac{35.36}{52} = 0.68$	$\frac{0.68}{0.68} = 1$
O = 38.07	$\frac{38.07}{16} = 2.38$	$\frac{2.38}{0.68} = 3.5$

Multiplication by a suitable integer to get whole number ratio.

K	Cr	O
(1 × 2)	(1 × 2)	(3.5 × 2)
2	2	7

Therefore the empirical formula of the compound is $K_2Cr_2O_7$.

3. Determine the empirical formula for a compound with the following elemental composition:

40.00% C, 6.72% H, 53.29% O

And also find out the molecular formula if the molecular weight of the compound is 180 g/mol.

Solution: The first step will be to assume exactly 100 g of this substance. This means in 100 g of this compound, 40.00 g will be due to carbon, 6.72 g will be due to hydrogen, and 53.29 g will be due to oxygen. We will need to compare these elements to each other stoichiometrically. In order to compare these quantities, they must be expressed in terms of moles. So the next task will be to convert each of these masses to moles, using their respective atomic weights:

$$40.00 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.331 \text{ mol C}$$

$$6.72 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 6.667 \text{ mol H}$$

$$53.29 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.331 \text{ mol O}$$

Take notice that since the composition data was given to four significant figures, the atomic weights used in the calculation were to at least four significant figures. Using fewer significant figures may actually lead to an erroneous formula.

Now that the moles of each element are known, a stoichiometric comparison between the elements can be made to determine the empirical formula. This is achieved by dividing through each of the mole quantities by which ever mole quantity is the smallest number of moles. In this example, the smallest mole quantity is either the moles of carbon or moles of oxygen (3.331 mol):

$$\frac{3.331 \text{ mol C}}{3.331 \text{ mol}} = 1.000 \text{ C} = 1 \text{ C}$$

$$\frac{6.667 \text{ mol H}}{3.331 \text{ mol}} = 2.001 \text{ H} = 2 \text{ H}$$

$$\frac{3.331 \text{ mol O}}{3.331 \text{ mol}} = 1.000 \text{ O} = 1 \text{ O}$$

The ratio of C:H:O has been found to be 1:2:1, thus the empirical formula is: CH_2O. Again, as a reminder, this is the simplest formula for the compound.We know that the molecular weight of this compound is 180 g/mol. With this information, the molecular formula may be determined. The formula weight of the empirical formula is 30 g/mol. Divide the molecular weight by the empirical formula weight to find a multiple:

$$\frac{180 \text{ g/mol}}{30 \text{ g/mol}} = 6$$

The molecular formula is a multiple of 6 times the empirical formula:

$C_{(1 \times 6)}$ $H_{(2 \times 6)}$ $O_{(1 \times 6)}$ which becomes $C_6H_{12}O_6$(glucose)

4. A sample contains C, H and S. Suppose 7.96 mg sample of this compound is burned in oxygen and found to form 16.65 mg of CO_2. The sulphur in 4.31 mg of the compound is converted into sulfate by a series of reactions, and precipitated as $BaSO_4$. The $BaSO_4$ was found to have a mass of 11.96 mg. The molecular weight of the compound was found to be 168 g/mol. Using this data, find out the molecular formula of the compound?

Solution:

The strategy will be to use stoichiometry to determine the mass percent of each of the elements in the compound, and then use the mass percentages to determine the empirical formula. Notice that since all the data is in milligrams, we may carry out the calculations using milli- units throughout.

The only source of carbon for the CO_2 formed came from the compound; thus, determine the milligrams of carbon found in 16.65 mg of CO_2:

$$16.65 \text{ mg } CO_2 \times \frac{1 \text{ mmol } CO_2}{44.01 \text{ mg } CO_2} \times \frac{1 \text{ mmol C}}{1 \text{ mmol } CO_2} \times \frac{12.02 \text{ mg C}}{1 \text{ mmol C}} = 4.544 \text{ mg C}$$

Now that the "part" of the sample due to carbon is known, one may calculate the percent carbon in the compound, using the mass the sample as the "whole":

$$\frac{4.544 \text{ mg C}}{7.96 \text{ mg sample}} \times 100 = 57.1 \text{ \%C}$$

The only source of sulfur for the precipitate of $BaSO_4$, came from the compound, thus, determine the milligrams of sulfur in 11.96 mg of $BaSO_4$:

$$11.96 \text{ mg } BaSO_4 \text{ x } \frac{1 \text{ mmol } BaSO_4}{233.39 \text{ mg } BaSO_4} \text{ x } \frac{1 \text{ mmol S}}{1 \text{ mmol } BaSO_4} \text{ x } \frac{32.06 \text{ mg S}}{1 \text{ mmol S}} = 1.643 \text{ mg S}$$

Similarly, determine the percent sulfur in the compound, using the mass of sulfur as the "part" and the mass of compound as the "whole":

$$\frac{1.643 \text{ mg S}}{4.31 \text{ mg sample}} \text{ x } 100 = 38.1 \text{ \%S}$$

The percentage of hydrogen may determine by difference:

%H = 100.0% - 57.1 %C - 38.1 %S = 4.8 %H

From the elemental composition, we may determine the empirical formula, in the same manner as used in the first example. First, assume exactly 100 g of the compound. In 100 grams of the compound, 57.1 g would be due to carbon, 38.0 g would be due to sulfur and 4.9 g would be due to hydrogen. Convert each of these masses into moles using the corresponding atomic weight for each element:

$$57.1 \text{ g C x } \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.75 \text{ mol C}$$

$$4.8 \text{ g H x } \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 4.8 \text{ mol H}$$

$$38.0 \text{ g S x } \frac{1 \text{ mol S}}{32.06 \text{ g S}} = 1.19 \text{ mol S}$$

Now that the moles of each element are known, the empirical formula may be determined by dividing the moles of each element by the smallest number of moles. This yields a ratio of the number of each element in the empirical formula.

$$\frac{4.75 \text{ mol C}}{1.19 \text{ mol}} = 3.99 \text{ C} = 4 \text{ C}$$

$$\frac{1.19 \text{ mol S}}{1.19 \text{ mol}} = 1.00 \text{ S} = 1 \text{ S}$$

$$\frac{4.9 \text{ mol H}}{1.19 \text{ mol}} = 4.03 \text{ H} = 4 \text{ H}$$

The ratio of C:H:S has been found to be 4:4:1, thus the empirical formula is: C_4H_4S. The molar mass of the empirical formula is 84 g/mol. Since the molecular weight of the actual compound is 168 g/mol, and is double the molar mass of the empirical formula, the molecular formula must be twice the empirical formula:

$$C_{(4 \times 2)}\ H_{(4 \times 2)}\ S_{(1 \times 2)} \text{ which becomes } C_8H_8S_2$$

Problem Set:

1. Ascorbic acid (vitamin C) cures scurvy (A disease). It is composed of 40.92 % carbon (C), 4.58 % hydrogen (H), and 54.50 % oxygen (O) by mass. Determine its empirical formula.
(Atomic masses: C = 12; H = 1.0; O = 16)

Solution:

In a chemical formula, the subscripts represent the ratio of the number of moles of each element that combine to form one mole of the compound.

If we have 100 g of ascorbic acid, there will be 40.92 g of C, 4.58 g of H, and 54.50 g of O. Because the subscripts in the formula represent a mole ratio, we need to convert the grams of each element to moles. $\text{No. of moles of C} = n_C = 40.92 \text{ g} \times \frac{1 \text{ mol}}{12.01 \text{ g}} = 3.407 \text{ mol}$

Simple atomic ratio of C= $\frac{3.407}{3.406} = 1$

$$\text{No. of moles of H} = n_H = 4.58 \text{ g} \times \frac{1 \text{ mol}}{1.008 \text{ g}} = 4.54 \text{ mol}$$

Simple atomic ratio of H= $\frac{3.407}{4.54} = 1.33$

$$\text{No. of moles of O} = n_O = 54.50 \text{ g} \times \frac{1 \text{ mol}}{16.00 \text{ g}} = 3.406 \text{ mol}$$

Simple atomic ratio of O= $\frac{3.406}{3.406} = 1$

Thus we arrive at the formula $C_1H_{1.33}O_1$, which gives the identity and the mole ratios of atoms present. However, chemical formulas are written with whole numbers,so all the subscripts are multiplied by 3,we get the simple atomic ratio is 3:4:3.

Thus, $C_3H_4O_3$ is the empirical formula for ascorbic acid.

2. 0.200 g of an organic compound gave, on combustion, 0.147 g of carbon dioxideand 0.12 g of water and 46.03 % of N_2. Calculate the empirical formula of the compound.

Solution:Calculation of percentage composition

a. The amount of C in 0.147 g of CO_2

$$= \frac{(\text{Wt of } CO_2)(\text{At. wt of C})}{(\text{Mol. wt of } CO_2)} = \left(\frac{0.147 \text{ g} \times 12 \text{ g}}{44 \text{ g}}\right)$$

$$\text{The percentage of C} = \left(\frac{0.147 \text{ g} \times 12 \text{ g}}{44 \text{ g}}\right) \times \frac{100 \text{ g}}{0.200 \text{ g}} = 20.014$$

b. The amount of H_2 in 0.12 g of H_2O

$$= \frac{(\text{Wt of } H_2O)(\text{At. wt of } H_2)}{(\text{Mol. wt of } H_2O)} = \left(\frac{0.12 \text{ g} \times 2 \text{ g}}{18 \text{ g}}\right)$$

$$\text{The percentage of H} = \left(\frac{0.12 \text{ g} \times 2 \text{ g}}{18 \text{ g}}\right) \times \frac{100 \text{ g}}{0.200 \text{ g}} = 6.66$$

c. The percentage of $N = 46.03$

d. The percentage composition of oxygen = [100 – (20.04 + 6.66 + 46.03)]
= 26.67

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
C = 20.04	$\frac{20.04}{12} = 1.67$	$\frac{1.67}{1.66} = 1$
H = 6.6	$\frac{6.66}{1} = 6.66$	$\frac{6.66}{1.66} = 4$

N = 46.03	$\frac{46.03}{14} = 3.3$	$\frac{3.3}{1.66} = 2$
O = 26.67	$\frac{26.67}{16} = 1.66$	$\frac{1.66}{1.66} = 1$

Therefore the empirical formula of the compound CH_4N_2O

3. A carbon compound contains 12.8% carbon, 2.1% hydrogen, 85.1% bromine. The molecular weight of the compound is 187.9. Calculate the molecular formula. (Atomic masses: C = 12; H = 1.0; Br = 80)

Solution:

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
C = 12.8	$\frac{12.8}{12} = 1.067$	$\frac{1.067}{1.067} = 1$
H = 2.1	$\frac{2.1}{1} = 2.1$	$\frac{2.1}{1.067} = 2$
Br = 85.1	$\frac{85.1}{80} = 1.067$	$\frac{1.067}{1.067} = 1$

The empirical formula is CH_2Br

Empirical formula weigh 12 + (2 × 1) + 80 = 94.

The molecular weight = 187.9 (given)

$$\therefore \quad n = \frac{187.9}{94} = 2$$

Molecular formula = $(CH_2Br)_2 = C_2H_4Br_2$

4. A sample of a compound containing boron (B) and hydrogen (H) contains 6.444 g of B and 1.803gof H. The molar mass of the compound is about 30 g. What is its molecular formula?(B = 11.0; H = 1.0)

Solution:

Given that;B = 6.444g, H = 1.803g

Molar mass of the compound = 30 g.

Percentage of the elements	Dividing the % composition by their atomic weight	Simple atomic ratio
B = 6.444	$\frac{6.444}{11} = 0.58$	$\frac{0.58}{0.58} = 1$
H = 1.803	$\frac{1.803}{1} = 1.803$	$\frac{1.803}{0.58} \approx 3$

Empirical formula = BH_3.

Empirical formula mass = 14

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{30}{14} \approx 2$$

Therefore molecular formula = (empirical formula)$_2$ = $(BH_3)_2$ = B_2H_6.

Exercise Questions:

1. Peroxyacetylnitrate (PAN) is one of the components of smog. It is a compound of C, H, N, and O. Determine the percent composition of oxygen and the empirical formula from the following percent composition by mass: 19.8 percent C, 2.50 percent H, 11.6 percent N. What is its molecular formula given that its molar mass is about 131 g mol^{-1}? (N = 14; O = 16; C = 12; H = 1)
   (Ans: $C_2H_3NO_5$)

2. What are the empirical formulas of the compounds with the following compositions? (C = 12; H = 1; O = 16; N = 14)

   a. 40.1 percent C, 6.6 percent H, 53.3 percent O **(Ans: CH_2O)**
   b. 18.4 percent C, 21.5 percent N, 60.1 percent K **(Ans: CNK)**
3. The empirical formula of a compound is CH. If the molar mass of this compound is about 78 g, what is its molecular formula? **(Ans: C_6H_6)**
4. Mono sodium glutamate (MSG), a food-flavor enhancer, has been blamed for "Chinese restaurant syndrome," the symptoms of which are headaches and chest pains. MSG has the following composition by mass: 35.51 percent C, 4.77 percent H,

37.85 percent O, 8.29 percent N, and 13.60 percent Na. What is its molecular formula if its molar mass is about 169 g mol^{-1}. (C = 12, H = 1; O = 16; N=14; Na=23)
(Ans: $C_5H_8O_4NNa$)

5. Determine the empirical formula of a compound having the following percent composition by mass: K : 24.72 percent; Mn : 34.77 percent; O : 40.51 percent. (K = 39,; Mn = 54.94; O = 16)

Stoichiometry

Chemical reactions and Equations

Chemical reaction is a process in which a substance (or substances) is changed into one or more new substance(s). To communicate with one another about chemical reactions, chemists have devised a standard way using chemical equations. A chemical equation uses chemical symbols to show what happens during a chemical reaction.

Ex: Metallic zinc and sulfur (a yellow powder) react when heated to produce zinc sulfide, a white salt.

$$Zn + S \text{ ---->} ZnS$$

- Carbon dioxide and water react in the presence of sunlight and chlorophyll to produce oxygen gas and sugar (the photosynthesis reaction). Our life on earth depends on this process.

$$CO_2 + H_2O \text{--->} C_6H_{12}O_6 + O_2$$

- Hydrogen gas burns in air to produce water, with the evolution of heat and light. This reaction powers the liftoff of the space shuttle, and may soon power automobiles and heat homes.

Writing Chemical Equations:

Consider what happens when hydrogen gas (H_2) burns in air (which contains oxygen, O_2) to form water (H_2O). This reaction can be represented by the chemical equation

$$H_2 + O_2 \rightarrow H_2O$$

Where the "plus" sign means "reacts with" and the arrow means "to yield." Thus, this symbolic expression can be read: "Molecular hydrogen reacts with molecular oxygen to yield water." The reaction is assumed to proceed from left to right as the arrow indicates.

The above equation is not complete, however, because there are twice as many oxygen atoms on the left side of the arrow (two) as on the right side (one). To confirm with the law of conservation of mass, there must be the same number of each type of atom on both sides of the arrow; that is, we must have as many atoms after the reaction ends as we did before it started. We can balance this equation by placing the appropriate coefficient (2 in this case) in front of H_2 and H_2O:

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

We use the law of conservation of mass as our guide in balancing chemical equations.

“The balanced chemical equation represents a stoichiometric equation. The exact quantities of the reactants and the products that appear in the balanced chemical equation are known as stoichiometric quantities”.

The *balanced chemical equation* of water shows that “two hydrogen molecules can combine or react with one oxygen molecule to form two water molecules”.

Because the ratio of the number of molecules is equal to the ratio of the number of moles and also based on the molar mass, we can read the equation in three ways as shown below.

$2H_2$	$+ O_2$	$\rightarrow 2H_2O$
Two molecules	+ one molecule	→ two molecules
2 moles	+ 1 mole	→ 2 moles
2(2.02 g)	+ 32.oo g	→ 2(18.02 g)

36.04 g reactants equal 36.04 g product.

We refer to H_2 and O_2 in the equation as ***reactants***, which are the starting materials in a chemical reaction. Water is the ***product***, which is the substance formed as a result of a chemical reaction. A chemical equation, then, is just the chemist’s shorthand description of a reaction. In a chemical equation, the reactants are changed into one or more new substances.

Reactants → products

To provide additional information, chemists often indicate the physical states of the reactants and products by using the letters *g*, *l*, and *s* to denote gas, liquid, and solid, respectively. For example,

$$2\ CO_{(g)} + O_{2(g)} \rightarrow 2\ CO_{2(g)}$$
$$2\ HgO_{(s)} \rightarrow 2\ Hg_{(l)} + O_{2(g)}$$

To represent what happens when sodium chloride (NaCl) is added to water, we write

$$NaCl_{(s)} \xrightarrow{H_2O} NaCl_{(aq)}$$

Where ‘*(aq)*’ denotes the aqueous (that is, water) environment. Writing H_2O above the arrow symbolizes the physical process of dissolving a substance in water, although it is sometimes left out for simplicity.

Knowing the states of the reactants and products is especially useful in the laboratory. For example, when potassium bromide (KBr) and silver nitrate ($AgNO_3$) react in an aqueous environment, a solid, silver bromide (AgBr) is formed. This reaction can be represented by the equation:

$$KBr_{(aq)} + AgNO_{3(aq)} \rightarrow KNO_{3(aq)} + AgBr_{(s)}$$

If the physical states of reactants and products are not given, an uninformed person might try to bring about the reaction by mixing solid KBr with solid $AgNO_3$. These solids would react very slowly or not at all. We can understand the reasons for this if we look at the process at the molecular level. For a product like silver bromide to form, the Ag^+ and Br^- ions would have to come in contact with each other. However, these ions are locked in place in their solid compounds and have little mobility.

Balancing Chemical Equations

Suppose we want to write an equation to describe a chemical reaction. The first step is to identify the reactants and products. The next step is to write their chemical formulas. We assemble them in the conventional sequence – reactants on the left separated by an arrow from products on the right. The equation written at this point is likely to be *unbalanced chemical equation (skeleton equation)*; that is the number of each type of atom on one side of the arrow differs from the number on the other side.

For balancing the equation,

- We look for elements that appear only once on each side of the equation with the same number of atoms on each side: The formula containing these elements must have the same coefficient.
- Next, look for elements that appear only once on each side of the equation but in unequal number of atoms. Balance these elements.
- Finally, balance elements that appear in two or more formulas on the same side of the equation.

Let us consider a specific example. In the laboratory, a small amount of oxygen gas can be prepared by heating potassium chlorate ($KClO_3$). The products are oxygen gas (O_2) and potassium chloride (KCl). From this information, we write

$$KClO_3 \rightarrow KCl + O_2$$

All three components (K, Cl, and O) appear only once on either side of the equation, but only for K and Cl do we have equal numbers of atoms on both sides. Thus, $KClO_3$ and KCl must have the same coefficient. The next step is to make the number of O atoms the same on both sides of the equation. Then, to balance oxygen atoms, we write;

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

Now K and Cl become unbalanced. Therefore we balance the K and Cl atoms. Then we have;

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

Now let us consider the combustion (that is, burning) of the natural gas component ethane (C_2H_6) in oxygen or air, which yields carbon dioxide (CO_2) and water. The unbalanced equation is

$$C_2H_6 + O_2 \rightarrow CO_2 + H_2O$$

We see that the number of atoms for any of the elements (C, H, and O) is not the same on both sides of the equation. In addition, C and H appear only once on each side of the equation; O appears in two compounds on the right side (CO_2 and H_2O). To balance the C atoms, we place a 2 in front of CO_2:

$$C_2H_6 + O_2 \rightarrow 2CO_2 + H_2O$$

To balance H atoms, we place a 3 in front of H_2O:

$$C_2H_6 + O_2 \rightarrow 2CO_2 + 3H_2O$$

At this stage, the C and H atoms are balanced, but the O atoms are not balanced because there are seven O atoms on the right-hand side and only two O atoms on the left-hand side of the equation. This inequality of O atoms can be eliminated by writing $\frac{7}{2}$ in front of the O_2 on the left-hand side:

$$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

The equation is now balanced. However, we normally prefer to express the coefficients as whole numbers rather than as fractions.
Therefore, we multiply the entire equation by 2:

$$2\ C_2H_6 + 7\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O$$

We note that the coefficients used in balancing the last equation are the smallest possible set of whole numbers. And finally we get the balanced equation.

Classification of Chemical Reactions:

There are literally millions of known chemical reactions. To learn them all individually is a hopeless task. Instead, we attempt to classify reactions into a manageably small number of categories, and learn the fundamental characteristics of each category. We can then make statements about a reaction category that apply to all individual reactions in the category. In this text, we will be concerned with three major reaction types that we will now define and describe. We are not yet equipped to fully understand certain aspects of these reactions; however, it is best to begin practicing the recognition of reaction type as early as possible, even though it may seem difficult at first. It will become easier. The following three classes of chemical reactions will be discussed in this text:

- Electron Transfer reactions (also known as oxidation-reduction, or red-ox reactions)
- Proton Transfer reactions (also known as acid-base reactions)

- Double Displacement reactions

We will define each type, and briefly discuss its characteristics.

Electron Transfer Reactions:

These are reactions in which electrons are transferred from one atom, *molecule*, or ion to another atom, molecule, or ion. The substance that provides the electrons becomes more positive as a result of the process; the substance that receives the electrons becomes more negative. Some electron transfer reactions are very easy to recognize. For example, the reaction of sodium and chlorine is an electron transfer process, because sodium becomes more positive and chlorine more negative in the process:

$$2Na_{(s)} + Cl_{2(g)} \text{--->} 2NaCl_{(s)}$$

Sodium is in the elemental (uncharged) form prior to reaction; after reaction, it exists as Na^+ ions in NaCl. Clearly, each sodium atom has lost one electron. At the same time, each Cl atom of Cl_2 has gained an electron to become Cl^-. The reaction of magnesium and oxygen is also an electron transfer process:

$$2Mg_{(s)} + O_{2(g)} \text{--->} 2MgO_{(s)}$$

Each magnesium atom loses two electrons; each oxygen atom accepts two electrons; electrons are therefore transferred from Mg to O.

Proton Transfer Reactions:

These are processes in which a proton, H^+, is transferred from one species to another. The species losing the proton is called an acid; the species gaining the proton is called a base. An example of a proton transfer reaction is shown below.

$$HCl_{(aq)} + Mg(OH)_{2(aq)} \text{--->} MgCl_{2(aq)} + H_2O_{(l)}$$

Here a proton, H^+, is transferred from HCl to the OH^- portion of magnesium hydroxide. Water is produced by combination of H^+ and OH^-; magnesium chloride is also produced.

$$H_2SO_{4(aq)} + Na_2CO_{3(aq)} \text{--->} Na_2SO_{4(aq)} + H_2CO_{3(aq)}$$

Here H_2SO_4 transfers two protons to CO_3^{2-} to produce H_2CO_3; sodium sulfate is also produced. If protons are transferred in a reaction, the reaction is an acid-base process.

Double Displacement Reactions:

In a double displacement process, the positive and negative parts of two reacting substances exchange: the positive part of one substance ends up with the negative part of the other. For example, the reactions below are double displacement processes:

$$NaCl_{(aq)} + AgNO_{3(aq)} \text{--->} NaNO_{3(aq)} + AgCl_{(s)}$$
$$BaCl_{2(aq)} + K_2SO_{4(aq)} \text{--->} KCl + BaSO_{4(s)}$$

You may notice that the proton transfer reactions are also double displacement reactions. This is certainly true. But because acid-base processes play such a central role in chemistry, chemists choose to classify them separately. We will stick on to this convention.

Now we will learn combustion reactions, which constitute an important subclass of electron transfer reactions.

Combustion Reactions:

In this section, we introduce and discuss an important category of chemical reactions: combustion reactions. A combustion reaction involves the reaction of a substance, element or compound, with oxygen, usually with the accompanying production of heat or light or sound energy. The balanced equations representing the combustion reactions of elemental phosphorus and of methane are shown in equation form below:

$4P_{(s)} + 5\ O_{2(g)} \text{--->} P_4O_{10(s)}$
$CH_{4(g)} + 2O_{2(g)} \text{--->} CO_{2(g)} + 2H_2O_{(g)}$

P_4O_{10} is called the oxide of phosphorus; similarly, CO_2 is an oxide of carbon, and H_2O is the oxide of hydrogen. Using this terminology, we generalize from these typical combustion processes as follows:

Element + O_2 ---> oxide of element
Compound + O_2 ---> oxides of all elements in the compound

The Chemical Equation as a Recipe (formula/ technique):

Frequently, people who are first learning about chemical equations interpret the meaning of the equation incorrectly. In this section, we will attempt to concretize chemical equations, which admittedly relate symbols of atoms and molecules and are therefore abstract, by drawing an similarity between a chemical equation and a recipe. The analogy is very close; all of the important quantitative aspects of chemical reactions apply equally to recipes. A recipe is a prescription for a process by which specified relative amounts of ingredients are transformed into a desired product. It is a written representation of the process of producing the product. Similarly, a chemical equation is a description of a process by which appropriate relative amounts of reactants are transformed into products. It is a written representation of the process of chemical change. A recipe for a simple fruit salad is given below:

1 apple + 2 oranges + 10 grapes --> 1 fruit salad

Reaction Stoichiometry as a Recipe:

A chemical equation for a reaction is essentially a recipe. Our purpose in doing that was to ground the rather abstract notions of chemical formulas and equations to something concrete, with which almost everyone has experience. All of the important quantitative aspects of chemical equations--collectively known as *reaction stoichiometry*--can be understood in terms of the recipe idea. It is instructive to return to the fruit salad recipe for our first example.

Example:

You intend to make 20 fruit salads for a large dinner party according to the following recipe:

1 apple + 5 oranges + 10 grapes → 1 fruit salad

You go to the store to purchase starting materials, and come home with the 10 pounds of apples, 15 pounds of oranges, and 1 pound of grapes. Are these materials sufficient to produce 20 fruit salads?

<u>Solution</u>:

The equation is expressed in terms of *numbers* of apples, oranges, and grapes; however, we know only the total amounts of each fruit by *mass*. Clearly we need more information, specifically, the average mass of an apple, an orange, and a grape. Suppose that we can weigh a typical apple, orange, and grape on a simple kitchen scale. Suppose further that the apples, oranges, and grapes are of unusually uniform size, so that the weight of one apple faithfully represents the weight of any apple. Our weighing gives the following results:

1 apple-weight = 0.25 lb/apple
1 orange-weight = 0.33 lb/orange
1 grape-weight = 0.00033 lb/grape

These unit weights enable us to convert grocery store masses into numbers of apples, oranges, and grapes:

Number of apples = 10 lbs/(0.25 lb/apple) = 40 apples
Number of oranges = 10 lbs/(0.33 lb/orange) = 30 oranges
Number of grapes = 1 lb/(0.00033 lb/grape) = 3000 grapes

Now we are in a position to apply the recipe, which tells us that for each apple used, we must use 5 oranges and 10 grapes. To use 40 apples would require 200 oranges and 400 grapes. We have more than enough grapes to use up all of the apples, but we do not have enough oranges. We can conclude that the number of fruit salads will be limited by the number of oranges that we have. Because we need 5 oranges per fruit salad, we can make only 6 fruit salads from 30 oranges. This will require 6 apples and 6(10) = 60 grapes. We will need to return to the store to get quite a few more oranges. Specifically, we will require enough for 14 more fruit salads, or a total of 14(5) = 70 oranges. Since each orange weighs a third of a pound, we need somewhat over 20 pounds more of oranges.

From this example we learn a few important ideas. First, the recipe is expressed in numbers of units of each ingredient, not in terms of their masses. Similarly a chemical equation is expressed in terms of numbers of atoms, molecules, or formula units, not in terms of their masses. Second, the amounts of our fruit salad ingredients are expressed as masses when we buy them at the store. Similarly, when we buy chemical substances, the amounts are expressed as masses. Third, to apply the recipe, we must convert the masses to numbers of things using the mass per thing. Having done this, we figure out how many fruit salads it is possible to make with the given amounts of ingredients. We must do the same thing with a chemical equation. Finally, one of the ingredients is found to limit the number of fruit salads that can be made. We will find that in many cases, one of the reactants limits the amount of product that can be formed in a chemical reaction. This will be the reactant that is used up first; it is called the *limiting reagent*. Let's now see how the recipe analogy helps us in doing stoichiometric calculations for chemical reactions.

Let us examine one example to understand limiting reagent.

Ex 1:

A 50.6 g sample of $Mg(OH)_2$ is reacted with 45.0 g of HCl according to the reaction:

$$Mg(OH)_2 + 2\ HCl \text{ --> } MgCl_2 + 2\ H_2O$$

Form the equation find out the limiting reagent?

Solution:

First, calculate the moles of each reactant using their molar mass:

$$50.6 \text{ g } Mg(OH)_2 \text{ x } \frac{1 \text{ mol } Mg(OH)_2}{58.3 \text{ g } Mg(OH)_2} = 0.868 \text{ mol } Mg(OH)_2 \text{ available}$$

$$45.0 \text{ g HCl x } \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} = 1.23 \text{ mol HCl available}$$

Consider the balanced reaction:

$$Mg(OH)_2 + 2\ HCl \text{ --> } MgCl_2 + 2\ H_2O$$

Form the balanced equation it is clear that 2 moles of HCl is needed to react with 1 mole of $Mg(OH)_2$.

Therefore the actual no. of moles of HCl needed to react with 0.8688 mole of $Mg(OH)_2$ is; 0.8688 x 2 = 1.737 mole

But 1.23 mole of HCl is available, so there not enough HCl, hence HCl must be the limiting reagent. Since HCl is the limiting reagent, use the moles of HCl available to calculate the theoretical yield of $MgCl_2$:

$$1.23 \text{ mol HCl x } \frac{1 \text{ mol } MgCl_2}{2 \text{ mol HCl}} \text{ x } \frac{95.3 \text{ g } MgCl_2}{1 \text{ mol } MgCl_2} = 58.6 \text{ g } MgCl_2$$

Ex 2:

Methane, CH_4, burns in oxygen to give carbon dioxide and water according to the following equation:

$$CH_4 + 2O_2 \text{------>} CO_2 + 2\,H_2O$$

In one experiment, a mixture of 0.250 mol of methane was burned in 1.25 mol of oxygen in a sealed steel vessel. Find the limiting reagent, if any, and calculate the theoretical yield, (in moles) of water.

Solution:

According to the equation: 1 mol CH_4 = 2 mol O_2

If we use up all the methane then:

$$\frac{1 \text{ mol } CH_4}{0.25 \text{ mol}} = \frac{2 \text{ mol } O_2}{x}$$

x = 0.50 mol of O_2 would be needed.

We have 1.25 mol of O_2 on hand. Therefore we have 0.75 mol of O_2 in excess of what we need.

If the oxygen in is excess, then the methane is the limiting reagent.

Confirmation: If we use up all the oxygen then

$$\frac{1 \text{ mol } CH_4}{x} = \frac{2 \text{ mol } O_2}{1.25 \text{ mol}} \qquad x = 0.625 \text{ mol of methane.}$$

We don't have 0.625 moles of methane. We have only 0.25 moles. Therefore the methane will be used up before all the oxygen is. Again the methane is the limiting reagent.

Finally we say that 0.25 mole of methane and 1.25 mole of oxygen are mixed and reacted according to the equation, the methane is the limiting reagent and the maximum yield of water will be 0.50 moles.

SAQs:

1. $H_2 + O_2 \rightarrow H_2O$ reaction is

a) Balanced chemical equation
b) Unbalanced chemical equation
c) Skeleton equation
d) Both b) and c)

Solution: d)

2. In the reaction, $2\,CO_{(g)} + O_{2(g)} \rightarrow 2\,CO_{2(g)}$ the reactants are

a) CO and CO_2
b) CO_2
c) CO_2 and O_2
d) CO and O_2

Solution: d)

3. Balanced equation for the combustion of ethane is,

a) $C_2H_6 + O_2 \rightarrow CO_2 + H_2O$
b) $2\ C_2H_6 + 3\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O$
c) $C_2H_6 + 3\ O_2 \rightarrow 2\ CO_2 + 6\ H_2O$
d) $2\ C_2H_6 + 7\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O$

Solution: d)

4. What are the steps involved in a balanced chemical equation?

Solution:

- For balancing the equation, we look for elements that appear only once on each side of the equation with the same number of atoms on each side.
- The formula containing these elements must have the same number of atoms of each kind.
- Next, look for elements that appear only once on each side of the equation but in unequal number of atoms. Balance these elements.
- Finally, balance elements that appear in two or more formulas on the same side of the equation.

5. Use the formation of water from hydrogen and oxygen to explain the following terms: chemical reaction, reactant, and product.

Solution:

Consider what happens when hydrogen gas (H_2) burns in air (which contains oxygen, O_2) to form water (H_2O). This reaction can be represented by the chemical equation

$$H_2 + O_2 \rightarrow H_2O$$

H_2 and O_2 in the equation are ***reactants***, which are the starting materials in a chemical reaction. Water is the ***product***, which is the substance formed as a result of a chemical reaction.

LAQs:

1. When aluminum metal is exposed to air, a protective layer of aluminum oxide (Al_2O_3) forms on its surface. This layer prevents further reaction between aluminum and oxygen, and it is the reason that aluminum beverage cans do not corrode. [In the case of iron, the rust, or Iron(III) oxide, that forms is too porous to protect the iron metal underneath, so rusting continues.] Write a balanced equation for the formation of Al_2O_3.

Solution:

The unbalanced equation is

$$Al + O_2 \rightarrow Al_2O_3$$

In a balanced equation, the number and types of atoms on either side of the equation must be the same. We see that there is one Al atom on the reactants side and there are two Al atoms on the products side. We can balance the Al atoms by placing a coefficient of 2 in front of the Al on the reactants side.

$$2\ Al + O_2 \rightarrow Al_2O_3$$

There are two O atoms on the reactants side, and three O atoms on the product side of the equation. We can balance the O atoms by placing a coefficient of $\frac{3}{2}$ in front of O_2 on the reactants side.

$$2\ Al + \frac{3}{2} O_2 \rightarrow Al_2O_3$$

This is a balanced equation. However, equations are normally balanced with the smallest set of whole number coefficients. Multiplying both sides of the equation by 2 gives whole number coefficients.

$$4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$$

The equation is balanced. Also, the coefficients are reduced to the simplest set of whole numbers.

2. balance the following reaction:
$N_2O_5 \rightarrow N_2O_4 + O_2$

Solution:

The unbalanced equation is

$$N_2O_5 \rightarrow N_2O_4 + O_2$$

In a balanced equation, the number and types of atoms on either side of the equation must be the same. We see that there are two N atoms on the reactants side and there are two N atoms on the products side. So the atoms on each side of the equation are same. i.e., the reaction is balanced.

Next, there are five O atoms on the reactants side, and six O atoms on the product side of the equation. We can balance the O atoms by multiplying with 2 in front of N_2O_5 on the reactants side. Now the total number of oxygen atoms on reactant side is 10 and products side is 6, number of nitrogen on reactant side is 4 and products side is 2.

$$2N_2O_5 \rightarrow N_2O_4 + O_2$$

We can balance the N atoms by multiplying with 2 in front of N_2O_4. Now the number of O atoms and N atoms in both reactant side and products side are balanced. The balanced chemical equation is,

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

3. What are chemical reactions? Classify them with examples.

Solution:

Chemical reaction is a process in which a substance (or substances) is changed into one or more new substance(s). To communicate with one another about chemical reactions, chemists have devised a standard way using chemical equations. A chemical equation uses chemical symbols to show what happens during a chemical reaction. The types of chemical reactions are given below.

Electron Transfer Reactions:

These are reactions in which electrons are transferred from one atom, *molecule*, or ion to another atom, molecule, or ion. The substance that provides the electrons becomes more positive as a result of the process; the substance that receives the electrons becomes more negative. Some electron transfer reactions are very easy to recognize. For example, the reaction of sodium and chlorine is an electron transfer process, because sodium becomes more positive and chlorine more negative in the process:

$$2Na_{(s)} + Cl_{2(g)} \text{--->} 2NaCl_{(s)}$$

Sodium is in the elemental (uncharged) form prior to reaction; after reaction, it exists as Na^+ ions in NaCl. Clearly, each sodium atom has lost one electron. At the same time, each Cl atom of Cl_2 has gained an electron to become Cl^-. The reaction of magnesium and oxygen is also an electron transfer process:

$$2Mg_{(s)} + O_{2(g)} \text{--->} 2MgO_{(s)}$$

Each magnesium atom loses two electrons; each oxygen atom accepts two electrons; electrons are therefore transferred from Mg to O.

Proton Transfer Reactions:

These are processes in which a proton, H^+, is transferred from one species to another. The species losing the proton is called an acid; the species gaining the proton is called a base. An example of a proton transfer reaction is shown below.

$$HCl_{(aq)} + Mg(OH)_{2(aq)} \text{--->} MgCl_{2(aq)} + H_2O_{(l)}$$

Here a proton, H^+, is transferred from HCl to the OH^- portion of magnesium hydroxide. Water is produced by combination of H^+ and OH^-; magnesium chloride is also produced.

$$H_2SO_{4(aq)} + Na_2CO_{3(aq)} \text{--->} Na_2SO_{4(aq)} + H_2CO_{3(aq)}$$

Here H_2SO_4 transfers two protons to CO_3^{2-} to produce H_2CO_3; sodium sulfate is also produced. If protons are transferred in a reaction, the reaction is an acid-base process.

Double Displacement Reactions:

In a double displacement process, the positive and negative parts of two reacting substances exchange: the positive part of one substance ends up with the negative part of the other. For example, the reactions below are double displacement processes:

$$NaCl_{(aq)} + AgNO_{3(aq)} \text{--->} NaNO_{3(aq)} + AgCl_{(s)}$$
$$BaCl_{2(aq)} + K_2SO_{4(aq)} \text{--->} KCl + BaSO_{4(s)}$$

You may notice that the proton transfer reactions are also double displacement reactions. This is certainly true. But because acid-base processes play such a central role in chemistry, chemists choose to classify them separately. We will stick on to this convention.

Now we will learn combustion reactions, which constitute an important subclass of electron transfer reactions.

Combustion Reactions:

In this section, we introduce and discuss an important category of chemical reactions: combustion reactions. A combustion reaction involves the reaction of a substance, element or compound, with oxygen, usually with the accompanying production of heat or light or sound energy. The balanced equations representing the combustion reactions of elemental phosphorus and of methane are shown in equation form below:

$4P_{(s)} + 5\ O_{2(g)} \text{--->} P_4O_{10(s)}$
$CH_{4(g)} + 2O_{2(g)} \text{--->} CO_{2(g)} + 2H_2O_{(g)}$

P_4O_{10} is called the oxide of phosphorus; similarly, CO_2 is an oxide of carbon, and H_2O is the oxide of hydrogen.

Problem Set:

1. **What is the difference between a chemical reaction and a chemical equation?**

Solution:

Chemical reaction is a process in which a substance (or substances) is changed into one or more new substances.

A chemical equation, then, is just the chemist's shorthand description of a reaction. In a chemical equation, the reactants are conventionally written on the left and the products on the right of the arrow:

$$\text{Reactants} \rightarrow \text{products}$$

2. **Balance the equation representing the reaction between N_2 and O_2 to yield NH_3**

$$\mathbf{N_2 + H_2 \rightarrow NH_3}$$

Solution:

The unbalanced equation is

$$N_2 + H_2 \rightarrow NH_3$$

In a balanced equation, the number and types of atoms on either side of the equation must be the same. We see that there are two N atoms on the reactants side and there is one N atom on the products side. We can balance the N atoms by placing a coefficient of 2 in front of the NH_3 on the products side.

$$N_2 + H_2 \rightarrow 2NH_3$$

There are two H atoms on the reactants side, and six H atoms on the product side of the equation. We can balance the H atoms by placing a coefficient of 3 in front of the H_2 on the reactant side. Now the atoms on each side of the equation are same. i.e., the reaction is balanced.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

3. **Balance the equation representing the reaction between iron (Fe) and oxygen (O_2) to yield Iron(III) oxide, Fe_2O_3.**

Solution:

The unbalanced equation is

$$Fe + O_2 \rightarrow Fe_2O_3$$

In a balanced equation, the number and types of atoms on either side of the equation must be the same. We see that there is one Fe atom on the reactants side and there are two Fe atoms on the product side. We can balance the Fe atoms by placing a coefficient of 2 in front of the Fe on the reactants side.

$$2\,Fe + O_2 \rightarrow Fe_2O_3$$

There are two O atoms on the reactants side, and three O atoms on the product side of the equation. We can balance the O atoms by placing a coefficient of $\frac{3}{2}$ in front of O_2 on the reactants side.

$$2\,Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3$$

This is a balanced equation. However, equations are normally balanced with the smallest set of whole number coefficients. Multiplying both sides of the equation by 2 gives whole number coefficients.

$$4\,Fe + 3\,O_2 \rightarrow 2\,Fe_2O_3$$

The equation is balanced. Also, the coefficients are reduced to the simplest set of whole numbers.

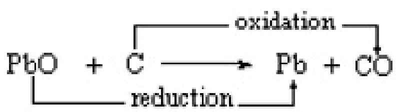
Stoichiometry

Oxidation number Concept

In our daily life we come across processes like rusting of iron articles, fading of colour of clothes, burning of combustible substances such as cooking gas, wood, coal *etc.* All such processes fall in the category of specific type of chemical reactions called reduction- oxidation reactions or *Red-ox reactions*. A large number of industrial processes like electroplating, manufacture of caustic soda, extraction of metals like aluminium and sodium ***etc.,*** are based on red-ox reactions. Red-ox reactions form the basis of *electrochemical* and *electrolytic cell*.

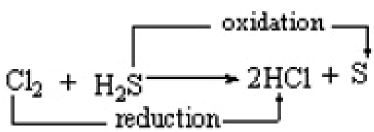
Oxidation and Reduction Reactions

Oxidation is a process of addition of oxygen or removal of hydrogen.
Reduction is the process of removal of oxygen or addition of hydrogen.
Examples:**Reaction of PbO on carbon.**



Here oxygen is being removed from lead oxide (PbO) and is being added to carbon C. Therefore PbO is reduced while C is oxidised.

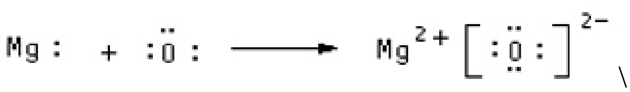
Reaction of H_2 S and Cl_2



Here hydrogen being removed from hydrogen sulphide (H_2S) and is being added to chlorine (Cl_2). Thus H_2S is oxidised and $Cl_2$is reduced.

Electronic concept of Oxidation and Reduction

Electrochemical reactions occur as a result of transference of electrons from one species to the other. For example, if magnesium is burnt in oxygen it gets oxidised to magnesium oxide (MgO). In the formation of magnesium oxide, two electrons from magnesium atom are transferred to oxygen atom.



The process of transference of electrons is described as *red-ox process*.

Oxidation

It is a process in which an atom or group of atoms taking part in chemical reaction loses one or more electrons. Loss of electrons results in the increase of positive charge or decrease in negative charge of the species.

For example :

$Na \rightarrow Na^{+} + e$ (*increase of positive charge*)
$Mg \rightarrow Mg^{2+} + 2\,e$ (*increase in positive charge*)
$Fe^{2+} \rightarrow Fe^{3+} + e$ (*increase of positive charge*)
$MnO_4^{2-} \rightarrow MnO_4^{-} + e$ (*decrease in negative charge*)
$[Fe(CN)_6\,]^{4-} \rightarrow [Fe(CN)_6\,]^{3-} + e$ (*decrease in negative charge*)

- The species which undergo the loss of electrons during the reactions are called *reducing agents* or *reductants.*
- MnO_4^{2-}, Fe^{2+}, and Mg are reducing agents in the above examples.

Reduction

It is a process in which an atom or group of atoms taking part in a chemical reaction *gains* one or more electrons. The gain of electrons results in the decrease of positive charge or increase in negative charge of the species.

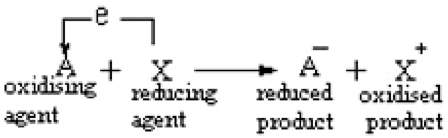
For example:

$Ag^{+} + e \rightarrow Ag$ (*decrease in positive charge*)
$Fe^{3+} + e \rightarrow Fe^{2+}$ (*decrease in positive charge*)
$[Fe(CN)_6]^{3-} + e \rightarrow [Fe(CN)_6]^{4-}$ (*increase in negative charge*)
$MnO_4^{-} + e \rightarrow MnO_4^{2-}$ (*increase in negative charge*)

- The species which undergo *gain* of electrons during the reactions are called oxidising agents *or oxidants*.
- In the above example, Ag^{+}, Fe^{3+}, $[Fe(CN)_6]^{3-}$ ions are oxidising agents.

Simultaneous occurrence of Oxidation and Reduction

In any process, oxidation can occur only if reduction is also taking place side by side and *vice versa.* Thus neither oxidation nor reduction can occur alone. That is why chemical reactions involving reduction-oxidation are called *red-ox* reactions. During the *red-ox reaction* there is transference of electrons from *reducing agent* to the *oxidising agent* as shown below :



For example, consider a reaction between zinc and copper ions :

$Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu(s)$

In this reaction, zinc lose electrons and are *oxidised*to zinc ions(Zn^{2+}) whereas cupric ions (Cu^{2+}) gain electrons and are *reduced* to copper atoms. The cupric ions act as oxidising agent and zinc act as reducing agent. In fact, the oxidising agent gets *reduced* while reducing agents *oxidised*during redox reactions.

Oxidation: *Loss of electrons.*
Reduction: *Gain of electrons*
Oxidising agent: *Species which gains electrons*
Reducing agent: *Species which loses electrons*

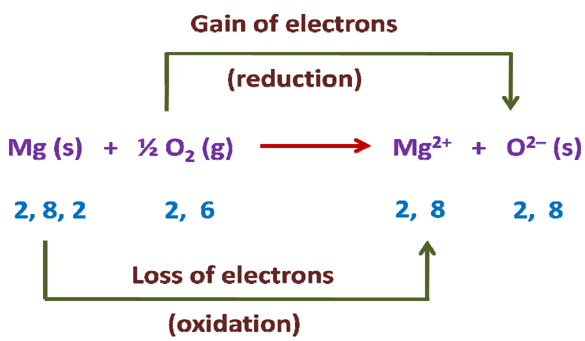
Competitive Electron Transfer Reactions

Example 1:

Magnesium burns in air with a brilliant white light giving white substance, magnesium oxide. The reaction is represented by the equation.

$$2\ Mg\ (s) + O_2\ (g) \rightarrow 2\ MgO\ (s)$$

This may be rewritten as an equation, indicating the electronic configuration of various atoms of the elements participating in the reaction.



In the above equation, magnesium gives up two electrons or transfers them to oxygen atom. This process can be considered to take place; in two separate steps one involved the loss of two electrons by the magnesium atom and the other the gain of the two electrons by oxygenatom.

Thus, $Mg \rightarrow Mg^{2+} + 2\ e^-$

$$\frac{1}{2}O_2 + 2\ e^- \rightarrow O^{2-}$$

"The reaction that involves loss of electrons is called an oxidation reaction and that involving gain of electrons is called a reduction reaction. The overall reaction is called as "oxidation – reduction". The number of electrons lost in the oxidation reaction is equal to the number of electrons gained in the reduction reaction. In the above reaction this number is equal to two.

Example 2:

When a piece of zinc metal is placed in a blue solution of copper nitrate, red metallic copper is deposited on the zinc, and at the same time the blue colourof the copper nitrate solution disappears.

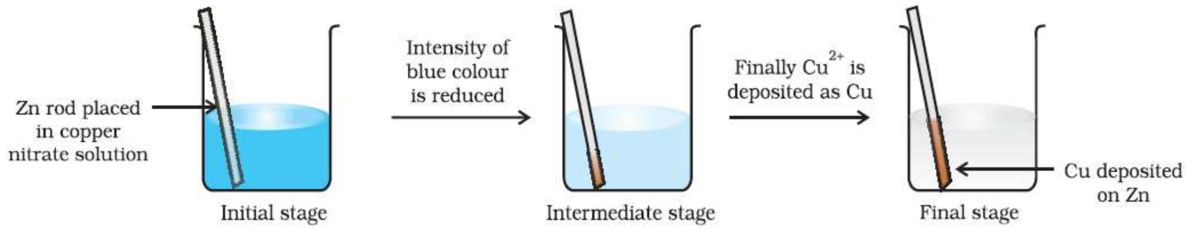


Fig.Redox reaction between zinc and aqueous solution of copper nitrate occurring in a beaker.

The reaction may be represented as

$$\text{Zn (s)} + \text{Cu}(\text{NO}_3)_2\text{(aq)} \rightarrow \text{Zn}(\text{NO}_3)_2\text{(aq)} + \text{Cu (s)}$$

Gain of electrons (reduction)

$$\text{Zn (s)} + \text{Cu}^{2+}\text{(aq)} \longrightarrow \text{Zn}^{2+}\text{(aq)} + \text{Cu (s)}$$

Loss of electrons (oxidation)

Hence Zn loses two electrons and forms Zn^{2+}, and thus undergoes oxidation while Cu^{2+} gains two electrons to form Cu, and undergoes reduction.Thus zinc is oxidized to Zn^{2+} ions and Cu^{2+} ions are reduced to metallic copper.

Let us extend electron transfer reaction to copper metal and silver nitrate solution in water and arrange a set-up as shown in following Fig.

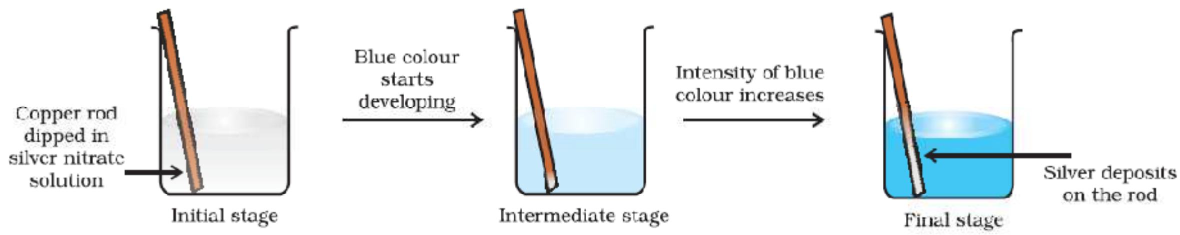


Fig: Red-ox reaction between copper and aqueous solution of silver nitrate occurring in a beaker.

The solution in the beaker develops blue colour due to the formation of Cu^{2+} ions on account of the reaction:

release of $2e^-$

$$\text{Cu(s)} + 2\text{Ag}^{+}\text{(aq)} \longrightarrow \text{Cu}^{2+}\text{(aq)} + 2\text{Ag(s)}$$

gain of $2e^-$ …..(2)

Here Cu(s) is oxidised to Cu^{2+}(aq) and Ag^{+}(aq) is reduced to Ag(s). Equilibrium greatly favoursthe products Cu^{2+}(aq) and Ag(s)Let us also compare the reaction of metallic cobalt placed in nickel sulphate solution. The reaction that occurs is :

release of $2e^-$

$$Co(s) + Ni^{2+}(aq) \longrightarrow Co^{2+}(aq) + Ni(s) \qquad \ldots\ldots (3)$$

gain of $2e^-$

At equilibrium, chemical tests reveal that both Ni^{2+} (aq) and Co^{2+}(aq) are present at moderate concentrations. In this case, neither the reactants [Co(s) and Ni^{2+} (aq)] nor products [Co^{2+}(aq) and Ni(s)] are greatly favoured.

By comparison we know that zinc releases electrons to copper and copper releases electrons to silver. The electron releasing tendency of the metals is in the order:

Zn > Cu > Ag

The competition for electrons between various metals helps us to design a class of cells, named as *galvanic cells* in which chemical reactions become the source of *electrical energy.*

Oxidation half and Reduction half reactions

Every reaction can be split up into half reactions, one representing loss of electrons *i.e.*, oxidation half-reaction, while other representing gain of electrons, *i.e.*, reduction half reaction. *Some examples are given below:*

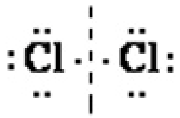
$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ (*complete reaction*)
$Zn - 2\,e \rightarrow Zn^{2+}$(*oxidation half reaction*)
$Cu^{2+} + 2\,e \rightarrow Cu$ (*reduction half reaction*)
$Sn^{2+} + 2\,Hg^{2+} \rightarrow Sn^{4+} + Hg_2{}^{2+}$(*complete reaction*)
$Sn^{2+} - 2\,e \rightarrow Sn^{4+}$ (*oxidation half*)
$2\,Hg^{2+} + 2\,e \rightarrow Hg\ 2^{2+}$ (*reduction half reaction*)

Oxidation number or Oxidation state:

Oxidation number (ON) of an element is defined as the residual charge which its atom appears to have when all other atoms from the molecule are removed as ions. ***Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that electron in a covalent bond belongsentirely to more electronegative element.***

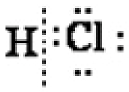
During the removal of atoms, the electrons are counted according to the following rules:

- Electrons shared between two similar atoms are divided equally between the sharing atoms. For example, in chlorine molecule (Cl_2) the electron pair is equally shared between two chlorine atoms. Therefore, one electron is counted with each chlorine atom as shown below:



Now there is no net charge on each atom of chlorine. In other words, oxidation number of chlorine in Cl_2 is zero.

- Electrons shared between two dissimilar atoms are counted with *more electronegative atom.* For example, in hydrogen chloride molecule chlorine is more electronegative than hydrogen. Therefore, the shared pair is counted towards chlorine atom as shown below:



As a result of this, chlorine gets one extra electron and acquires a unit negative charge. Hence oxidation number of chlorine is −1. On the other hand hydrogen atom without electron has a unit positive charge. Hence, oxidation number of hydrogen in hydrogen chloride is **+1**. Thus, atoms can have positive zero or negative value of oxidation numbers depending up on their state of combination. In fact, oxidation number is the charge assigned to the atom in a species according to some arbitrary rules as described below.

General rules for assigning Oxidation Number to an atom

The following rules are employed for determining oxidation number of the atoms.

1. The oxidation number of the element in the free or elementary state is always zero.
   For example
   Oxidation number of helium in He = 0
   Oxidation number of chlorine in Cl_2 = 0
   Oxidation number of sulphur in S_8 = 0
   Oxidation number of phosphorus in P_4= 0
2. The oxidation number of the element in the monoatomic ion is equal to the charge on the ion. For example, in K^+ Cl^-, the oxidation number of K is +1, while that of Cl is −1. In the similar way, oxidation number of all alkali metals (Li, Na, K, Rb, Cs and Fr)is + 1, while those of alkaline earth metals (Be, Mg, Ca, Sr, Ba and Ra) is +2 in their compounds.

3. The oxidation number of fluorine is −1 in all its compounds.
4. Hydrogen is assigned oxidation number of +1 in its compounds except in metal hydrides like NaH, MgH_2, CaH_2, LiH in which its oxidation number is −1.
5. Oxygen is assigned oxidation number of - 2 in most of its compounds, however in peroxides like H_2O_2, BaO_2, and Na_2O_2*etc*. Its oxidation number is −1. Similarly the exception also occurs in compounds of fluorine like OF_2 and O_2F_2 in which the oxidation number of oxygen is+2 and + 1 respectively. In super oxides like KO_2 it is – 1/2.

6. The algebraic sum of the oxidation numbers of all the atoms in neutral molecule is zero. But in the case of compound ion, the sum of the oxidation numbers of all its atoms is equal to the charge on the ion.

STOCK NOTATIONS

The names of compounds are written by the use of O. N's of the metal atoms. The O.N's are written in the form of Roman numerals in brackets after the name of the metal. For example, O.N of copper in Cu_2O is +1 and that in CuO is +2. Thus their name are copper (I) oxide and copper(II)oxide. This system of naming the compounds by the use of the oxidation numbers of representative metal atoms was proposed by *Albert Stock* and is referred as *System of Stock Notations* after his name. Some more examples are given below.

Cr_2O_3	:	Chromium (III)Oxide.
$SnCl_2$	:	Tin (II) chloride
V_2O_5	:	Vanadium (V) Oxide.
$SnCl_4$	:	Tin (IV) Chloride
$Fe_2(SO_4)_3$	:	Iron (III)sulphate
$FeSO_4$	:	Iron(II) sulphate

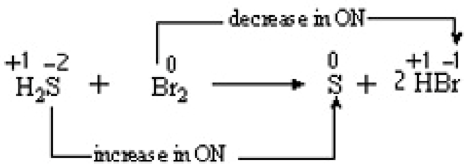
Although the Stock Notations are generally used for metals, yet some compounds of non-metals have been named by this system. Some examples are given below:

SO_2	:	Sulphur (IV) Oxide
SO_3	:	Sulphur (VI) Oxide

Oxidation and Reduction in terms of Oxidation Number

Oxidation is defined as a chemical process in which oxidation number of the element increases. **Reduction** is defined as the chemical process in which oxidation number of the element decreases.

Consider the reaction between hydrogen sulphide and bromine to give hydrogen bromide and sulphur.



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

Oxidising agent

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

Reducing agent

Reducing agent is a substance which undergoes the increase in the oxidation number of one or more of its elements. In the above example H_2S is the reducing agent while Br_2 is the oxidising agent.

TYPES OF REDOX REACTIONS

1. **Combination reactions**

A combination reaction can be denoted in the manner:
$A + B \rightarrow C$

Either A and B or both A and B must be in elemental form for such a reaction to be a red-ox reaction. All combustion reactions, which make use of elemental dioxygen, as well as other reactions involving elements other than dioxygen, are red-ox reactions. Some important examples of this category are:

$$\overset{0}{C}(s) + \overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4\ -2}{CO_2}(g)$$

$$3\overset{0}{Mg}(s) + \overset{0}{N_2}(g) \xrightarrow{\Delta} \overset{+2\ -3}{Mg_3N_2}(s)$$

$$\overset{-4+1}{CH_4}(g) + 2\overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4\ -2}{CO_2}(g) + 2\overset{+1\ -2}{H_2O}(l)$$

2. **Decomposition reactions**

Decomposition reactions are the opposite of combination reactions. A decomposition reaction leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state. Examples of this class of reactions are:

$$2\overset{+1\ -2}{H_2O}(l) \xrightarrow{\Delta} 2\overset{0}{H_2}(g) + \overset{0}{O_2}(g)$$

$$2\overset{+1\ -1}{NaH}(s) \xrightarrow{\Delta} 2\overset{0}{Na}(s) + \overset{0}{H_2}(g)$$

$$2\overset{+1\ +5\ -2}{KClO_3}(s) \xrightarrow{\Delta} 2\overset{+1\ -1}{KCl}(s) + 3\overset{0}{O_2}(g)$$

It may be noted that there is no change in the oxidation number of hydrogen in methane under *combination reactions* and that of potassium in potassium chlorate (above). This may be noted here that all *decomposition reactions are not red-ox reactions.* For example decomposition of calcium carbonate is not a red-ox reaction.

$$\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O_3}(s) \xrightarrow{\Delta} \overset{+2}{Ca}\overset{-2}{O}(s) + \overset{+4}{C}\overset{-2}{O_2}(g)$$

3. **Displacement reactions**

In displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be noted as:

$$\mathbf{X + YZ \rightarrow XZ + Y}$$

Displacement reactions fit into two categories; metal displacement and non-metal displacement.

(a) Metal displacement: A metal in a compound can be displaced by another metal in the uncombined state. Metal displacement reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores.

A few such examples are:

$$\overset{+2}{Cu}\overset{+6}{S}\overset{-2}{O_4}(aq) + \overset{0}{Zn}(s) \rightarrow \overset{0}{Cu}(s) + \overset{+2}{Zn}\overset{+6}{S}\overset{-2}{O_4}(aq)$$

$$\overset{+5}{V_2}\overset{-2}{O_5}(s) + 5\overset{0}{Ca}(s) \xrightarrow{\Delta} 2\overset{0}{V}(s) + 5\overset{+2}{Ca}\overset{-2}{O}(s)$$

$$\overset{+3}{Cr_2}\overset{-2}{O_3}(s) + 2\overset{0}{Al}(s) \xrightarrow{\Delta} \overset{+3}{Al_2}\overset{-2}{O_3}(s) + 2\overset{0}{Cr}(s)$$

In each case, reducing metal is a better reducing agent than the one that is being reduced which evidently shows more capability to lose electrons as compared to the one that is reduced.

(b) Non-metal displacement

The non-metal displacement red-ox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement. All alkali metals and some alkaline earth metals (Ca, Sr and Ba) which are very good *reductants,* will displace hydrogen from cold water.

$$2\overset{0}{Na}(s) + 2\overset{+1}{H_2}\overset{-2}{O}(l) \rightarrow 2\overset{+1}{Na}\overset{-2}{O}\overset{+1}{H}(aq) + \overset{0}{H_2}(g)$$

$$\overset{0}{Ca}(s) + 2\overset{+1}{H_2}\overset{-2}{O}(l) \rightarrow \overset{+2}{Ca}(\overset{-2}{O}\overset{+1}{H})_2(aq) + \overset{0}{H_2}(g)$$

Less active metals such as magnesium and iron react with steam to produce dihydrogen gas.

$$\overset{0}{Mg}(s) + 2\overset{+1}{H_2}\overset{-2}{O}(l) \xrightarrow{\Delta} \overset{+2}{Mg}(\overset{-2}{O}\overset{+1}{H})_2(s) + \overset{0}{H_2}(g)$$

$$2\overset{0}{Fe}(s) + 3\overset{+1}{H_2}\overset{-2}{O}(l) \xrightarrow{\Delta} \overset{+3}{Fe_2}\overset{-2}{O_3}(s) + 3\overset{0}{H_2}(g)$$

Many metals including those which do not react with cold water are capable of displacing hydrogen from acids. Dihydrogen from acids may even be produced by such metals which do not react with steam. A few examples for the displacement of hydrogen from acids are:

$$\overset{0}{Zn}(s) + 2\overset{+1}{H}\overset{-1}{Cl}(aq) \rightarrow \overset{+2}{Zn}\overset{-1}{Cl_2}(aq) + \overset{0}{H_2}(g)$$

$$\overset{0}{Mg}(s) + 2\overset{+1}{H}\overset{-1}{Cl}(aq) \rightarrow \overset{+2}{Mg}\overset{-1}{Cl_2}(aq) + \overset{0}{H_2}(g)$$

$$\overset{0}{Fe}(s) + 2\overset{+1}{H}\overset{-1}{Cl}(aq) \rightarrow \overset{+2}{Fe}\overset{-1}{Cl_2}(aq) + \overset{0}{H_2}(g)$$

The above reactions are used to prepare dihydrogen gas in the laboratory. Here, the reactivity of metals is reflected in the rate of hydrogen gas evolution , which is the slowest for the least active metal Fe, and the fastest for the most reactive metal Mg. Very less active metals , which may occur in the native state such as silver (Ag) and gold (Au) do not react even with hydrochloric acid.

The metals Zn, Cu and Ag through tendency to lose electrons show their reducing activity in the order *Zn* > *Cu* > *Ag*. Like metals, activity series also exists for the halogens. The power of these elements as *oxidising agents* decreases as we move down from fluorine to iodine in group 17 of the periodic table. This implies that fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it displaces the oxygen of water:

$$2\overset{+1\;-2}{H_2O}\,(l) + 2\overset{0}{F_2}\,(g) \rightarrow 4\overset{+1\;-1}{HF}(aq) + \overset{0}{O_2}(g)$$

It is for this reason that the displacement reactions of chlorine, bromine and iodine using fluorine are not generally carried out in aqueous solution. On the other hand, chlorine can displace bromide and iodide ions in an aqueous solution as shown below:

$$\overset{0}{Cl_2}\,(g) + 2\overset{+1\;-1}{KBr}\,(aq) \rightarrow 2\,\overset{+1\;-1}{KCl}\,(aq) + \overset{0}{Br_2}\,(l)$$

$$\overset{0}{Cl_2}\,(g) + 2\overset{+1-1}{KI}\,(aq) \rightarrow 2\,\overset{+1\;-1}{KCl}\,(aq) + \overset{0}{I_2}\,(s)$$

As Br_2 and I_2 are coloured and dissolve in CCl_4, can easily be identified from the colour of the solution. The above reactions can be written in ionic form as:

$$\overset{0}{Cl_2}\,(g) + 2\overset{-1}{Br^-}\,(aq) \rightarrow 2\overset{-1}{Cl^-}\,(aq) + \overset{0}{Br_2}\,(l)$$

$$\overset{0}{Cl_2}\,(g) + 2\overset{-1}{I^-}\,(aq) \rightarrow 2\overset{-1}{Cl^-}\,(aq) + \overset{0}{I_2}\,(s)$$

The reactions (above) form the basis of identifying Br - and I - in the laboratory through the test popularly known as '**Layer *test*** '. Bromine displace iodide ion in solution.

$$\overset{0}{Br_2}\,(l) + 2\overset{-1}{I^-}\,(aq) \rightarrow 2\overset{-1}{Br^-}\,(aq) + \overset{0}{I_2}\,(s)$$

The halogen displacement reactions have a direct industrial application. The recovery of halogens from their halides requires an oxidation process, which is represented by:

$$\mathbf{2\,X_2 \rightarrow X_2 + 2e^-}$$

here X denotes a halogen element. Whereas chemical means are available to oxidise Cl^-, Br^- and I^-, as fluorine is the strongest oxidisingagent ; there is no way to convert F^- ions to F_2 by chemical means. The only way to achieve F_2 from F^- is to oxidiseelectrolytically.

4. **Disproportionation reactions**

Disproportionation reactions are a special type of red-ox reactions. In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substance is in the intermediate oxidation state; and both higher and lower oxidation states of that element are formed in the reaction. The decomposition of hydrogen peroxide is a familiar example of the reaction, where oxygen experience disproportionation.

$$\overset{+1\;-1}{2H_2O_2}(aq) \rightarrow \overset{+1\;-2}{2H_2O}(l) + \overset{0}{O_2}(g)$$

Here the oxygen of peroxide, which is present in −1 state, is converted to zero oxidation state in O_2 and decreases to −2 oxidation in water.

Phosphorous, sulphur and chlorine undergo disproportionation in the alkaline medium as shown below:

$$\overset{0}{P_4}(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow \overset{-3}{P}H_3(g) + 3H_2\overset{+1}{P}O_2^-$$

$$\overset{0}{S_8}(s) + 12\ OH^-(aq) \rightarrow 4\overset{-2}{S^{2-}}(aq) + 2\overset{+2}{S_2}O_3^{2-}(aq) + 6H_2O(l)$$

$$\overset{0}{Cl_2}(g) + 2\ OH^-(aq) \rightarrow \overset{+1}{Cl}O^-(aq) + \overset{-1}{Cl^-}(aq) + H_2O(l) \ ....(1)$$

The above reaction describes the formation of household bleaching agents. The hypochlorite ion (ClO^-) formed in the reaction oxidises the colour bearing stains of the substance to colourless compounds.

Bromine and iodine follow the same trend as exhibited by chlorine in reaction (1), fluorine shows deviation from this behaviour when it reacts with alkali. The reaction that takes place in the case of fluorine is as follows.

$$2\ F_2(g) + 2\ OH^-(aq) \rightarrow 2\ F^-(aq) + OF_2(g) + H_2O(l)$$

Fluorine in the above reaction will attack water to produce some oxygen also . This departure shown by fluorine is due its most electronegative character. It cannot exhibit any positive oxidation state. This means that among halogens, fluorine does not show disproportionation tendency.

Nitrogen and its compounds	**Oxidation number of nitrogen**
NH_4^+	– 3
NH_3	– 3
N_2H_4	– 2
NH_2OH	– 1
N_2	0
NO	+2
N_2O_3	+ 3
NO_2	+ 4
N_2O_5	+ 5

Calculation of oxidation number:

1. $Ba(NO_3)_2$

   Steps to solve the problem:

   - Barium ion = Ba^{2+}
   - Oxidation number for Ba = +2
   - Oxygen has a rule....-2 in most compounds
   - Oxidation number for O = -2
   - By using the above values we will find the oxidation number of N
   - Let x = Oxidation number for nitrogen
   - Oxidation number of N is calculated by the formula, Sum of oxidation numbers = 1(+2) + 2(x) + 6(-2) = 0
   - x = +5

2. NF_3

Steps to solve the problem:

- Oxidation number of F = -1
- find the oxidation number of N
- Let x = oxidation number of N
- Sum of oxidation numbers = 1(x) + 3(-1) = 0
- x = +3

SAQs:

1. In a reaction, loss of electrons is termed as
   a) Oxidation
   b) Reduction
   c) Ionization
   d) Both a) and b)

Solution: a)

2. A compound is said to be reduced, when its oxidation number is----------
   a) Increased
   b) Decreased
   c) Either increased or decreased
   d) Remaining constant

Solution: b)

3. Oxidation number of C in CH_4 is
   a) +1

b) +4
c) -4
d) -1

Solution: c)

4. Calculate the oxidation number of sulphur in S_8.

Solution:

This is a polyatomic molecule, but it is in the elementary state. Therefore, the oxidation number of sulphur in this molecule is zero.

5. Calculate the oxidation number of sulphur in H_2SO_4.

Solution:

Let the oxidation number of sulhpur in H_2SO_4 be equal to x.

Oxidation number of hydrogen per atom = + 1.

Oxidation number of oxygen per atom = – 2

Total charge on the molecule is zero.

i.e. 2 (+1) + 1(x) + 4 (-2) = 0

2 + x – 8 = 0

x = 8 – 2 = + 6.

∴ Oxidation number of sulphur in H_2SO_4 is + 6.

6. What is the oxidation number of chromium in $Cr_2O_7^{2-}$ ion?

Solution:

Oxidation number of oxygen per atom = – 2

Oxidation number of Chromium = x

Total charge on the ion is −2.

i.e.,2(x) + 7(-2) = – 2

2x – 14 = – 2

2x = – 2 + 14

$2x = 12$

$x = +6$

∴ The oxidation number of chromium in $Cr_2O_7^{2-}$ is + 6.

Problem Set:

1. Calculate the oxidation number of manganese in MnO_4^{2-} ion.

Solution:

Oxidation number of oxygen = – 2

Oxidation number manganese = x

Total charge on the ion is −2.

i.e., 1(x) + 4(-2) = – 2

x – 8 = – 2

x = – 2 + 8 = + 6

∴ The oxidation number of manganese in manganate ion MnO_4^{2-} is +6.

2. Calculate the oxidation number of manganese in permanganate ion (MnO_4^-)

Solution:

Oxidation number of oxygen = – 2

Oxidation number of manganese = x

Total charge on the ion is -1.

i.e.,1(x) + 4(-2) = – 1

x – 8 = – 1

x = – 1 + 8 = + 7.

∴ The oxidation number of manganese in permanganate ion is + 7.

3. Calculate the oxidation number of chromium in Cr_2O_3.

Solution:

Oxidation number of oxygen = – 2

Oxidation number of chromium = x

Total charge on the molecule is zero.

i.e., $2(x) + 3(-2) = 0$
$2x – 6 = 0$
$2x – 6 = 0$
$2x = +6$
$x = + 3.$

∴ The oxidation number of chromium in Cr_2O_3 is + 3.

4. Calculate the oxidation number of Fe in $[Fe(H_2O)_6]^{3+}$.

Solution:

Oxidation number of $H_2O = 0$ (since $[+2+(-2)]=0$)

Oxidation number of iron (Fe) = x

Total charge on the molecule $[Fe(H_2O)_6]^{3+}$ is +3.

i.e., $1(x) + 0 = +3$
$x = + 3$

The oxidation number of Fe in $[Fe(H_2O)_6]^{3+}$ is + 3.

Exercise Questions:

1. Calculate the oxidation number of S in $Na_2S_4O_6$. (Ans: +2.5)
2. Calculate the oxidation number of Cr in $[Cr(NH_3)_6]Cl_3$. (Ans: +3)
3. Calculate the oxidation number of Fe in $[Fe(H_2O)_5(NO)^{+}]^{+2}$. (Ans: +1)
4. Calculate the oxidation number of Cl atom present in Ca(OCl)Cl (bleaching powder). (Ans: +1 , -1)
5. Explain competitive electron transfer reactions?
6. What are the types of red-ox reactions? Explain the reactions with oxidation number concept.

Solutions:

1.

Oxidation number of oxygen = – 2

Oxidation number of sodium = +1

Oxidation number of sulphur = x

Total charge on the molecule is zero.

i.e. 2(+1) + 4(x) + 6(-2) = 0
2+4x – 12 = 0
4x – 10 = 0
4x = + 10
x = + 2.5.

The oxidation number of sulphur in $Na_2S_4O_6$ is + 2.5.

2.

Oxidation number of chlorine = – 1

Oxidation number of NH_3 = 0 (since [−3+3(+1)]=0)

Oxidation number of chromium (Cr) = x

Total charge on the molecule $[Cr(NH_3)_6]Cl_3$ is zero.

i.e., 1(x) + 0 + 3(−1) = 0
x – 3 = 0
x = + 3

The oxidation number of chromium in $[Cr(NH_3)_6]Cl_3$ is + 3.

3.

Oxidation number of $(NO)^+$ = +1

Oxidation number of H_2O = 0 (since [2(+1) + (−2)]=0)

Oxidation number of Iron (Fe) = x

Total charge on the ion $[Fe(H_2O)_5(NO)^+]^{+2}$ is +2.

i.e., x + 0 + (+1) = +2
x = 2 - 1

$x = +1$

The oxidation number of Iron in $[Fe(H_2O)_5(NO)^+]^{+2}$ is + 1.

4.

Oxidation number of $(OCl)^-$ that is from HOCl = -1

Oxidation number of Cl present as $(OCl)^-$ is $(-2 + x = -1)$ or $x = +1$

Oxidation number of Ca = +2

Oxidation number of Cl = x

Total charge on the Ca(OCl)Cl is zero.

i.e., $+2 - 1 + x = 0$

$x = -1$

Thus two Cl atoms are present in Ca(OCl)Cl as +1 and −1.

Stoichiometry

Balancing of Red-ox reactions by ion-electron method

Balancing red-ox reactions:

A chemical reaction is necessarily represented as a balanced equation. To get a balanced equation two different methods can be adopted. Both the methods are based on the calculation of oxidation numbers of the elements constituting the reactants and the products. The methods are

i. Oxidation number method
ii. Ion – electron method or half reaction method.

The first method is based on the change in the oxidation number of the reductant and the oxidant and the second method is based on splitting the red-ox reaction into two half reactions one involving oxidation and another involving reduction. Both methods work very well.

Now let us discuss balancing of a chemical reaction by Ion – electron method.

Balancing of a reaction by this method is done in the following stages.

1. Write an ionic equation with the participating substances. i.e., reactants and products. Locate the oxidation and reduction reactions in it.
2. The oxidation half reaction and the reduction half reaction are written separately.
3. Each of the half reactions is separately balanced according to the following steps.
   a. Balance all the elements, except hydrogen and oxygen.
   b. To balance hydrogen atoms, a necessary number of hydrogen ions (H^+ ions) are added on the side deficient in hydrogen atoms, if the reaction takes place in acid medium.
   c. If the reaction takes place in alkaline medium, the hydrogen atoms are balanced by adding necessary number of water (H_2O) on the side deficient in hydrogen.
   d. In acid medium, the oxygen atoms are balanced by adding necessary number of H_2O molecules on the side deficient in oxygen.
   e. If the reaction takes place in alkaline medium, the oxygen atoms are balanced by adding necessary number of OH^- ions on the side deficient in oxygen.
   f. The operations b), c), d) and e)are repeated until the hydrogen atoms and oxygen atoms are perfectly balanced in both the half reactions.
   g. Balance the negative charges by adding necessary number of electrons on the side deficient in negative charges.
   h. The two half reactions are multiplied by suitable integers so as to get identical number of electrons participating in each of the half reactions.

i. The balanced half reactions are added in such a manner as to cancel the number of electrons involved.
j. Needless to say that the equation thus obtained is completely balanced with respect to atoms as well as charges.

Example – 1:

Balance the following chemical reaction by ion – electron method.

$$Cr_2O_7^{2-} + NO_2^- \rightarrow Cr^{3+} + NO_3^- \quad \text{in acid medium}$$

Solution:

The oxidation is NO_2^- to NO_3^- since the oxidation state of nitrogen atom increases from +3 to +5

$\therefore$ The oxidation half reaction is $NO_2^- \rightarrow NO_3^-$

The reduction is $Cr_2O_7^{-2}$ to Cr^{+3} since the oxidation state of Cr decreases from +6 to +3. The reduction half reaction is $Cr_2O_7^{-2} \rightarrow Cr^{+3}$

Write the two half reactions as shown below

Reduction half reaction oxidation half reaction

$$Cr_2O_7^{-2} \rightarrow Cr^{+3} NO_2^- \rightarrow NO_3^-$$

Balance all the other elements. Except H_2 and O_2

$$Cr_2O_7^{-2} \rightarrow 2\,Cr^{+3} NO_2^- \rightarrow NO_3^-$$

Balance hydrogen's by adding H^+ ions as the reaction takes place in acid medium.

No hydrogens are present. So need balanced H – atoms.

Balance oxygens by adding necessary number of H_2O molecules on the side deficient in oxygen.

$$Cr_2O_7^{-2} \rightarrow 2\,Cr^{+3} + 7\,H_2O NO_2^- + H_2O \rightarrow NO_3^-$$

Balance the hydrogens by adding H^+ ions on the side deficient in hydrogens.

$14\,H^+ + Cr_2O_7^{-2} \rightarrow 2\,Cr^{+3} + 7\,H_2O \qquad NO_2^- + H_2O \rightarrow NO_3^- + 2\,H^+$

Balance the negative charges by adding electrons on the side deficient in negative charges.

$$14\,H^+ + Cr_2O_7^{-2} + 6\,e^- \rightarrow 2\,Cr^{+3} + 7\,H_2O NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$

Multiplying the two half reactions with suitable integers to equalize the number of electrons participating in each of the half reactions.

$1 \times [6e^{-}+14H^{+}+Cr_2O_7^{-2}] \rightarrow 2Cr^{+3}+7H_2O$ $[NO_2^{-}+H_2O \rightarrow NO_3^{-}+2H^{+}+2e^{-}] \times 3$

Adding the two half reactions, the overall balanced reaction is obtained.

$$\boxed{Cr_2O_7^{-2} + 3NO_2^{-} + 8\,H^{+} \rightarrow 2\,Cr^{+3} + 4\,H_2O + 3\,NO_3^{-}}$$

Example – 2:

Balance the following chemical reaction by ion – electron method

In alkaline medium

$$P_4 \rightarrow PH_3 + H_2PO_2^{-}$$

Solution:

In the reaction P_4 undergoes both oxidation and reduction

The oxidation half reaction is given by,

$$P_4 \rightarrow H_2PO_2^{-}$$

Here the oxidation state of Phosphorousincreases from '0' to +1.

The reduction half reaction is

$$P_4 \rightarrow PH_3$$

Here the oxidation state of Phosphorous decreasesfrom '0' to −3

Write the two half reactions as shown below.

Reduction half reaction oxidation half reaction

$P_4 \rightarrow PH_3$ $P_4 \rightarrow H_2PO_2^{-}$

Balance all the other elements except H_2 and O_2

$P_4 \rightarrow 4\,PH_3$ $P_4 \rightarrow 4\,H_2PO_2^{-}$

Balance the hydrogen atoms by adding necessary number of H_2O molecules on the side deficient in hydrogen's.

$P_4 + 6\,H_2O \rightarrow 4\,PH_3$ $P_4 + 4\,H_2O \rightarrow 4\,H_2PO_2^{-}$

Balance the oxygen atoms by adding necessary number of OH^- ions on the side deficient in oxygen atoms.

$P_4 + 6\,H_2O \rightarrow 4\,PH_3 + 6\,OH^-$ $\qquad$ $P_4 + 4\,H_2O + 4\,OH^- \rightarrow 4\,H_2PO_2^-$

Repeating the balancing of hydrogen and oxygen atoms alternatively

$P_4 + 6\,H_2O \rightarrow 4\,PH_3 + 6\,OH^-$ $\qquad$ $P_4 + 4\,H_2O + 4\,OH^- \rightarrow 4\,H_2PO_2^-$

1st time $+3H_2O \rightarrow + 3OH^-$ $\qquad$ 1st time $+2OH^- \rightarrow +2H_2O$

2nd time $+3H_2O \rightarrow +3\,OH^-$ $\qquad$ 2nd time $+2OH^- \rightarrow +2H_2O$

Adding to get balanced half reactions

$P_4+12H_2O \rightarrow 4PH_3+12OH^-$ $\qquad$ $P_4+8OH^- \rightarrow 4\,H_2PO_2^-$

Balance the charges by adding electrons on the side deficient in negative charges.

$P_4+12H_2O+12e^- \rightarrow 4PH_3+12OH^-$ $\qquad$ $P_4+8OH^- \rightarrow 4\,H_2PO_2^-+4e^-$

Multiply the half reactions with suitable integers.

$1 \times [P_4+12H_2O+12e^- \rightarrow 4PH_3+12OH^-]$ and

$3 \times [P_4+8OH^- \rightarrow 4\,H_2PO_2^-+4e^-] = 3P_4+24OH^- \rightarrow 12\,H_2PO_2^-+12e^-$

Adding the two half reactions and then simplifying we get,

$P_4+12H_2O+3P_4+24OH^- \rightarrow 4PH_3+12OH^-+12\,H_2PO_2^-$

⇨ $4P_4+12H_2O+12OH^- \rightarrow 4PH_3+12\,H_2PO_2^-$

⇨ $\boxed{P_4 + 3\,H_2O + 3\,OH^- \rightarrow PH_3 + 3\,H_2PO_2^-}$

Assignment questions:

1. To balance a chemical equation, how many systematic methods can be possible? What are they?
2. Write the postulates followed in the balancing of reactions by ion – electron method.
3. Balance oxidation of NO_2^- with $Cr_2O_7^{-2}$ in acid medium (ion – electron method)
4. Balance the following reaction in basic medium (ion – electron method)

$$P_4 \rightarrow PH_3 + H_2PO_2^-$$

SAQs:

1. Ion electron method is also known as,
    a. Oxidation number method
    b. Half reaction method
    c. Both a) and b)
    d. Neither a) nor b)

Solution: b)

2. While balancing,reaction is carried out in presence of alkali; oxygen atoms are balanced by adding on the side deficient in oxygen with
    a. H_2O
    b. OH^- ion
    c. Both a) and b)
    d. O^{-2} ion

Solution: b)

3. In balancing an equation in acidic medium, hydrogen is balanced by adding necessary number of
    a. H^+ ions
    b. OH^- ion
    c. Both a) and b)
    d. Neither a) nor b)

Solution: a)

LAQs:

1. Balance the equation $H_2SO_{4(aq)} + HBr_{\,(aq)} \longrightarrow SO_{2(g)} + Br_2$

Solution:

Write the skeleton equation in the ionic form for the reaction. Both H_2SO_4 and HBr are strong acids. They ionize in solutions. Therefore

The reaction is written as

$$\underset{+6}{2\,H^+(aq) + SO_4^{2-}(aq)} + H^+(aq) + \underset{-1}{Br^-(aq)} \rightarrow \underset{+4}{SO_2(g)} + \underset{0}{Br_2(I)}$$

The half reactions are

Oxidation is $Br^- \longrightarrow Br_2$ and reduction is $SO_4^{2-} \rightarrow SO_2$

Reduction half reaction	**Oxidation half reaction**
• $SO_4^{2-} \rightarrow SO_2$ • $SO_4^{2-} \rightarrow SO_2$ • $SO_4^{2-} \rightarrow SO_2 + 2\,H_2O$ (Balancing O) • $SO_4^{2-} + 4\,H^+ \rightarrow SO_2 + 2\,H_2O$ (Balancing H) • $SO_4^{2-} + 4\,H^+ + 2\,e^- \rightarrow SO_2 + 2\,H_2O$ (Balancing and equalizing charges)	• $Br^- \rightarrow Br_2$ • $2\,Br^- \rightarrow Br_2$ (Balancing Br^-) • $2\,Br^- \rightarrow Br_2$ • $2\,Br^- \rightarrow Br_2$ • $2\,Br^- \rightarrow Br_2 + 2\,e^-$ (balancing and equalizing charges)

$2\,Br^- + SO_4^{2-} + 4\,H^+ \rightarrow Br_2 + SO_2 + 2\,H_2O$ (Final Balanced equation)

2. Write the balanced ionic equation which represents the oxidation of iodide ion(I^-) by permanganate ion in basic medium to give iodine (I_2) and manganese dioxide (MnO_2).

Solution:

The skeleton equation is written as

$$\overset{+7}{MnO_4^-} + \overset{-1}{I^-} \rightarrow \overset{+4}{MnO_2} + \overset{0}{I_2}$$

The oxidation half reaction is $I^- \rightarrow I_2$ (oxidation no. changes from – 1 to 0)

The reduction half reaction is $MnO_4^- \rightarrow MnO_2$ (oxidation no. changes from +7 to +4)

Hence the two half reactions are as follows:

Reduction half reaction	**Oxidation half reaction**
• $MnO_4^- \rightarrow MnO_2$ • $MnO_4^- \rightarrow MnO_2$ (Mn atoms are already balanced) • $MnO_4^- \rightarrow MnO_2 + 2\,OH^-$ (Oxygen atoms balanced)	• $I^- \rightarrow I_2$ • $2I^- \rightarrow I_2$ (I atoms are balanced) • $2I^- \rightarrow I_2$ (Oxygen atoms are not present)

• $MnO_4^- + 2\,H_2O \rightarrow MnO_2 + 2\,OH^- + 2\,OH^-$ (H – atoms and O atoms are balanced in basic medium) • $MnO_4^- + 2\,H_2O + 3\,e^- \rightarrow MnO_2 + 4\,OH^-$ (Charges balanced) • $2(MnO_4^- + 2H_2O + 3\,e^- \rightarrow MnO_2 + 4OH^-)$ [Multiplying above equation with 2] • $2\,MnO_4^- + 4\,H_2O + 6\,e^- \rightarrow 2\,MnO_2 + 8\,OH^-$	• $2I^- \rightarrow I_2$ (Hydrogen atoms are not present) • $2I^- \rightarrow I_2 + 2e^-$ (Charges balanced) • $3\,(2I^- \rightarrow I_2 + 2e^-)$ [Multiplying above equation with 3, then electrons balanced] • $6I^- \rightarrow 3I_2 + 6e^-$

Adding

$2\,MnO_4^- + 4\,H_2O + 6\,I^- \rightarrow 2\,MnO_2 + 8\,OH^- + 3\,I_2$ (Balanced equation)

Problem Set:

1. Write the balanced equation for the oxidation of sulphite ions to sulphate ions (in acid medium) by permanganate ions.

Solution:

The ionic skeleton reaction is

$$\overset{+7}{MnO_4^-} + \overset{+4}{SO_3^{2-}} \rightarrow \overset{+2}{Mn^{2+}} + \overset{+6}{SO_4^{2-}}$$

The oxidation half reaction $SO_3^{2-} \rightarrow SO_4^{2-} (+4 \text{ to } +6)$

The reduction half reaction $MnO_4^- \rightarrow Mn^{2+} (+7 \text{ to } +2)$

Reduction half reaction	**Oxidation half reaction**
• $MnO_4^- \rightarrow Mn^{2+}$ • $MnO_4^- \rightarrow Mn^{2+}$ (Mn is already balanced) • $MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O$ (O is balanced)	• $SO_3^{2-} \rightarrow SO_4^{2-}$ • $SO_3^{2-} \rightarrow SO_4^{2-}$ (S is already balanced) • $SO_3^{2-} + H_2O \rightarrow SO_4^{2-}$ (O is balanced) • $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2\,H^+$

• $MnO_4^- + 8\,H^+ \rightarrow Mn^{2+} + 4\,H_2O$ (H balanced in acid medium) • $MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$ (Charges balanced) • $2\,(MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O)$ (Electrons balanced) • $2\,MnO_4^- + 16\,H^+ + 10\,e^- \rightarrow 2\,Mn^{2+} + 8\,H_2O$	(H balanced in acid medium) • $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2\,H^+ + 2\,e^-$ (Charges balanced) • $5\,(SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2\,H^+ + 2\,e^-)$ (Electrons balanced) • $5SO_3^{2-} + 5H_2O \rightarrow 5\,SO_4^{2-} + 10H^+ + 10e^-$

Adding

- $5\,SO_3^{2-} + 2\,MnO_4^- + 16\,H^+ + 5H_2O \rightarrow 5\,SO_4^{2-} + 10\,H^+ + 2\,Mn^{2+} + 8\,H_2O$

or

- $2\,MnO_4^- + 5\,SO_3^{2-} + 6\,H^+ \rightarrow 2\,Mn^{2+} + 5\,SO_4^{2-} + 3\,H_2O$

2. Balance the following equation $Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} I^- + CrO_4^{-2}$

Solution:

Oxidation half reaction $Cr(OH)_3 \xrightarrow{OH^-} CrO_4^{-2}$

(The oxidation no. of Cr changes from + 3 to + 6)

Reduction half reaction $IO_3^- \rightarrow I^-$

(The oxidation no. of 'I' changes from +5 to – 1)

Reduction half reaction	**Oxidation half reaction**
1. $IO_3^- \rightarrow I$ 2. $IO_3^- \rightarrow I$ (I already balanced) 3. $IO_3^- \rightarrow I + 3OH^-$ (O balanced) 4. $IO_3^- + 3H_2O \rightarrow I + 3OH^- + 3OH^-$	1. $Cr(OH)_3 \rightarrow CrO_4^{-2}$ 2. $Cr(OH)_3 \rightarrow CrO_4^{-2}$ (Cr already balanced) 3. $Cr(OH)_3 + OH^- \rightarrow CrO_4^{-2}$ (O balanced) 4. $Cr(OH)_3 + OH^- + 4OH^- \rightarrow CrO_4^{-2} + 4\,H_2O$ (H and O balanced in basic medium)

(H and again O are balanced in basic medium) 5. $IO_3^- + 3\,H_2O + 6\,e^- \rightarrow I + 6\,OH^-$ (Charges balanced) 6. $IO_3^- + 3H_2O + 6e^- \rightarrow I^- + 6\,OH^-$ (Electrons balanced)	5. $Cr(OH)_3 + 5OH^- \rightarrow CrO_4^{-2} + 4H_2O + 3e^-$ (Charges balanced) 6. $2Cr(OH)_3 + 10\,OH^- \rightarrow 2CrO_4^{-2} + 8H_2O + 6e^-$ (Electrons balanced)

Adding

$$2\,Cr(OH)_3 + 10\,OH^- + IO_3^- + 3\,H_2O + 6\,e^- \rightarrow 2CrO_4^{2-} + 8\,H_2O + 6\,e^- + I^- + 6\,OH^-$$

$$2\,Cr\,(OH)_3 + IO_3^- + 4\,OH^- \rightarrow 2CrO_4^{2-} + 5\,H_2O + I^-$$

Exercise Questions:

1. Oxalic acid is oxidized by permanganate ion in acid medium to Mn^{2+}. Balance the reaction by ion – electron method.

   (Ans: $\mathbf{2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H^+ \rightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O}$**)**

Solution:

Skeleton equation

$$\overset{+7}{MnO_4^-} + \overset{+3}{C_2O_4^{2-}} \rightarrow \overset{+2}{Mn^{2+}} + \overset{+4}{CO_2}$$

The oxidation half reaction $C_2O_4^{2-} \rightarrow CO_2 (+3 \text{ to } +4)$

The reduction half reaction $MnO_4^- \rightarrow Mn^{2+} (+7 \text{ to } +2)$

Reduction half reaction	**Oxidation half reaction**
1. $MnO_4^- \rightarrow Mn^{2+}$ 2. $MnO_4^- \rightarrow Mn^{2+}$ (Mn is already balanced) 3. $MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O$	1. $C_2O_4^{2-} \rightarrow CO_2$ 2. $C_2O_4^{2-} \rightarrow 2\,CO_2$ (C balanced) 3. $C_2O_4^{2-} \rightarrow 2\,CO_2$ (O is already balanced)

(O is balanced) 4. $MnO_4^- + 8\,H^+ \rightarrow Mn^{2+} + 4\,H_2O$ (H balanced in acid medium) 5. $MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$ (Charges balanced) 6. $2\,(MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O)$ (Electrons balanced) 7. $2\,MnO_4^- + 16\,H^+ + 10\,e^- \rightarrow 2\,Mn^{2+} + 8\,H_2O$	4. $C_2O_4^{2-} \rightarrow 2\,CO_2$ (H is not present) 5. $C_2O_4^{2-} \rightarrow 2\,CO_2 + 2\,e^-$ (Charges balanced) 6. $5\,(C_2O_4^{2-} \rightarrow 2\,CO_2 + 2\,e^-)$ (Electrons balanced) 7. $5\,C_2O_4^{2-} \rightarrow 10\,CO_2 + 10\,e^-$

Adding the half reactions

$$5\,C_2O_4^{2-} + 2\,MnO_4^- + 16\,H^+ \rightarrow 10\,CO_2 + 10\,H^+ + 2\,Mn^{2+} + 8\,H_2O$$

$$2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H^+ \rightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O$$

2. Balance the equation $O_2 + Cr \xrightarrow{OH^-} [Cr\,(OH)_4]^-$

(Ans: 4 Cr + 3O_2 + 6 H_2O + 4 OH^- →4 $[Cr\,(OH)_4]^-$)

Solution:

$$\overset{(0)}{O_2} + \overset{(0)}{Cr} \xrightarrow{OH^-} [\overset{(+3)}{Cr}\,(\overset{(-2)}{O}H)_4]^-$$

Oxidation half reaction $Cr \rightarrow [Cr\,(OH)_4]^-$

(Oxidation number of Cr changes forms 0 to +3)

Reduction half reaction $O_2 \rightarrow [Cr\,(OH)_4]^-$

(Oxidation number of 'O' changes from 0 to – 2

Reduction half reaction	**Oxidation half reaction**
1. $O_2 \rightarrow [Cr\,(OH)_4]^-$ 2. $O_2 + Cr \rightarrow [Cr\,(OH)_4]^-$	1. $Cr \rightarrow [Cr\,(OH)_4]^-$ 2. $Cr \rightarrow [Cr\,(OH)_4]^-$

(Cr balanced) 3. $O_2 + Cr + 2\ OH^- \rightarrow [Cr\ (OH)_4]^-$ (O balanced) 4. $O_2 + Cr + 2OH^- + 2H_2O \rightarrow [Cr\ (OH)_4]^- + 2OH^-$ (H balanced) 5. $O_2 + Cr + 2\ H_2O + e^- \rightarrow [Cr\ (OH)_4]^-$ (Charges balanced) 6. $3\ [O_2 + Cr + 2\ H_2O + e^- \rightarrow 3\ [Cr\ (OH)_4]^-]$ (Electrons balanced)	(Cr already balanced) 3. $Cr + 4\ OH^- \rightarrow [Cr\ (OH)_4]^-$ (O balanced) 4. $Cr + 4\ OH^- \rightarrow [Cr\ (OH)_4]^-$ (H balanced in basic medium) 5. $Cr + 4OH^- \rightarrow [Cr\ (OH)_4]^- + 3e^-$ (Charges balanced) 6. $Cr + 4OH^- \rightarrow [Cr\ (OH)_4]^- + 3e^-$ (Electrons balanced)

Adding

$$Cr + 4\ OH^- + 3O_2 + 3Cr + 6H_2O + 3e^- \rightarrow [Cr\ (OH)_4]^- + 3e^- + 3[Cr(OH)_4]^-$$

i.e. $4\ Cr + 3O_2 + 6\ H_2O + 4\ OH^- \rightarrow 4\ [Cr\ (OH)_4]^-$

Stoichiometry

Balancing of Red-ox reactions by Oxidation number method

Oxidation number method:

This method is applied to both ionic as well as molecular reactions. The balancing of the equations is done in the following stages.

a. Assign the oxidation numbers to all the atoms participating in the reaction. i.e., skeleton equation
b. Identify the elements whose oxidation numbers have changed.
   i.e. Oxidant and reductant. Their atoms are balanced.
c. Then increase in oxidation number in the oxidation process is equalized with the decrease in oxidation number in the reduction process (only numerical). This is done by selecting suitable integral coefficients to the changes in oxidation number.
d. These coefficients are used for the chemical substances involved in the oxidation and the reduction processes and the equation is written again to get a balanced equation.

The following worked out example will make it clear.

Example – 1:

Balance the following equation by oxidation number method

$H_2SO_4 + HI \rightarrow H_2O + H_2S + I_2$

Solution:

Assign oxidation numbers to the elements in the reaction using theempirical rules.

$H_2SO_4 + HI \rightarrow H_2O + H_2S + I_2$
2(+1)(+6) 4(-2)   (+1)(-1)   2(+1)(-2)   (+1) 2(-2)   0

Identify the elements whose oxidation numbers have changed.

$S \rightarrow S^{-2}$ reduction process (+6)
(-2)

The decrease in oxidation number is [+6-(-2)] =8

$2I^- \rightarrow I_2$ Oxidation process

The increase in oxidation number is [0-(-2)]=2

Equalize the increase in oxidation number in oxidation process with the decrease in the oxidation number in reduction process.

Decrease in oxidation number in reduction = 8

[Increase in oxidation number in oxidation = 2] × 4

The equation is written again using the coefficients obtained above.

$$H_2SO_4 + 8HI \rightarrow 4H_2O + H_2S + 4I_2$$

Verify the equation to balance with respect to charges and the atoms.

Example – 2:

Balance the following equation by oxidation number method.

$$Zn_{(s)} + H^+_{(aq)} + NO_3^-{}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + NH_4^+{}_{(aq)} + H_2O$$

Solution:

Assign oxidation numbers to the elements in the reaction using the empirical rules.

$$Zn_{(s)} + H^+ + NO_3^- \rightarrow Zn^{+2}_{(aq)} + NH_4^+{}_{(aq)} + H_2O$$

0 +1 (+5)3(-2) +2 (-3)(4(+1)) 2(+1)(-2)

Identify the elements whose oxidation

$Zn_{(s)} \rightarrow Zn^{+2}_{(aq)}$ oxidation process

Change in oxidation number is [+2 – 0] =2

$NO_3^-{}_{(aq)} \rightarrow NH_4^+{}_{(aq)}$ Reduction process

Change in oxidation number is [+5-(-3)] = 8

Equalizing the increase in oxidation number in oxidation process with the decrease in oxidation number in reduction process.

[Increase in oxidation number in oxidation = 2] × 4

[Decrease in oxidation number in reduction = 8] × 1

The equation is written again using the coefficients obtained above.

$$4Zn_{(s)} + 10H^{+}_{(aq)} + NO^{-}_{3} \rightarrow 4Zn^{+2}_{(aq)} + NH_4{}^{+}_{(aq)} + 3H_2O$$

Verify the equation to balance with respect to charges and the atoms.

Assignment questions:

1. What are the stages in which the chemical equation is balanced by oxidation number method?
2. Balance the following equations by oxidation number method.
   a. $H_2SO_4 + I^{-} \rightarrow H_2O + H_2S + I_2$
   b. $Zn_{(s)} + H^{+}_{(aq)} + NO^{-}_{3(aq)} \rightarrow Zn^{+} + NH_4^{+} + H_2O$

SAQs:

1. Oxidation numbers to the elements are assigned in the equation by using _____
   a. Multiple rules
   b. Conservation of mass
   c. Properties of elements
   d. Empirical rules

Solution: d)

2. Oxidation number method is applied to,
   a. Ionic reactions
   b. Molecular reactions
   c. Both a) and b)
   d. Exchange reactions.

Solution: c)

LAQ:

1. Balance the following equation by the oxidation number method.

$$Cr_{(s)} + Pb\,(NO_3)_{2(aq)} \rightarrow Cr\,(NO_3)_{3(aq)} + Pb_{(s)}$$

Solution:

Step – 1:

Indicate the oxidation numbers of the elements participating in the reaction.

$$\overset{(0)}{Cr}_{(s)} + \overset{+2}{Pb}\,(\overset{+5}{N}\overset{-2}{O}_3)_{2(aq)} \rightarrow \overset{+3}{Cr}\,(\overset{+5}{N}\overset{-2}{O}_3)_{3(aq)} + \overset{(0)}{Pb}_{(s)}$$

Step – 2:

Identify the atoms whose oxidation states have changed.

a. The oxidation number of chromium is increased form 0 to + 3
b. The oxidation number of lead is decreased from + 2 to 0

Step – 3:

Equalize the increase in the oxidation number to the decrease in the oxidation number.

Increase +3, decrease; –2,

2 (+3) = +6, 3 (–2) = –6

Step – 4:

Write the equation using these coefficients.

$$2\ Cr\ (s) + 3\ Pb\ (NO_3)_2\ (aq) \rightarrow 2\ Cr\ (NO_3)_3\ (aq) + 3\ Pb\ (s)$$

Step – 5:

Check up whether the equation is balanced or not. Yes the equation is balanced.

Problem set:

1. Balance the following equation

$$H_2SO_4 + HI \rightarrow H_2S + I_2 + H_2O$$

Solution:

Step – 1:

Indicate the oxidation numbers of the elements in all the molecules.

$$H_2SO_4 \quad + \quad HI \quad \rightarrow \quad H_2S \quad + \quad I_2 \quad + \quad H_2O$$

Step – 2:

Identify the elements whose oxidation state (O.S) have changed and write the equation and balance them with respect to the number of atoms.

–1 0+6 -2

$2I^- \rightarrow I_2$ $S \rightarrow S^{2-}$

Total increase in O.S. is +2. Decrease in O.S. in – 8

Step – 3:

Equalize the increase in the oxidation number to the decrease in oxidation number.

Increase +2;decrease –8;

4 (+2) = +8 1 (–8) = –8

Step – 4:

Write down the equation using these coefficients

$H_2SO_4 + 8\,HI \rightarrow H_2S + 4\,I_2 + 4\,H_2O$

Step – 5:

Check up whether the equation is balanced or not.

Check the whether the charge is balanced or not. All the reactants and products are in molecular state, the charge on a molecule is zero. Therefore, the equation is balanced with respect to charge.

Check whether the number of atoms is balanced or not.

Reactants	Products
10 H	10 H
1 S	1 S
4 [O]	4 [O]
8 [I]	8 [I]

The balanced chemical equation is: $H_2SO_4 + 8\,HI \rightarrow H_2S + 4\,I_2 + 4\,H_2O$

Exercise questions:

1. Balanced the following equation by the oxidation number method.

$$MnO_4^{2-} + Cl_2 \rightarrow MnO_4^{-} + Cl^{-}$$

Solution:

Step – 1:

Indicate the oxidation numbers of the elements.

$$\overset{+6\ -2}{MnO_4^{2-}} + \overset{0}{Cl_2} \rightarrow \overset{+7\ -2}{MnO_4^{-}} + \overset{-1}{Cl^{-}}$$

Step – 2:

Identify the elements whose oxidation states have changed and write the equation and balance them with respect to atoms.

$$\overset{+6}{MnO_4^{2-}} \rightarrow \overset{+7}{MnO_4^{-}} \qquad \overset{0}{Cl_2} \rightarrow 2\,\overset{-1}{Cl^{-}}$$

Increase in oxidation number

$+ 7 – 6 = + 1$

Decrease in oxidation number

$(–2) – 0 = (–2)$

Step – 3:

Equalize the increase in oxidation number, with the decrease in oxidation number.

Increase + 1

$2 \times (+1) = + 2$

decrease – 2

$1 \times (– 2) = – 2$

Step – 4:

Write the equation using these coefficients.

$$2\ MnO_4^{2-} + Cl_2 \rightarrow 2\ MnO_4^{-} + 2\ Cl^{-}$$

Step – 5:

Check whether the equation is balanced with respect to charge

Reactants	Products
$2\ MnO_4^{2-} + Cl_2$	$2\ MnO_4^{-} + 2\ Cl^{-}$
$2\ (–2) + 0$	$2\ (–1) + 2\ (–1)$
$= –4 + 0 = –4$	$= – 2 –2 = –4.$

Check whether the equation is balanced with respect to number of atoms or not.

Reactants

Products

2 Mn	2 Mn
8 [O]	8 [O]
2 [Cl]	2 [Cl]

$$2\ MnO_4^{2-} + Cl_2 \rightarrow 2\ MnO_4^{-} + 2\ Cl^{-}$$

Unit-6

Solution

A solution may be regarded as a single phase containing more than one component.

Every solution consists of a solvent and one or more solutes.

Solvent in a solution is its constituent substances which has the same state of aggregation as that of the solution. Generally the component present in greater amount than any or all the other components is called the solvent.

Solutions containing relatively high concentration of solute are called concentrated solutions.

Solutions containing relatively low concentration of solute are called dilute solutions.

Properties of liquids

Vapour pressure:

The Pressure exerted by vapour molecules on the surface area of a liquid, when liquid phase and vapour phase are in equilibrium, at a given temperature, is called vapour pressure of the liquid.

When temperature of a liquid is increased, the rate of vapourisation increases. The temperature at which the vapour pressure of a liquid becomes equal to the external pressure, the liquid boils. The temperature at which the liquid boils is called boiling point.

Thus, the temperature at which the vapour pressure of liquid is equal to the atmospheric pressure is called boiling point.

The boiling temperature of a liquid at 1 atm pressure is called normal boiling point.

The boiling temperature of a liquid at 1 bar pressure is called standard boiling point.

a) Surface Tension:

The force acting along the surface of a liquid at right angles to any line of unit length is called surface tension (γ).

Units: dynes cm^{-1} (C.G.S system)

Nm^{-1} (S.I system)

The phenomenon of surface tension is due to the existence of strong intermolecular forces of attraction in liquids.

Effect of temperature: Increase in the temperature increases the kinetic energy of molecules, then their inter molecular attractions decreases. So surface tension decreases with the increase of temperature.

Examples:

1) The liquid drops are spherical, due to surface tension.
2) The rise of liquid in a capillary tube is due to surface tension.

b) **Viscosity:**

The property of resistance flow is called Viscosity. Viscosity of a liquid is a measure of its frictional resistance to the flow of liquid. If viscosity increases then flow of liquid is decreases. Liquid which flow rapidly have low internal resistance. So their viscosity is less. Liquids which flow slowly have high internal resistance. So their viscosity is high.

Examples:

1) Glass is not a solid. It is a super-cooled liquid with a very high viscosity.
2) H_2SO_4 is viscous, due to H-bonding.

Concentration terms:

Molarity (M):

The number of moles of the solute per litre of the solution, *i.e.*,

Molarity (M) = Number of moles of solute/number of litres of solution

Or Molarity X number of litres of solution = Number of moles of solute

Let w_A g of the solute of molecular mass m_A be dissolved in V litre of solution.

$$\textbf{Molarity of the solution (M)} = \left(\frac{w_A}{m_A}\right)\left(\frac{1}{V}\right)$$

Or

If V is taken in mL, then

$$\textbf{Molarity of the solution (M)} = \left(\frac{w_A}{m_A}\right)\left(\frac{1000}{V}\right)$$

Unit of molarity is mol litre^{-1}

Molality (m):

The number of moles of the solute present in 1 kg of the solvent,

Molality (m) = Number of moles of solute/number of kilo-grams of the solvent

Let w_A grams of the solute of molecular mass m_A be present in w_B grams of the solvent, then

$$\textbf{Molality (m)} = \left(\frac{w_A}{m_A}\right)\left(\frac{1000}{w_B}\right)$$

Normality (N):

The number of gram equivalents of solute present per litre of solution.

Normality = Number of gram equivalents of solute/Number of litres of the solution

Let w_A g of the solute of equivalent mass E_A be present in V litres of the solution, then,

$$\textbf{Normality (N)} = \left(\frac{w_A}{E_A}\right)\left(\frac{1}{V}\right)$$

<u>Relation between normality and molarity</u>:

Normality = n X Molarity

<u>Mole fraction</u>:

This method is used when the solution is constituted by mixing two or more components.

It is defined as the ratio of number of moles of one component to the total number of moles of the solution (*i.e.,* all the components).

For example taking three components A, B and C containing solution.

Components	**A**	**B**	**C**
Mass (in grams)	w_1	w_2	w_3
Molecular mass	m_1	m_2	m_3
No.of g moles	w_1/m_1	w_2/m_2	w_3/m_3

$$\textbf{Total number of gram moles} = \left(\frac{w_1}{m_1}\right) + \left(\frac{w_2}{m_2}\right) + \left(\frac{w_3}{m_3}\right)$$

Thus,

Mole fraction of A = $(w_1/m_1) / (w_1/m_1 + w_2/m_2 + w_3/m_3) = f_A$

Mole fraction of B = $(w_2/m_2) / (w_1/m_1 + w_2/m_2 + w_3/m_3) = f_B$

Mole fraction of C = $(w_3/m_3) / (w_1/m_1 + w_2/m_2 + w_3/m_3) = f_C$

The sum of mole fractions of a solution is equal to 1,

i.e., $f_A + f_B + f_C = 1$.

In a binary solution,

Mole fraction of solute + Mole fraction of solvent =1

Let n moles of solute (A) and N moles of solvent (B) be present in a solution.

$$\textbf{Mole fraction of solute} = \left(\frac{n}{n+N}\right) = X_A$$

$$\textbf{Mole fraction of solvent} = \left(\frac{N}{n+N}\right) = X_B$$

Thus, $X_A + X_B = 1$

Mole fraction is independent of temperature of the solution.

Colligative properties of dilute solutions:

Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the **number of solute particles** present in the solution irrespective of their nature. These properties are termed as **colligative properties**.

The colligative properties are,

1) Lowering in the vapour pressure,
2) Elevation in the boiling point,
3) Depression in the freezing point, and
4) Osmotic pressure.

Colligative properties are the properties of dilute solutions, that is why these are termed as colligative properties of dilute solutions.

The importance of these properties lies in the fact that they provide methods for the determination of **molecular masses** of dissolved solutes. The results are excellent if the following 3 conditions are satisfied.

1) The solution should be very dilute.
2) The solute should be non-volatile.
3) The solute does not dissociate or associate in solution.

1) Lowering in the vapour pressure:

When a non-volatile solute is added to a solvent, the vapour pressure is lowered due to the following reasons.

(i) Solvent occupied surface area percentage is decreases. Thus, the rate of evaporation and vapour pressure decreases. The solute molecules occupy the surface, and so the percentage of surface area occupied by the solvent decreases.

(ii) According to Graham's law of evaporation,

$$\textbf{Rate of evaporation} \propto \frac{1}{\sqrt{\textbf{density}}}$$

When a non-volatile solute is dissolved in a liquid, its density increases. Thus both rate of evaporation and vapour pressure are lowered.

If p_0 is the vapour pressure of pure solvent and p_s is the vapour pressure of solution, the difference $(p_0 - p_s)$ is known as lowering in vapour pressure and the ratio $[p_0 - p_s / p_0]$ is known as relative lowering in vapour pressure

Raoult established a relationship between relative lowering in vapour pressure and composition of the solution after a series of experiments in various solvents. The relationship is known as **Raoult's law**. It states that "**the relative lowering in vapour pressure of a dilute solution is equal to mole fraction of the solute present in the solution."**

If n moles of solute be dissolved in N moles of the solvent, the mole fraction of the solute will be n/n+N.

According to Raoult's law,

$$\frac{P_o - P_s}{P_o} = \frac{n}{n+N}$$

This is mathematical expression for Raoult's law.

Modified form of Raoult's law: the above relationship can be written as,

$$\frac{P_o}{P_o - P_s} = \frac{n+N}{n} = 1 + \frac{N}{n}$$

$$\Longrightarrow \frac{P_o}{P_o - P_s} - 1 = \frac{N}{n}$$

$$\Longrightarrow \frac{P_s}{P_o - P_s} = \frac{N}{n}$$

$$\Longrightarrow \frac{P_o - P_s}{P_s} = \frac{n}{N}$$

$$\Longrightarrow \frac{P_o - P_s}{P_s} = \left(\frac{w_A}{m_A}\right)\left(\frac{m_B}{w_B}\right)$$

2) <u>Elevation of boiling point (</u>ΔT_b)(Ebullioscopy):

The boiling point of the solvent is elevated by the addition of non-volatile solute. **The difference in the boiling point of the solution and the boiling point of the pure solvent is known as elevation of boiling point**.

Elevation of boiling point (ΔT_b) = boiling point of the solution – boiling point of pure solvent

From Raoult's law for dilute solution

$$\frac{P_o - P_s}{P_o} = \left(\frac{w_A}{m_A}\right)\left(\frac{m_B}{w_B}\right)$$

where, p_s = vapour pressure of solution

p_o = vapour pressure of solute

$$P_o - P_s = \left(\frac{w_A}{m_A}\right)\left(\frac{m_B}{w_B}\right) P_o$$

For the pure solvent, p_o (its vapour pressure at the boiling point) and m_B (its molecular mass) are constant.

Therefore,

$$P_o - P_s \propto \left(\frac{w_A}{m_A}\right)\left(\frac{1}{w_B}\right)$$

$$\Longrightarrow \Delta P \propto \Delta T_b \propto \left(\frac{w_A}{m_A}\right)\left(\frac{1}{w_B}\right)$$

$$\Longrightarrow \Delta T_b = k_b \left(\frac{w_A}{m_A}\right)\left(\frac{1}{w_B}\right)$$

Where K_b is called as elevation constant.

3) <u>Depression of Freezing point</u> (ΔT_f) (Cryoscopy):

Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour pressure of the corresponding solid.

When non volatile solute is added to the solvent, lowers the vapour pressure of the solvent, therefore it will be in equilibrium with solid phase at a lower pressure and hence at lower temperature.

The difference between the freezing points of the pure solvent and its solution is called depression of freezing point.

Depression of freezing point (ΔT_f) = freezing point of the solvent – freezing point of the solution

From Raoult's law for dilute solution

$$\frac{P_o - P_s}{P_o} = \left(\frac{w_A}{m_A}\right)\left(\frac{m_B}{w_B}\right)$$

Where, p_s = vapour pressure of solution

p_o = vapour pressure of solute

$$P_o - P_s = \left(\frac{w_A}{m_A}\right)\left(\frac{m_B}{w_B}\right) P_o$$

For the pure solvent, p_o and m_B are constant.

Therefore,

$$P_o - P_s \propto \left(\frac{w_A}{m_A}\right)\left(\frac{1}{w_B}\right)$$

$$\Longrightarrow \Delta P \propto \Delta T_f \propto \left(\frac{w_A}{m_A}\right)\left(\frac{1}{w_B}\right)$$

$$\Longrightarrow \Delta T_f = k_f \left(\frac{w_A}{m_A}\right)\left(\frac{1}{w_B}\right)$$

Where K_f is called as depression constant.

4) <u>Osmosis and osmotic pressure:</u>

Osmosis: The spontaneous flow of solvent molecules through semi permeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.

Osmotic pressure:

It is defined as the hydrostatic pressure built up on the solution which just stops the osmosis.

Osmotic pressure = hydrostatic pressure

<u>van't Hoff theory of dilute solutions</u>:

van't Hoff realized that an analogy exists between gases and solutions provided osmotic pressure of solutions is used in place of ordinary gas pressure. He showed that for dilute solutions of non-electrolytes the following laws hold good.

1) **Boyle-van't Hoff law:** the osmotic pressure (P or π) of a solution is directly proportional to its concentration (C) when the temperature is kept constant. The concentration of the solution containing one gram mole in V litres is equal to 1/V (C = 1/V)

   Thus $P \propto C$

   $$P \propto \frac{1}{V}$$

   or $PV = \text{constant}$ or $\pi V = \text{constant}$

2) **Gay-Lussac-van't Hoff law:**

   Concentration remaining same, the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T), *i.e.*,

   $$P \propto T$$

   $$\Longrightarrow \frac{P}{T} = \text{Constant} \text{ or } \frac{\pi}{T} = \text{Constant}$$

   Combining above two laws,

   $$P \propto CT$$

   $$P = SCT$$

   $$\Longrightarrow P = (S)\left(\frac{1}{V}\right)T$$

   $PV = ST$ or $\pi V = ST$

   Where S is called molar solution constant. $S = 0.082$ lit atm K^{-1} mol^{-1}

   If solution contains n gram moles in V litres, the general equation would become

   $PV = nST$ or $\pi V = nST$

3) **Third law:**

   Equimolecular solutions of different solutes exert equal osmotic pressure under identical conditions of temperature. Such solutions which have the same osmotic pressure are termed as **isotonic solutions**.

   Avogadro hypothesis, "equal volumes of dilute solutions of different solutes, having the same temperature and osmotic pressure, contain equal number of molecules."

   For solution I, $PV = n_1ST$

   For solution II, $PV = n_2ST$

   Thus, n_1 must be equal to n_2 when P, V and T are same.

Determination of molecular masses:

For dilute solutions PV = nST,

Instead of one gram mole of the solute present in V litres of solution, let w_A gram of solute (mol. Mass m_A) be present in V_1 litres of solution, then

thus, the equation PV = nST becomes

$$PV_1 = \left(\frac{w_A}{m_A}\right)(ST)$$

$$\Longrightarrow m_A = \frac{(w_A)(S)(T)}{PV^1}$$

Knowing the value of P experimentally, the value of m_A, i.e., molecular mass of the solute can be determined.

Consider two solutions I and II having n_1 and n_2 moles of the solute in V_1 and V_2 litres of solution respectively. Let P_1 and P_2 be their osmotic pressures at the same temperature (T).

From the equation, PV = nST,

For solution I, $P_1V_1 = n_1ST$

$$\Longrightarrow P_1 = \left(\frac{n_1}{V_1}\right) ST$$

For solution II, $P_2V_2 = n_2ST$

$$\Longrightarrow P_2 = \left(\frac{n_2}{V_2}\right) ST$$

If both solutions are isotonic, i.e., $P_1 = P_2$

$$\left(\frac{n_1}{V_1}\right) ST = \left(\frac{n_2}{V_2}\right) ST$$

$$\Longrightarrow \frac{n_1}{V_1} = \frac{n_2}{V_2}$$

$$\Longrightarrow \frac{(w_1/m_1)}{V_1} = \frac{(w_2/m_2)}{V_2}$$

This is the condition for isotonic solutions.

Raoult's Law:

According to this law, the partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.

Let a mixture (solution) be prepared by mixing n_A moles of liquid A and n_B moles of liquid B. Let p_A and p_B be the partial pressures of two constituents A and B in solution and p_A^0 and p_B^0 the vapour pressures in pure state respectively.

Thus, according to Raoult's law,

$$p_A = (n_A/n_A+n_B)\, p_A^0 = (\text{mole fraction of A})\, (p_A^0) = X_A\, p_A^0$$

and $$p_B = (n_B/n_A+n_B)\, p_B^0 = (\text{mole fraction of B})\, (p_B^0) = X_B\, p_B^0$$

If the total pressure be P, then

$$P = p_A + p_B$$

$$= (n_A/n_A+n_B)\, p_A^0 + (n_B/n_A+n_B)\, p_B^0$$

$$= X_A\, p_A^0 + X_B\, p_B^0$$

Ideal solutions obey Raoult's law at every range of concentration. Non-ideal solution does not obey Raoult's law. They show either positive or negative deviation from Raoult's law.

Relation between dalton's law and Raoult's law:

The composition of the vapour in equilibrium with the solution can be calculated applying Dalton's law of partial pressures. Let the mole fractions of vapours A and B be Y_A and Y_B. Let p_A and p_B be the partial pressures of vapours A and B respectively and total pressure P.

$$p_A = Y_A\, P \text{ -------------------(i)}$$

$$p_B = Y_B\, P \text{ -------------------(ii)}$$

$$p_A = X_A\, p_A^0 \text{ -------------------(iii)}$$

$$p_B = X_B\, p_B^0 \text{ -------------------(iv)}$$

Equating (i) and (iii)

$$\mathbf{Y_A\, P = X_A\, p_A^0}$$

$$\Longrightarrow \mathbf{Y_A = \frac{X_A\, P_A^o}{P} = \frac{P_A}{P}}$$

Similarly equating (ii) and (iv)

$$\mathbf{Y_B = \frac{X_B\, P_B^o}{P} = \frac{P_B}{P}}$$