

മലപ്പുറം ജില്ലാ പഞ്ചായത്ത് വിജയഭേരി വിദ്യാഭ്യാസ പദ്ധതിയുടെ ഭാഗമായി കഴിഞ്ഞ വർഷം പ്ലസ് ടു വി എച്ച് എസ് ഇ രണ്ടാം വർഷ വിദ്യാർത്ഥികൾക്കായി ഫോക്കസ് 21 എന്ന പേരിൽ തയ്യാറാക്കിയ സ്റ്റഡി മെറ്റീരിയലുകൾക്ക് അധ്യാപകരിൽ നിന്നും വിദ്യാർത്ഥികളിൽ നിന്നും വളരെ നല്ല പ്രതികരണമാണ് ലഭിച്ചത്. കോവിഡ് മഹാമാരിമൂലം സാധാരണ ക്ലാസുകൾ ലഭിക്കാത്ത വിദ്യാർത്ഥികൾക്ക് പ്രസ്തുത മെറ്റീരിയൽ ഏറെ സഹായകരമായെന്ന് അവർ സാക്ഷ്യപ്പെടുത്തുന്നു.

ഒന്നാം വർഷ വിദ്യാർത്ഥികൾക്കുള്ള പരീക്ഷ സെപ്റ്റംബർ ആദ്യവാരം നടക്കുകയാണ്. ഫോക്കസ് പാഠഭാഗങ്ങൾക്കായി വിജയഭേരി ഫോക്കസ് +1 എന്ന പേരിൽ കഴിഞ്ഞ വർഷത്തേതു പോലെ ഈ വർഷവും വിവിധ വിഷയങ്ങൾക്ക് പ്രത്യേക സ്റ്റഡിമെറ്റീരിയൽ മലപ്പുറം ജില്ലാ പഞ്ചായത്ത് വിജയഭേരി വിദ്യാഭ്യാസ പദ്ധതിയുടെ ഭാഗമായി പുറത്തിറക്കുകയാണ്. മലപ്പുറം ഡയറ്റാണ് പ്രസ്തുത മെറ്റീരിയലിനുള്ള അക്കാദമിക പിന്തുണ നൽകിയിട്ടുള്ളത്. വിവിധ വിഷയങ്ങളുടെ ജില്ലാ തല അധ്യാപകരുടെ അസോസിയേഷനാണ് ഈ പ്രവർത്തനങ്ങൾക്ക് തങ്ങളുടെ കൂടെ നിന്നത്. എല്ലാവരേയും ഈ അവസരത്തിൽ നന്ദിയോടെ സ്മരിക്കുന്നു.

ഈ ഉദ്യമം അധ്യാപകർക്കും വിദ്യാർത്ഥികൾക്കും ഏറെ ഉപകാരപ്പെടുമെന്ന് പ്രതീക്ഷിക്കുന്നു. എല്ലാ വിദ്യാർത്ഥികൾക്കും മികച്ച വിജയം കൈവരിക്കാൻ കഴിയട്ടെ എന്നാശംസിക്കുന്നു.

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Content

Unit 1	Some Basic Concepts of Chemistry	4
Unit 2	Structure of Atom	6
Unit 3	Classification of Elements and Periodicity in Properties	14
Unit 4	Chemical Bonding and Molecular Structure	16
Unit 5	States of Matter	22
Unit 6	Thermodynamics	25
Unit 7	Equilibrium	32
Unit 8	Redox Reactions	37
Unit 9	Hydrogen	43
Unit 10	The s-Block Elements	45
Unit 11	The p - Block Elements	52
Unit 12	Organic Chemistry: Some Basic Principles and Techniques	56
Unit 13	Hydrocarbons	63
Unit 14	Environmental Chemistry	69

1. SOME BASIC CONCEPTS OF CHEMISTRY

Laws of Chemical Combination:

The combination of elements to form compounds is governed by the following basic laws called Laws of chemical combinations

1. Law of Definite Proportions (Law of definite composition) - Joseph Proust

It states that a given compound always contains exactly the same proportion of elements by weight. Or every compound has a fixed composition by weight

Illustration: CO₂ always contains carbon and oxygen in the ratio 3:8

2. Law of Multiple Proportions – John Dalton

It states that if two elements can combine to form more than one compound, the different masses of one of the elements that combine with a fixed mass of the other element, are in small whole number ratio.

Illustration: Carbon combine with Oxygen to form CO & CO₂

$C(12g) + O(16g) \rightarrow CO$ $C(12g) + O_2(32g) \rightarrow CO_2$ Ratio of Oxygen is 1:2

3. Law of conservation of mass - A. Lavoisier

It States that matter can neither be created nor be destroyed

Illustration: 12g Carbon react with 32g Oxygen to form 44g CO₂

4. Avogadro's Law

Under similar conditions of temperature and pressure equal volume of all gases contain the same number of molecules

5. Gay Lussac's Law of gaseous volumes

It states that when gases combine to form gaseous products, a simple ratio exist between the volumes of the reactants and products at constant temperature and pressure

Atomic mass

Atomic mass of an element is a number that expresses how many times the mass of an atom of the element is greater than 1/12th the mass of a C-12 atom.

Atomic mass unit (amu): 1/12th the mass of a C-12 atom is called atomic mass unit (amu).

i.e. 1 amu = 1/12 x mass of a C-12 atom

$$= 1.66 \times 10^{-24} \text{ g} = 1.66 \times 10^{-27} \text{ kg}$$

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

Average atomic mass: Almost all the elements have isotopes. So we can calculate an average atomic mass of an element by considering the atomic mass of the isotopes and their relative abundance.

For e.g. chlorine has two isotopes ^{35}Cl and ^{37}Cl in the ratio 3:1.

So the average atomic mass $\text{Cl} = (3 \times 35 + 1 \times 37) / 4 = 35.5$

Molecular mass:

Molecular mass is the sum of atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together.

For e.g. molecular mass of H_2SO_4 is calculated as: $2 \times 1 + 32 + 4 \times 16 = 98 \text{ u}$.

Mole concept: Mole is the unit of amount of substance. It is defined as the amount of substance that contains as many particles as there are atoms in exactly 12 g C-12 isotope or it is the amount of substance which contains Avogadro number (6.022×10^{23}) of particles (atoms/ions/molecules).

This number is known as Avogadro number or Avogadro constant (N_A)

1 mole of hydrogen atoms = 6.022×10^{23} atoms

1 mole of water molecules = 6.022×10^{23} water molecules

1 mole = 1GAM= 1GMM= 6.022×10^{23} atoms= 6.022×10^{23} molecules=22.4L of any gas at STP

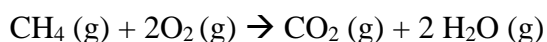
Molar mass: The mass of one mole of a substance in gram is called its molar mass (gram molecular mass). The molar mass in grams is numerically equal to molecular mass in u.

Molar mass of oxygen = 32g Molar mass of hydrogen = 2g etc.

Limiting Reactant: The reactant which is completely consumed in a reaction is called limiting reactant. The reactant which is not completely consumed in the reaction is called excess reactant

Practice Questions:

1. Calculate the amount of carbon dioxide formed by the complete combustion of 80g of methane as per the reaction:



Hint: According to the equation, 16 g CH_4 gives 44 g CO_2

So 80 g CH_4 gives $44 \times 80/16 = 220 \text{ g } \text{CO}_2$

2. Find the number of oxygen atoms in 4 g of O_2

Hint: 4/32

3. Which of the following contains the maximum number of molecules?

a) 1g N_2 b) 1g CO_2 c) 1g H_2 d) 1g NH_3

Hint: 1g H₂

4. Calculate the volume of 10 mole NH₃ at STP?

Hint: 10x22.4L

5. 3g of hydrogen reacts with 30g of oxygen to yield H₂O. Which is limiting reactant?

Hint: H₂ is limiting Reactant (mass of Oxygen required here is 24g)

6. Calculate the number of molecules in the following

a) 88g CO₂ b) 170 g NH₃ c) 112L CO₂

Hint: a) 2xN_A b) 10xN_A c) 5xN_A

7. Calculate number of hydrogen atoms present in 64g CH₄?

Hint: Number of moles = 64/16=4, Number of molecules = 4xN_A, Number of Hydrogen atoms = 4x4xN_A (Methane contains 4 hydrogen atoms)

8. Find out the odd one from the following

a) 224L NH₃ at STP b) 440g CO₂ c) 40g He d) 36g H₂O

Hint: 36g H₂O (difference in number of moles)

9. Calculate the molar mass of the following

a) HNO₃ b) Na₂SO₄ c) C₆H₁₂O₆

Hint: a) 63g b) 142g c) 180g

10. Find out the number of moles in the following

a) 11.2L CO₂ b) 88g CO₂ c) 170g NH₃

Hint : a) 0.5mole b) 2mole c) 10 mole

2 STRUCTURE OF ATOM

Electron: Discovered by J J Thomson by Cathode ray discharge tube experiment. These rays start from the cathode and move in straight lines are called *cathode rays or cathode ray particles*.

Properties of Cathode Rays: $e/m_e = 1.758 \times 10^{11} \text{ C kg}^{-1}$, m_e is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C).

Charge on the Electron (e): Charge on the electron is $-1.6022 \times 10^{-19} \text{ C}$.

Mass of electron (m_e): Mass of electron (m_e) = $9.1 \times 10^{-31} \text{ kg}$

Protons : E. Goldstein discovered anode rays or canal rays.

The smallest and lightest positive ion was obtained from hydrogen and was called proton.

Neutrons: Discovered by Chadwick by bombarding a thin sheet of beryllium by α -particles. They are electrically neutral particles having a mass slightly greater than that of the protons.

Rutherford's Nuclear Model of Atom: Rutherford proposed an atom model based on his α -particle scattering experiment. He bombarded a very thin gold foil with α -particles.

The Experiment: A stream of high energy α -particles from a radioactive source was directed at a thin gold foil. The thin gold foil had a circular fluorescent screen around it. Whenever α -particles struck the screen, a tiny flash of light was produced at that point.



Observations:

1. Most of the α - particles passed through the gold foil without any deviation.
2. A small fraction of the α -particles was deflected by small angles.
3. A very few α - particles bounced back, that is, were deflected by nearly 180° .

Conclusions:

1. Since most of the α -particles passed through the foil without any deviation, most space in the atom is empty.
2. A few positively charged α - particles were deflected. This is because the positive charge of the atom is concentrated in a very small volume at the centre called nucleus.
3. The volume occupied by the nucleus is negligibly small as compared to the total volume of the atom.

Nuclear model of atom.

1. All the positive charge and most of the mass of the atom were concentrated in an extremely small region called nucleus.
2. Electrons are revolving round the nucleus with a very high speed in circular paths called orbits.
3. Electrons and the nucleus are held together by electrostatic forces of attraction.

Drawbacks or Limitations of Rutherford's atom model:

1. Rutherford model cannot explain the stability of the atom.
2. He cannot explain the electronic structure of atom.

Q 1. What are the important observations and conclusions made by Rutherford from his alpha ray scattering experiment? Give any two limitations of Rutherford's nuclear model of atom.

Particle Nature of Electromagnetic Radiation:

Black body radiation: An ideal body which emits and absorbs all frequencies is called a black body and the radiation emitted by such a body is called black body radiation.

The phenomenon of black body radiation was first explained by Max Planck by his Quantum theory.

Q 2. Mention two observations which could not be explained by wave nature of electromagnetic radiations. (*Hint: Blackbody radiation, photoelectric effect*)

Planck's Quantum Theory:

Atoms and molecules could emit (or absorb) energy only in discrete quantities and not in a continuous manner, but in small packets of energy called quantum.

The energy (E) of each quantum of radiation is proportional to its frequency (ν). It is expressed by the equation,

$E = h\nu$, Where 'h' is known as Planck's constant and its value is 6.626×10^{-34} J s.

Photoelectric effect: (H. Hertz). It is the ejection of electrons by certain metals (like potassium, rubidium, caesium etc.) when light of suitable frequency incident on them. The electrons ejected are called photoelectrons.

The results observed during photoelectric effect are:

1. The electrons are ejected from the 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 minimum frequency (known as threshold frequency [ν_0]) below which photoelectric effect is not observed.
4. The kinetic energy of the ejected electrons is directly proportional to the frequency of the incident light.

Einstein explained the effect using Planck's quantum theory. When a photon of sufficient energy strikes the metal surface, it transfers its energy to the electron of the atom of the metal instantaneously and the electron is ejected without any time delay.

The kinetic energy of the ejected electrons is directly proportional to the frequency (ν) of the incident light. The minimum energy required to eject electron is $h\nu_0$, *work function*, then the difference in energy ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron.

According to law of conservation of energy, the kinetic energy of the ejected electron is given by,

$$K.E = h\nu - h\nu_0 \quad \text{Or,} \quad h\nu = h\nu_0 + \frac{1}{2}m_e v^2$$

Where m_e is the mass of the electron and v is the velocity of the ejected electron.

A more intense beam of light contains larger number of photons, so the number of electrons

ejected is also larger.

Q 3. Write two important results observed during photoelectric effect.

Q 4. The threshold frequency for a metal is $7.0 \times 10^{14} \text{ s}^{-1}$. Calculate the kinetic energy of an emitted electron when radiation of frequency (ν) $1.0 \times 10^{15} \text{ s}^{-1}$ hits the metal. (Hint: $K.E \text{ of electron} = h\nu - h\nu_0 = h(\nu - \nu_0)$)

Atomic spectra:

Spectrum is the arrangements of electromagnetic waves with all the wavelengths arranged in order of wavelengths or frequencies.

Emission spectra: An emission electromagnetic radiations composed of a number of discrete frequencies or wavelengths. They do not show a continuous spread of wavelength.

The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as finger prints.

Line Spectrum of Hydrogen: When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies (Line Spectrum).

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1}$$

where $n_1 = 1, 2, \dots$, $n_2 = n_1 + 1, n_1 + 2, \dots$. The value $109,677 \text{ cm}^{-1}$ is called the Rydberg constant (R_H) for hydrogen.

Series	n_1	n_2	Spectral region
Lyman	1	2,3,4....	Ultra violet
Balmer	2	3,4,5....	Visible
Paschen	3	4,5,6....	Infra red
Brackett	4	5,6,7....	Infra red
Pfund	5	6,7,8....	Infra red

Among these lines, the Balmer series is the only series that we can be visible.

The features of line spectra:

1. Line spectrum of element is unique
2. There is regularity in the line spectrum of each element.

Q 5. The Balmer series of lines in the hydrogen spectrum appear in the visible region of the electromagnetic spectrum. Calculate the wave number of the second line in the Balmer series.

Bohr's model for hydrogen atom: Niels Bohr. The important postulates:

1. The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits or stationary states or allowed energy states. These energy levels are numbered as 1,2,3 etc or designated as K, L, M, N, etc. These

numbers are known as *Principal quantum numbers*.

- The energy of an electron in the orbit does not change with time. However, when an electron absorbs energy, it will move away from the nucleus (i.e. to a higher energy level) and when it loses energy, it will move towards the nucleus (i.e. to a lower energy level).
- The radius of orbits can be given by the equation: $r_n = a_0 n^2$ where $a_0 = 52.9$ pm. Thus the radius of the first stationary state is 52.9 pm (called *the Bohr radius*).
- The energy of electron in an orbit is given by the expression: $E_n = -R_H (1/n^2)$, where $n = 1, 2, 3, \dots$ and R_H is a constant called Rydberg constant. Its value is 2.18×10^{-18} J.
- The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE .



Where E_i and E_f are the energies of lower and higher energy levels respectively.

This expression is commonly known as *Bohr's frequency rule*.

- The angular momentum of an electron is an integral multiple of $h/2\pi$.
i.e. $m_e v r = nh/2\pi$, where m_e is the mass of electron, v is the velocity of electron and r is the radius of Bohr orbit. $n = 1, 2, 3, \dots$

Bohr atom model could explain the stability and line spectra of hydrogen atom and hydrogen like ions.

Limitations of Bohr Atom Model:

- It could not explain the fine spectrum of hydrogen atom.
- It could not explain the spectrum of atoms other than hydrogen.
- It could not explain the splitting of spectral lines in the presence of electric field (Stark effect) and in magnetic field (Zeeman effect).
- It could not explain the ability of atoms to form molecules by chemical bonds.
- It did not consider the wave character of matter and Heisenberg's uncertainty principle.

In Bohr model,

- electrons are moving in well defined circular orbits about the nucleus.
- The wave character of the electron is not considered in Bohr model.

Reasons for the Failure of the Bohr Model:

- Bohr model of the hydrogen atom ignores dual behaviour of matter.
- Bohr model contradicts Heisenberg uncertainty principle.

Give the postulates of Bohr model of hydrogen atom. Also write two merits and two limitations of this model.

Dual Behaviour of Matter – de-Broglie’s equation:

De-Broglie proposed that like radiation, matter also exhibit dual behaviour i.e., *both particle and wave like properties*. This means that electrons should also have momentum as well as wavelength.

$$\lambda = \frac{h}{mv}$$

λ = wavelength in m
 h = 6.626×10^{-34}
 m = mass in kg
 v = velocity in m/s.

Where m is the mass of the particle, v is the velocity and mv is the momentum. The above equation is known as de-Broglie’s equation.

Q 6. A photon has a wavelength of 3.5 \AA . Calculate its mass (Given $h = 6.626 \times 10^{-34} \text{ Js}$. Velocity of light = $3 \times 10^8 \text{ m/s}$)
 (Hint: $\lambda = h/mv$)

Heisenberg’s Uncertainty Principle:

It states that, “it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of a moving microscopic particle like electron”.

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

Δx = Uncertainty of Position
 Δp = Uncertainty of Momentum

Q 7. The minimum value for the product of uncertainties in position and momentum of a moving microscopic particle is equal to.....
 (Ans: $h/4\pi$)

Quantum mechanical model of atom:

The fundamental equation of quantum mechanics was developed by Schrodinger and is known as Schrodinger equation. It is written as: $\hat{H} \psi = E\psi$, where \hat{H} is a mathematical operator called Hamiltonian operator, E is the total energy of the system (K.E + P.E) and ψ is called the wave function. On solving the above equation, we get different values for E and ψ . When Schrodinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function (ψ). These quantized energy states and corresponding wave functions are characterized by a set of three quantum numbers.

Orbitals and Quantum Numbers:

Atomic orbitals can be distinguished by their size, shape and orientation. These orbitals are precisely distinguished by quantum numbers.

1. Principal Quantum Number (n):

The following informations are obtained from n.

1. It gives the size the orbit.
2. It gives the energy of electron in an orbit.

3. It gives the shell in which the electron is found.
4. It also gives the average distance between the electron and the nucleus.

2. Azimuthal Quantum Number (Subsidiary or orbital angular momentum Quantum number (l)):

1. It gives the shape of the orbital.
2. It gives the sub shell or sub level in which the electron is located.
3. It also gives the orbital angular momentum of the electron.

For a given value of n, l can have n values ranging from 0 to n – 1. That is, for a given value of n, the possible value of l are : l = 0, 1, 2, (n-1).

3. Magnetic Quantum Number (m or ml):

It gives information about the orientation of orbitals in space. For a given ‘l’ value, there are 2l+1 possible values for m and these values are given by :m = – l to 0 to + l

4. Spin Quantum Number (s or ms):

It is the only experimental Quantum number and it gives the spin orientation of electrons. This spin may be either clockwise or anticlockwise. So the values for s may be +. or -. +. represents clock-wise spin and-. represents anticlockwise spin.

Q 8. Represent the orbital with quantum numbers n=5 and l=3. (Ans: 5f)

Q 9. Explain quantum numbers. Give the importance of quantum numbers in Pauli’s Exclusion Principle. (*Hint: Pauli’s exclusion principle, no two electrons in an atom can have the same set of four quantum numbers.*)

Q 10. Name the quantum number which gives the spatial orientation of an orbital with respect to standard set of co-ordinate axes. (Ans: Magnetic Quantum number)

Q 11. Which of the following sets of quantum numbers are NOT possible?

- 1) n = 2, l = 2, m_l = 0, m_s = + ½
- 2) n = 1, l = 0, m_l = 0, m_s = - ½
- 3) n = 3, l = 2, m_l = -3, m_s = + ½
- 4) n = 2, l = 1, m_l = 1, m_s = + ½

[Hint: (a)]

Rules for Filling of electrons in various orbitals:

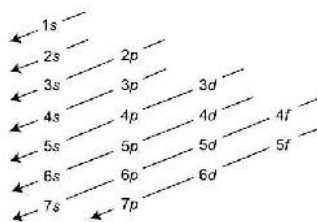
1. Aufbau principle:

The building up of orbitals means the filling up of orbitals with electrons. *It states that, the orbitals are filled in order of their increasing energies. In other words, electrons first occupy the lowest energy orbital and then to higher energy orbitals.*

1. The various orbitals are filled in the increasing order of their (n+l) value.

2. If two orbitals have the same $(n+l)$ values, the orbital with the lower n value is filled first.

It follows the order: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p



2. Pauli's Exclusion Principle:

It states that no two electrons in an atom can have the same set of four quantum numbers. i.e. an orbital can accommodate maximum 2 electrons with opposite spin.

3. Hund's rule of maximum multiplicity:

It states that electron pairing takes place only after partially filling all the degenerate orbitals. Orbitals having same energies are called degenerate orbitals.

Q 12. State and explain Hund's rule of maximum multiplicity.

Q 13. Quantum number gives the address of electrons. Explain the quantum number which determines: 1. Distance of electron from nucleus. 2. The orbital angular momentum of electron.

Electronic Configuration of Atoms:

The distribution of electrons into various orbitals of an atom is called its electronic configuration.

For hydrogen atom the electronic configuration is $1s^1$ meaning that it has one electron in the 1s orbital. The second electron in helium (He) the configuration is, therefore, $1s^2$.

Boron (B, $1s^2 2s^2 2p^1$), carbon (C, $1s^2 2s^2 2p^2$), nitrogen (N, $1s^2 2s^2 2p^3$), oxygen (O, $1s^2 2s^2 2p^4$), fluorine (F, $1s^2 2s^2 2p^5$) and neon (Ne, $1s^2 2s^2 2p^6$),

Stability of Completely Filled and Half Filled Subshells:

For atoms having half filled or completely filled electronic configurations have extra stability compared to other atoms.

This is due to their symmetrical distribution of electrons and greater exchange energy.

For example, the electronic configuration of Cr is $[\text{Ar}] 3d^5 4s^1$ and not $3d^4 4s^2$. This is because d^5 represents a half filled configuration and has extra stability. Similarly for Cu the electronic configuration is $[\text{Ar}] 3d^{10} 4s^1$ and not $3d^9 4s^2$.

Q 14. Write the subshell-wise electronic configurations of the following elements: Cr, Cu (*Hint: This is because half-filled and completely filled electronic configurations have extra stability.*)

3 CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Mendeleev's Periodic Law (1905)

The law states that “the physical and chemical properties of elements are periodic functions of their atomic weights”.

Mendeleev's Periodic Table

Mendeleev arranged elements in horizontal rows and vertical columns of a table in order of their increasing atomic weights in such a way that the elements with similar properties occupied the same vertical column or group.

He realized that some of the elements did not fit in with his scheme of classification if the order of atomic weight was strictly followed. He left the gap under Aluminium and a gap under Silicon, and called these elements Eka- Aluminium and Eka-Silicon.

MODERN PERIODIC LAW (1913) (Henry Mosely)

The law states that “the physical and chemical properties of elements are periodic functions of their atomic numbers”.

LONG FORM OF THE PERIODIC TABLE

Group and Period

Vertical columns are called groups and Horizontal rows are called periods. There are 7 periods and 18 groups in modern periodic table

The first period consists of 2 elements. Second and third period consists of 8 elements each. Fourth and fifth period consists of 18 elements. Sixth period consists of 32 elements. The last seventh period is an incomplete period.

Trends in Physical Properties

(i) Atomic Radius

Half of the distance between nuclei in covalently bonded diatomic molecule.

Variation of Atomic radius in a periodic table

Across the period atomic radius decreases because nuclear charge increases and atomic size decreases.

Down the group atomic radius increases because nuclear charge decreases and atomic size increases.

(a) Ionic Radius

The ionic radii can be estimated by measuring the distances between cations and anions in ionic crystals.

Cations are smaller than their parent atoms. Anions are larger than their parent atoms.

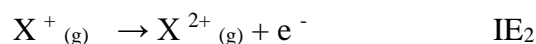
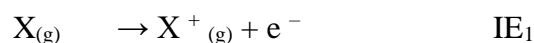
Iso electronic species

Some atoms and ions which contain the same number of electrons, we call them iso electronic species.

For example, O^{2-} , F^- , Na^+ , Mg^{2+} These have the same number of electrons (10).

(ii) Ionization Enthalpy (IE)

It is the amount of energy required to remove an electron from an isolated gaseous atom (X) in its ground state. The unit of ionization enthalpy is kJ mol^{-1} . Ionization enthalpies are always positive.

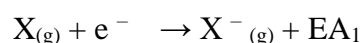
**Variation of Ionisation Energy**

Across the period ionisation energy increases because atomic size decreases and nuclear charge increases.

Down the group ionisation energy decreases because atomic size increases and nuclear charge decreases.

(iii) Electron Gain Enthalpy

It is the amount of energy liberated when an electron is added to an isolated gaseous atom (X) in its ground state. The unit of electron gain enthalpy is KJ mol^{-1} .



Noble gases have large positive electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration.

Across a period, electron gain enthalpy increases, because effective nuclear charge increases and atomic size decreases. Down the group, electron gain enthalpy decreases, because effective nuclear charge decreases and atomic size increases.

(iv) Electronegativity

It is defined as the tendency of atom to attract a shared pair of electrons.

Variation of Electronegativity

Across a period, electronegativity increases, because effective nuclear charge increases and atomic size decreases. Down the group, electronegativity decreases, because effective nuclear charge decreases and atomic size increases.

Questions and Answers

1. Second ionisation enthalpy is greater than first why?

Ans: The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom.

2. The most electronegative element is _____

Ans: Fluorine

3. Give the IUPAC name of the element with atomic number 117.

Ans: Ununseptium

4. Consider the following species N^{3-} , O^{2-} , F^- , Na^+ , Mg^{2+} , Al^{3+}

What is common in them?

Ans: They are isoelectronic species. (10 electrons)

5. Match the following

A	B
Sodium	f-block
Oxygen	s-block
Uranium	d-block
Silver	p-block

Ans: Sodium - s-block, Oxygen - p-block, Uranium- f-block, Silver - d-block,

6. Which one has greater size: Sodium or potassium? Justify your answer?

Ans: Potassium. Because down the group no of shells increases so atomic size increases.

7. The first ionisation enthalpy of sodium is lower than that of Magnesium, but its second ionisation enthalpy is higher than that of Magnesium. Why?

Ans: Na - $1s^2 2s^2 2p^6 3s^1$

Mg - $1s^2 2s^2 2p^6 3s^2$

By removing one electron, Na gets stable noble gas configuration(octet).But, since the s orbital of Mg is completely filled , removal of first electron will be difficult. So the first ionisation enthalpy of Na is lower than that of Mg. Removal of 2nd electron from Na is difficult due to its octet configuration but by removing 2nd electron from Mg, it gets stable noble gas configuration. So the second ionisation enthalpy of Na is higher than that of Mg.

8. Electron gain enthalpy of Fluorine is lower than that of Chlorine why?

Ans: Due to small size and greater electronic repulsion in fluorine.

9. What is meant by electron gain enthalpy? What are the factors affecting it?

Ans: It is the heat change (enthalpy change) when an electron is added to the outer most shell of an isolated gaseous atom. Size of the atom and nuclear charge.

10. What is meant by electronegativity? How does electronegativity vary in the periodic table? Justify

Ans: It is defined as the tendency of atom to attract a shared pair of electrons.

Electronegativity decreases down the group because atomic size increases and nuclear attraction decreases. Electronegativity increases along the period due to decrease in size and increase in nuclear charge.

11. Account for the following

(i) Ionization enthalpy of Nitrogen is greater than that of Oxygen

(ii) Atomic radius decreases from left to right along a period

Ans: (i) Due to the stable half-filled electronic configuration of Nitrogen.

(iii) Along a period, the no. of shells remains the same and the nuclear charge increases one by one. So, the atomic radius decreases.

4 CHEMICAL BONDING AND MOLECULAR STRUCTURE

Valence Shell Electron Pair Repulsion Theory (VSEPR Theory)

Main Postulates

- The shape of molecule depends on the number of electron pairs in the valence shell of central atom
- The negatively charged electron pairs repel each other
- To minimize repulsion, they stay as far as possible. This gives the geometry to the molecule
- A multiple bond is treated as a single super pair
- The repulsive interaction between electron pairs decreases in the order
lone pair – lone pair > lone pair – bond pair > bond pair – bond pair

Shape of molecules whose central atom has no lone pair of electrons

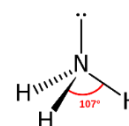
No. of electron pairs	Shape of molecule	Examples
2	Linear	BeF ₂ , BeCl ₂
3	Trigonal planar	BF ₃ , AlCl ₃
4	Tetrahedral	CH ₄ , NH ₄ ⁺ ,
5	Trigonal bipyramidal	PCl ₅
6	Octahedral	SF ₆

Shape of molecules whose central atom contains lone pairs

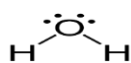
TYPE	Bond pairs	Lone pairs	Shape	Example
AB ₂ E	2	1	Bent	SO ₂ , O ₃
AB ₃ E	3	1	Trigonal pyramidal	NH ₃
AB ₂ E ₂	2	2	Bent	H ₂ O
AB ₄ E	4	1	See saw	SF ₄
AB ₃ E ₂	3	2	T-Shape	ClF ₃
AB ₅ E	5	1	Square pyramid	BrF ₅
AB ₄ E ₂	4	2	Square planar	XeF ₄

Structure of NH₃

Ammonia contains three bond pairs and one lone pair of electron, total four electron pairs around N atom. So expected geometry is tetrahedral. But due to the presence of lone pair, ammonia has **trigonal pyramidal** shape. Due to bond pair-lone pair repulsion the bond angle reduces to 107°


Structure of water

Water molecule contains 2 bond pairs and 2 lone pairs. Expected geometry is tetrahedral. Due to the presence of 2 lone pairs the actual geometry is bent. Due to lone pair – bond pair repulsion the bond angle reduces to 104.5°


Structure of ClF₃

ClF₃ contains 3 bond pairs and 2 lone pairs of electrons. Total 5 electron pairs. so the expected geometry is trigonal bipyramid. But due to the presence of two lone pairs, the geometry is T-shape



Structure of SF₄ It contains 4 bond pairs and 1 lone pair. Expected geometry is trigonal bipyramidal. But due the presence of lone pair the shape is see-saw.

Difference between sigma and pi-bond

SIGMA BOND	Pi-BOND
<ul style="list-style-type: none"> Formed by axial overlapping of half-filled atomic orbitals Extent of overlapping is large Strong bond is formed Free rotation is possible 	<ul style="list-style-type: none"> Formed by sidewise overlapping of atomic orbitals Extent of overlapping is small Weak bond is formed Free rotation is not possible

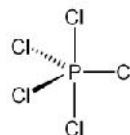
Hybridisation: Intermixing of atomic orbitals to get orbitals having same energy and identical shape is called hybridization

sp Hybridization: In this one s orbital and one p orbital hybridize to form two sp hybridized orbitals. These orbitals are arranged in **linear** position with a bond angle of 180° Eg: **BeCl₂** , **BeF₂** , **C₂H₂**

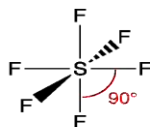
sp² HYBRIDISATION: One s orbital and two p orbitals hybridize together to form 3 sp² hybridized orbitals; these are oriented towards the vertices of an equilateral triangle. The shape is **trigonal planar**. Bond angle is 120° Eg : **BCl₃** , **C₂H₄**

sp³ HYBRIDISATION : In this one s orbital and three p orbitals hybridize to form four sp³ hybridized orbitals. They are oriented towards the corners of a regular tetrahedron giving **Tetrahedral** shape to the molecule. The **bond angle is $109^\circ 28'$** Eg: **CH₄** , **C₂H₆** , **H₂O** , **NH₃**

sp³d HYBRIDISATION: One s three p and one d orbitals hybridize to form five sp³d hybridized orbitals. **Trigonal bipyramidal** shape. Equatorial bond angle is 120° and axial bond angles are 90° . Eg : **PCl₅**



sp³d² Hybridisation: One s, three p, and two d orbitals hybridize to form six sp³d² orbitals. These are oriented towards the corners of an octahedron giving **octahedral** shape. Bond angles are 90° . Eg : **SF₆**



The F-S-F angles are all 90°



The red lines outline an octahedron. Black lines show the covalent bonds

MOLECULAR ORBITAL THEORY ---Postulates

1. In molecules electrons are present in new orbitals called molecular orbitals
2. Molecular orbitals are formed by the combination of atomic orbitals having nearly same energies
3. The number of molecular orbitals formed is equal to the number of combining atomic orbitals.
4. Half of the molecular orbitals have lower energy than combining atomic orbitals, they are called bonding molecular orbitals, and other half with higher energy than atomic orbitals are called antibonding molecular orbitals.
5. Molecular orbitals are associated with nuclei of all bonded atoms

6. Electrons are filled in molecular orbitals according to Pauli's exclusion principle, Hund's rule, and Aufbau principle

Differences Between Bonding And Antibonding Molecular Orbitals

Bonding molecular orbital	Antibonding molecular orbital
<ul style="list-style-type: none"> Formed by the addition of atomic orbitals Lower energy than that of atomic orbitals Electron density is concentrated in between the nuclei of bonded atoms Favours bonding between atoms 	<ul style="list-style-type: none"> Formed by the subtraction of atomic orbitals Higher energy than that of the atomic orbitals Electron density is concentrated away from the nuclei of bonded atoms Do not favours bonding between atoms

BOND ORDER: Bond order is half the difference between number of electrons present in bonding molecular orbitals and that present in antibonding molecular orbitals

$BO = \frac{1}{2} [N_b - N_a]$, N_b — No. of electrons in bonding molecular orbital

N_a --- No. of electrons in antibonding molecular orbital

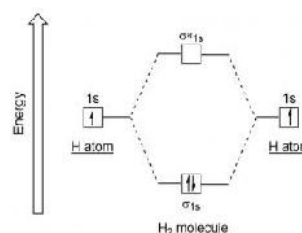
* bond order is directly proportional to stability

* bond order is inversely proportional to bond length

* -ve and zero value of bond order indicate that the molecule is unstable

* value of bond order is equal to the number of covalent bond present between atoms

Molecular Orbital Energy Level Diagram



1. **H₂** Number of electrons in H₂=2 ,

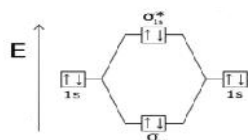
M.O configuration is $\sigma 1s^2$. Bond order of H₂ molecule = $\frac{1}{2} [N_b - N_a] = \frac{1}{2} [2 - 0] = 1$

Molecule is stable, diamagnetic, one covalent bond is present

2. Helium Molecule (He₂)

Total no. of electrons in He₂ molecule = 4 So its M.O configuration is = $\sigma 1s^2 \sigma^* 1s^2$

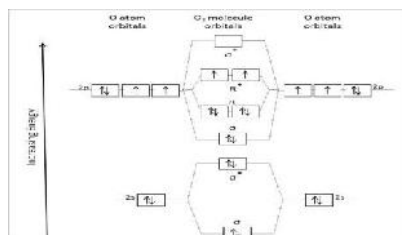
Bond order of He₂ molecule = $\frac{1}{2} [N_b - N_a] = \frac{1}{2} [2 - 2] = 0$ Since B.O is zero, He₂ molecule does not exist.



3. Oxygen (O₂) molecule

Total no. of electrons in O₂ molecule = 16 So its M.O configuration is = $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$

Bond order of O₂ molecule = $\frac{1}{2} [N_b - N_a] = \frac{1}{2} [10 - 6] = \frac{1}{2} \times 4 = 2$ i.e. in O₂ molecule,



two Oxygen atoms are bonded together by a double bond. Its M.O diagram is: Due to the presence of unpaired electrons, O₂ molecule is paramagnetic

Questions

1. Define bond order ? (Ans: Refer Note)
2. How many bond pairs and lone pairs present in NH₃ (Ans : 3 bp and 1 lp)
3. Shape of ClF₃ molecule is (T—shape)
4. Shape of NH₃ molecule is.....(Trigonal pyramidal)
5. Hybridization of B in BCl₃ is.....(sp²)
6. Hybridization of P in PCl₅ is(sp³d)
7. Shape of CH₄ is.....(Tetrahedral)
8. Bond order of He₂ is.....(0)
9. What is the magnetic property of oxygen molecule? (paramagnetic)
10. Define hybridization ? (Refer note)
11. Give any two point of differences between sigma and pi-bond ? (refer note)
12. Explain the structure of H₂O on the basis of VSEPR theory (Refer note)
13. Which one is more stable H₂ or O₂. Explain using MO theory ? (Ans. Hint, Write MO electronic config. of H₂ and O₂. Calculate bond order. BO of H₂ is 1 and that of O₂ is 2 . There fore O₂ is more stable)
14. Explain the structure of ethene on the basis of hybridization ? (Hint.-each carbon atom is SP² hybridized-one sp² hybridized orbital overlap to for c—c sigma bond –other two sp² hybridized orbitals of each c atom overlap with 1s orbital of H atom – unhybridized p orbital undergo side wise overlap to form c—c pi-bond. For diagram refer text.)
15. What are the postulates of VSEPR theory ? (refer note)
16. What are the postulates of MO theory ? (refer note)

17. Draw the molecular orbital energy level diagram of O₂ molecule and predict the properties. (Refer note)

5 STATES OF MATTER

1. The Gas Laws

Boyle's Law (Pressure – Volume Relationship)

At Constant temperature, the pressure of a fixed Amount of gas varies inversely with its volume.

$$P \propto \frac{1}{V}$$

$$V$$

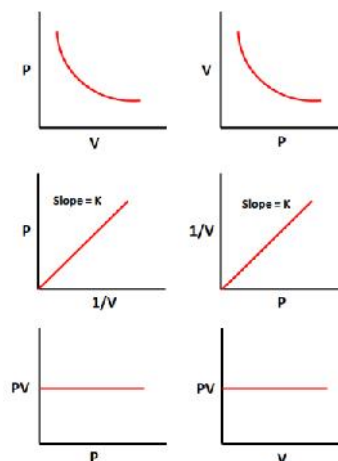
$$PV = k_1$$

$$P_1V_1 = P_2V_2 = \text{Constant}$$

Isotherm (Constant Temperature Plot)

Boyle prove that gases are highly compressible.

Gases become denser at high pressure.



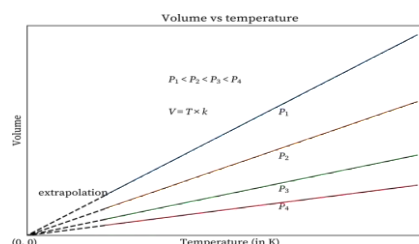
Charles's Law (Temperature – Volume Relationship)

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_1 \quad T_2$$

$$\frac{V}{T} = \text{Constant} = k_2$$

$$T$$



Charles's law states that if pressure remains constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.

Volume Vs temperature graph at constant pressure is called Isobar. Temperature at which gases are supposed to occupy zero volume is called Absolute zero.

Avogadro Law (Volume – Amount Relationship)

It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules. $V \propto n$

One mole of each gas at standard temperature and pressure (STP) will have same volume. Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar pressure. At STP molar volume of an ideal gas is 22.71098 L mol⁻¹.

A gas that follows Boyle's law, Charles's law and Avogadro law strictly is called an ideal gas.

Ideal Gas Equation: $pV=nRT$

R is called Universal Gas Constant. Ideal Gas equation is also called Equation of state.

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

This equation is also known as combined gas law.

Behaviour of real gases: Deviation from Ideal Gas behaviour

Why do gases deviate from the ideal behaviour?

This is because two assumptions of the kinetic theory do not hold good. These are

- There is no force of attraction between the molecules of a gas.
- Volume of gas molecules is negligibly small in comparison to the space occupied by the gas.

$$\left[p + \frac{an^2}{V^2} \right] (V-nb) = nRT$$

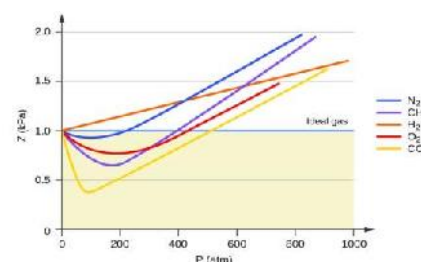
This equation is known as *Van der waals equation*.

Compressibility Factor Z

$$Z = \frac{pV}{nRT}$$

For Ideal Gas $Z = 1$.

The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle Temperature Or Boyle Point.



Model Questions and Hints

1. A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar. If at 1 bar pressure the gas occupies 2.27 L volume, up to what volume can the balloon be expanded?

Hint: According to Boyle's law $p_1 V_1 = p_2 V_2$

If p_1 is 1 bar, V_1 is 2.27 L.

If $p_2 = 0.2$ bar, Then $V_2 = \frac{p_1 V_1}{p_2}$

2. On a ship sailing in Pacific Ocean where temperature is 23.4°C , a balloon is filled with 2L air. What will be the volume of the balloon when the ship reaches Indian Ocean, where temperature is 26.1°C ?

Hint : $V_1 = 2L$ $T_2 = 26.1+273$

$T_1 = (23.4+273)K$ $= 299.1 K$

$= 296.4 K$

From Charles law

$\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$T_1 \quad T_2$

3.It is found that real gases do not obey ideal gas equation perfectly under all conditions.

a) Write the ideal gas equation and mention the terms

b) Why do real gases deviate from ideal behaviour?

Ans : a) $pV=nRT$ R is called Universal Gas Constant. Ideal Gas equation is also called Equation of state.

b) This is because two assumptions of the kinetic theory do not hold good. These are

i) There is no force of attraction between the molecules of a gas.

ii) Volume of gas molecules is negligibly small in comparison to the space occupied by the gas.

4.In the Celsius Scale, Melting point of ice is 0°C. Another Scale of temperature is based on absolute Zero.

a) Identify the scale?

b) What is the Volume of a gas at absolute zero temperature?

c) Draw a graph showing the relationship between volume and temperature of an ideal gas at a constant pressure.

d) Consider a gas at 0°C . At what temperature will the volume be doubled if the pressure is kept constant.

Ans : a) Kelvin Scale b) Zero

c) Isobar given above

(d) 546K

5.Consider the following isotherms of a gas.

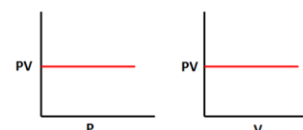
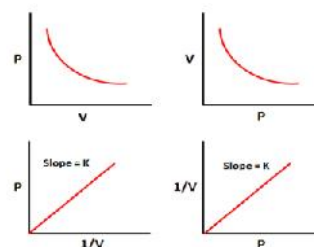
a) Which Gas law is illustrated by these diagrams ?

b) Draw the Diagram When PV is plotted against P ?

c) An air filled balloon has a volume of 125 L at a pressure of 760 mm of mercury and a temperature of 25°C.What will be its volume when the pressure is 670 mm of mercury and temperature is 18°C.

Ans : a) Boyle's Law.

b)



c) $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$ Find V_2

6. The gases which obey gas laws at all temperatures and pressures are called ideal gases.

- a) Give reasons for the deviation of real gases from the ideal gas behaviour.
 b) Calculate the minimum pressure required to compress 500 mL of air at 1 atm to 300 mL at the same temperature.

Ans : a) Refer the answer of 3) b

b) According to Boyle's Law $P_1 V_1 = P_2 V_2$

There pressure required,

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{500 \times 1}{300} = 5 \text{ atm.}$$

7. Ideal Gas equation is true for ideal gases only. There is a modified form of ideal gas equation applicable to all gases.

a) Give the name of modified form of ideal gas equation and write down it.

Ans : $\left[p + \frac{a n^2}{V^2} \right] (V - nb) = nRT$ a and b are called *Van der waals constant*

This equation is also known as *Van der waals equation*.

6 THERMODYNAMICS

Thermodynamics is a branch of chemistry that deals with macroscopic system . It deals with heat changes associated with chemical reactions .

Some Thermodynamic terms

System – The part of the universe which is under investigation .

Surroundings – The part of the universe other than system , which influences the system

Boundary - The real or imaginary separation between the system and surroundings

$$\text{System} + \text{surroundings} = \text{Universe}$$

Types of systems :

Open system – System exchanges both matter and energy with surroundings

Example – Hot water taken in an open vessel

Closed system – System exchanges energy but not matter with surroundings

Example – Hot water taken in a closed vessel

Isolated system – System exchanges neither energy nor matter with the surroundings

Example – Hot water taken in a thermos flask

Extensive property – Property which depends upon the amount of matter present in the system

Example – Volume , internal energy , enthalpy , entropy

Gibb's energy, heat capacity etc

Intensive property – Property which is independent of the amount of matter present in the system.

Example – Temperature,, density refractive index etc

State of the system – The condition of the system at a particular instant of time. It is represented by the state variables namely temperature , pressure and volume .

State function – A function or property which depends on the initial and final state of the system and not on the path through which the change is brought about.

Example – Temperature , pressure , volume , internal energy , enthalpy etc

Path function – Properties or functions which depend on the path followed .

Example – Work , heat

Thermodynamic process – A process is a method by which state of a system changes .

1) **Isothermal process** – Occurs at constant temperature . The system exchanges heat with surroundings .

$$\Delta T = 0 , \Delta q \neq 0$$

2) **Isobaric process** – Occurs at constant pressure ie , $\Delta P = 0$

3) **Isochoric process** – Occurs at constant volume ie , $\Delta V = 0$

4) **Adiabatic process** – Occurs at constant heat energy . Here no heat enters or leaves the system from the surroundings ie , $\Delta q = 0 , \Delta T \neq 0$

5) **Cyclic process** – The process occurs in a cyclic manner . ie , the system undergoes a series of changes and finally returns to the initial state .

$$\Delta U = 0 , \Delta H = 0$$

6) **Reversible process** – Every process is associated with 2 types of forces – driving force and opposing force . If the driving and opposing forces differ by a very small quantity , the process takes place in both directions .

7) **Irreversible process** – If the driving force and opposing force differ on a large quantity , the process takes place only in one direction .

Heat – Heat is a form of energy . It flows from a hot body to cold body , when there is thermal contact between the two . When a body absorbs heat , its heat increases (+q) when a body liberates heat , its heat decreases (-q)

Heat change is represented by q .

Work – A system does work when it cannot exchange heat . Work is done in the form of expansion work . It is represented as W .

Thermodynamically $W = P\Delta V$

When work is done on the system W is positive . ie , $W = +P\Delta V$

When work is done by the system W is negative . ie , $W = -P\Delta V$

For expansion work , $W = \pm P\Delta V$

For irreversible process , $W = \pm P\Delta V$

For reversible process , $W = -2.303nRT \log (V_2/V_1)$

V_1 = Initial volume

V_2 = Final volume

Free expansion – Expansion of a gas into vacuum . For free expansion $P = 0$

So , $W = 0$. ie, no work is done during free expansion .

Internal Energy

The sum of the different types of energies like potential energy , kinetic energy , electronic energy , translational energy etc

It is an extensive property and state function . It is denoted by U .

$$\Delta U = U_2 - U_1$$

U_1 = Initial internal energy

U_2 = Final internal energy

Internal energy of a system can be changed by

- 1) By exchanging heat between system and surrounding
- 2) By doing work

First law of thermodynamics

It states that energy can neither be created nor be destroyed but one form can be converted to another or The total energy of an isolated system is always constant .

Mathematical expression for first law - $\Delta U = q \pm W$ or $\Delta U = q \pm P\Delta V$

Significance of ΔU

$$\Delta U = q \pm P\Delta V$$

For a process at constant volume , $\Delta V = 0$

So $\Delta U = q_v$. ie , internal energy is the heat changed at constant volume .

Enthalpy

It is the total heat content of the system at constant pressure . It is denoted by H . It is a state function and extensive property .

Mathematically $H = U + PV$. ie , $\Delta H = \Delta U + P\Delta V$

For endothermic process ΔH is positive .

For exothermic process ΔH is negative .

Relation between ΔH and ΔU :

Consider a gaseous system with U_1 and H_1 as initial internal energy and enthalpy . Let it be changed to U_2 and H_2

$$H_1 = U_1 + PV_1$$

$$H_2 = U_2 + PV_2$$

$$\text{So , } H_2 - H_1 = (U_2 + PV_2) - (U_1 + PV_1)$$

$$\text{OR } \Delta H = (U_2 - U_1) + (PV_2 - PV_1)$$

$$\text{OR } \Delta H = \Delta U + P\Delta V$$

From ideal gas equation $PV = nRT$

If n_1 and n_2 are the total no. of moles of reactants and products respectively , then $PV_1 = n_1RT$,
 $PV_2 = n_2RT$

$$PV_2 - PV_1 = n_2RT - n_1RT$$

Ie , $P(V_2 - V_1) = (n_2 - n_1) RT$

ie , $P\Delta V = \Delta nRT$

so , $\Delta H = \Delta U + \Delta nRT$

Significance of ΔH

$$\Delta H = \Delta U + P\Delta V$$

From first law of thermodynamics , $\Delta U = q - P\Delta V$

So , $q = \Delta U + P\Delta V$

There fore , we can write $\Delta H = q_p$

That is enthalpy change is equal to heat of the reaction at constant pressure

Enthalpy of a reaction

During a chemical reaction , reactants are converted to products . The enthalpy change during a chemical reaction is called reaction enthalpy . It is denoted by $\Delta_r H$

$\Delta_r H = \text{sum of enthalpies of products} - \text{sum of enthalpies of reactants}$

Standard enthalpy of reactions($\Delta_r H^0$)

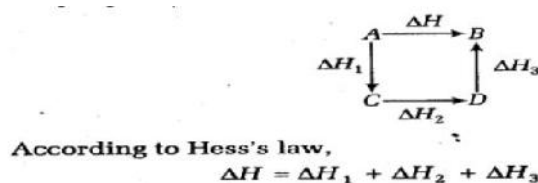
It is the enthalpy change for a reaction when the substances are in their pure form at 1 bar pressure. (Usually data are taken at 298K)

Hess's law of constant heat summation:

The law states that the total enthalpy change of a reaction will be the same whether the reaction takes place in a single step or in several steps .

Consider a reaction in which reactant A is converted to product B in a single step . Let the enthalpy change be ΔH . Let the same reactant A be converted to C , then D and finally to B . Let the heat changes be ΔH_1 , ΔH_2 and ΔH_3

According to Hess's law $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$



Spontaneous process – A process that takes place without the help of an external agency.

Example – All natural processes like water flowing from high level to low level, heat flowing from hot body to cold body, burning of fuels, evaporation of water.

A spontaneous process cannot reverse its direction by its own. Spontaneous processes are also called feasible or probable or irreversible reactions.

Non spontaneous process – A process that takes place with the help of an external agency.

Criteria For Spontaneity

Most of the reactions like burning of fuels, flowing of heat from hot body to cold body etc are accompanied by decrease in energy. So one of the criteria for spontaneity is decrease in energy.

But there are reactions like evaporation of water, melting of ice etc which occur by itself . Here the disorder or randomness of the system increases. So the second criteria for spontaneity is increase in disorder or randomness or entropy

Entropy

It is the measure of disorder or randomness of the system. It is denoted by S . S is a state function and extensive property. So only ΔS is considered.

Mathematically $\Delta S = q_{rev} / T$

Solid \longrightarrow Liquid \longrightarrow Gas – Entropy increases

Gas \longrightarrow Liquid. \longrightarrow Solid – Entropy decreases

For equilibrium entropy change = 0

Entropy and spontaneity

For a spontaneous process , disorder increases ie , ΔS is positive

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

For a spontaneous process , $\Delta S_{\text{total}} > 0$

For a non spontaneous process , $\Delta S_{\text{total}} < 0$

Second Law of Thermodynamics

It states that the entropy of universe always increases for every spontaneous process . So exothermic processes heat is released and disorder increases . So entropy change is positive and the reaction is spontaneous .

Third Law Of Thermodynamics

For a perfectly crystalline solid the entropy approaches zero when the temperature approaches absolute zero .

Gibb's Energy

It represents the overall criteria for spontaneity. It is denoted by G. It is a state function and extensive property.

Relation between ΔG , ΔH and ΔS – Gibb's equation

$$\Delta G = \Delta H - T\Delta S$$

For a reaction to be **spontaneous** ΔG Should be **negative**. Conditions for ΔG to be negative.

ΔH	ΔS	$-T\Delta S$	ΔG	Spontaneity
+	-	+	+	Nonspontaneous
-	+	-	-	Spontaneous
-	-	+	+ or -	Low Temp: Spontaneous High Temp: Nonspontaneous
+	+	-	+ or -	Low Temp: Nonspontaneous High Temp: Spontaneous

QUESTIONS AND ANSWERS

1 . Differentiate an isolated system from a closed system

Ans . Isolated system – It cannot exchange energy or matter with surroundings

Closed system – It can exchange energy but not matter with surroundings

2 . Classify the following into extensive and intensive properties. What are extensive and intensive properties?

Temperature, pressure, volume, internal energy, entropy, enthalpy

Ans . Extensive property – Internal energy , Entropy , Enthalpy, Volume

Intensive property – Temperature , Pressure

Extensive properties – Properties which depend on the amount of matter present in the system .

Intensive properties – Properties which are independent of the amount of matter present in the system

3 . Write the equations for the work done for the different thermodynamic processes .

Hint – For adiabatic process – $W_{adiabatic} = \Delta U$

For irreversible process – $W = -P\Delta V$

For reversible process – $W = -2.303nRT \log V_2 / V_1$

4 . What is free expansion

Ans . Expansion of gas into vacuum . $P = 0$, ie , $W = 0$

5 . State 1st law of thermodynamics. Give its mathematical statement.

Ans . It is law of conservation of energy. It states that energy can neither be created nor be destroyed.

Mathematical statement - $\Delta U = q \pm W$

6 . Write the significance of internal energy change and enthalpy change.

Ans . Internal energy change - $\Delta U = q_v$

Enthalpy change - $\Delta H = q_p$

q_v = Heat exchange at constant pressure

q_p = Heat exchanges at constant volume

7 . What is enthalpy of a reaction ?

Ans . Heat change accompanying conversion of reactant to product .

Enthalpy of reaction - $\Delta_r H = \text{Total enthalpy of products} - \text{total enthalpy of reactants}$

8 . State and explain Hess's law of heat summation

Ans . The law states that the total enthalpy change of a reaction will be the same whether the reaction takes place in a single step or in several steps .

Consider a reaction in which reactant A is converted to product B in a single step . Let the enthalpy change be ΔH . Let the same reactant A be converted to C , then D and finally to B . Let the heat changes be ΔH_1 , ΔH_2 and ΔH_3

According to Hess's law $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

9 . What is entropy ?

Ans . The degree of disorder or randomness . It is denoted by ΔS

$\Delta S = q_{rev} / T$

10 . Identify the entropy values in the following changes

1) Ice is changed to water

2) Dissolution of ammonium chloride

3) A gas adsorbed on a solid

Ans . 1) $\Delta S - +ve$

2) $\Delta S - +ve$

3) $\Delta S - -ve$

11 . State 2nd law of thermodynamics

Ans . It states that the entropy of universe always increases for every spontaneous process . So exothermic processes heat is released and disorder increases . So entropy change is positive and the reaction is spontaneous

12 . State the 3rd law of thermodynamics

Ans . For a perfectly crystalline solid the entropy approaches zero when the temperature approaches absolute zero .

13 . Write the Gibb's equation which connects ΔG , ΔH & ΔS

Ans . $\Delta G = \Delta H - T\Delta S$

14 . What is a spontaneous and a non-spontaneous process ?

Ans . Spontaneous process – A process which takes place by itself without the help of external energy

Non spontaneous process – A process which does not take place without the help of an external agency .

15 . How are enthalpy and free energy related ?

Ans . $\Delta H = \Delta U + P\Delta V$ or $\Delta H = \Delta U + nRT$

16 . How is spontaneity and Gibb's equation related?

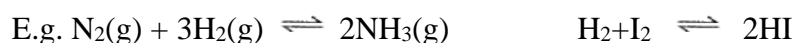
Ans . For a reaction to be spontaneous ΔG Should be negative.

$$\Delta G = \Delta H - T\Delta S$$

7 EQUILIBRIUM

Reversible reactions

Reversible reactions are those which take place in both directions. i.e. here reactants combined to form products and the products recombine to form reactants.



At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction. Thus equilibrium is a state in which the rates of forward and backward reactions are equal. Equilibrium is dynamic in nature. i.e. at equilibrium the reaction does not stop.

Law of Chemical Equilibrium and Equilibrium Constant

This law was proposed by C. M. Guldberg and Peter Waage. It states that at constant temperature, the product of concentration of the products to that of the reactants, in which each concentration term is raised to a power which is equal to the stoichiometric coefficients in the balanced chemical equation, has a constant value.

For a general reaction, $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad K_c \text{ is called equilibrium constant}$$

For the reaction $H_2 + I_2 \rightleftharpoons 2HI$; $K_c = \frac{[HI]^2}{[H_2][I_2]}$ For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

Equilibrium constant for the reverse reaction is the inverse of that for the forward reaction. i.e. if the equilibrium constant for the reaction

$H_2 + I_2 \rightleftharpoons 2HI$ is K_c , then that for the reverse reaction is $1/K_c$

Equilibrium constant for gaseous reactions

For a reaction involving gases, the concentration terms are replaced by partial pressures.

For example, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$K_p = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})}$$

Where K_p is called equilibrium constant in terms of partial pressure, p_{HI} , p_{H_2} and p_{I_2} are the partial pressures of HI, H_2 and I_2 respectively.

Relation between K_p and K_c

Consider a general reaction, $aA + bB \rightleftharpoons cC + dD$

The equilibrium constant in terms of concentration for this reaction is $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

the equilibrium constant in terms of partial pressures is $K_p = \frac{(p_C)^c \cdot (p_D)^d}{(p_A)^a \cdot (p_B)^b}$ (1)

From ideal gas equation, $PV = nRT$, $P = nRT/V = CRT$ (since $n/V = C$, the concentration)

Therefore, $(p_A)^a = [A]^a (RT)^a$, $(p_B)^b = [B]^b (RT)^b$, $(p_C)^c = [C]^c (RT)^c$

and $(p_D)^d = [D]^d (RT)^d$

Substitute these values in equation (1), we get

$$K_p = \frac{[C]^c(RT)^c [D]^d(RT)^d}{[A]^a(RT)^a [B]^b(RT)^b} = \frac{[C]^c[D]^d (RT)^c(RT)^d}{[A]^a[B]^b (RT)^a(RT)^b} = K_c \frac{(RT)^{c+d}}{(RT)^{a+b}} = K_c [RT]^{(c+d)-(a+b)}$$

$$K_p = K_c (RT)^{n_P - n_R} \quad \text{or} \quad K_p = K_c (RT)^{\Delta n}$$

Δn is the change in no. of moles of gaseous species. i.e. $\Delta n =$ no. of moles of gaseous products – no. of moles of gaseous reactants.

Special cases:

i) If $\Delta n = 0$, then $K_p = K_c$ ii) If $\Delta n > 0$, then $K_p > K_c$ and iii) If $\Delta n < 0$, then $K_p < K_c$

Acid – base concepts:

1. Arrhenius concept: According to this concept acids are substances which give hydrogen ion (H^+) or hydronium ion (H_3O^+) in aqueous solution and bases are substances which give hydroxyl ion (OH^-) in aqueous solution.

Arrhenius acids : HCl , H_2SO_4 , HNO_3 etc Arrhenius bases : $NaOH$, KOH , $Ca(OH)_2$ etc

Note: H^+ ions exist in water as hydronium ions (H_3O^+)

2. The Bronsted – Lowry concept: (protonic concept)

According to this concept acids are proton (H^+) donors and bases are (H^+) acceptors.

For example, in the reaction $NH_3(l) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Here NH_3 is a base since it accepts an H^+ ion to form NH_4^+ and H_2O is an acid since it donates an H^+ ion to form OH^- .

The acid base pair that differs by only one proton (H^+) is called a conjugate acid – base pair.

An acid formed from a base is called conjugate acid and a base formed from an acid is called conjugate base.

In general **Acid – $H^+ \rightarrow$ Conjugate base** **Base + $H^+ \rightarrow$ Conjugate acid**

(conjugate acid by the addition of H^+ ion and conjugate base is formed by the removal of H^+ ion)

If the acid is strong, its conjugate base is weak and vice versa.

Water can act both as acid and base. So it is an amphoteric substance.



3. Lewis concept: (electronic concept)

According to this concept acids are electron pair acceptors and bases are electron pair donors.

Substances which donate electron pair are called Lewis bases and substances which accept electron pair are called Lewis acids.

Example for Lewis acids are BF_3 , $AlCl_3$, H^+ , Co^{3+} , Mg^{2+} etc.

Example for Lewis bases are NH_3 , H_2O , OH^- , Cl^- , Br^- etc.

For a substance to act as Lewis acid, it should contain vacant orbitals and for a substance to act as Lewis base, it should contain lone pairs of electrons.

All cations are Lewis acids and all anions are Lewis bases.

The ionization constant of water (The ionic product of water) K_w

Water is a weak electrolyte and hence it ionizes only partially as:



The dissociation constant, $K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$

$$K [\text{H}_2\text{O}]^2 = K_w$$

$$\text{There for } K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

Where K_w is called ionization constant of water or ionic product of water. It is defined as the product of the molar concentration of hydronium ion and hydroxyl ion in water or in any aqueous solution.

For pure water at 298K, $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$.

Therefore, $K_w = [\text{H}^+][\text{OH}^-] = 10^{-7} \times 10^{-7} = 10^{-14} \text{ M}^2$

The value of K_w is temperature dependent. It increases when temperature is increased.

By knowing the concentrations of H_3O^+ and OH^- ions, we can predict the nature of an aqueous solution.

If $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, the solution is acidic If $[\text{H}_3\text{O}^+] < [\text{OH}^-]$, the solution is basic

If $[\text{H}_3\text{O}^+] = [\text{OH}^-]$, the solution is neutral

The p H scale

p H is defined as the negative logarithm of the hydrogen ion concentration or hydronium ion concentration in moles per litre (i.e. molarity). i.e. $\text{p H} = -\log[\text{H}^+]$ or $\text{p H} = -\log[\text{H}_3\text{O}^+]$

Negative logarithm of hydroxyl ion concentration in mol /L is called p OH .

i.e. $\text{p OH} = -\log[\text{OH}^-]$

For pure water, at 298K (25°C), $[\text{H}^+] = 10^{-7}$. Therefore p H of pure water is 7.

The pH scale is introduced by Sorensen. It contains numbers from 0 to 14. If the pH is less than 7, the solution is acidic, if it is greater than 7, it is basic and if it is 7, the solution is neutral.

p H + p OH = 14 Thus by knowing the p H , we can calculate p OH as $\text{p OH} = 14 - \text{p H}$

Buffer Solutions

Solution which resists the change in pH on dilution or with the addition of small amount of acid or alkali is called Buffer solution. There are two types of buffer solutions – acidic buffer and basic buffer.

Acidic buffer is a mixture of a weak acid and its salt with a strong base. E.g. a mixture of acetic acid and sodium acetate acts as an acidic buffer around p H 4.75.

Basic buffer is a mixture of a weak base and its salt with a strong acid. E.g. a mixture of NH_4OH and NH_4Cl acts as a basic buffer around pH 9.25

Human blood is a buffer solution. It contains weak acid carbonic acid and its salt bicarbonates.

Questions & Answers

1. For the equilibrium, $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$, the value of equilibrium constant K_p is 1.8×10^{-2} at 500 K. Calculate K_c for this reaction at the same temperature.

Ans: Here $K_p = 1.8 \times 10^{-2}$, $R = 0.083 \text{ L bar/K/mol}$, $\Delta n = n_{P(\text{g})} - n_{R(\text{g})} = 3 - 2 = 1$ and $T = 500\text{K}$

$$K_p = K_c(RT)^{\Delta n}$$

$$1.8 \times 10^{-2} = K_c(0.083 \times 500)^1 \quad K_c = 1.8 \times 10^{-2} / (0.083 \times 500) = 4.33 \times 10^{-4}$$

2. Give the Lewis concept of acids and bases with suitable example.

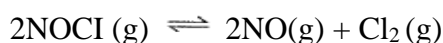
Ans: According to this concept, acids are electron pair acceptors and bases are electron pair donors. Example for Lewis acids are BF_3 , AlCl_3 etc. Example for Lewis bases are NH_3 , H_2O etc.

3. Examine the chemical equilibrium, $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$.

Write the expression for equilibrium constant (K_c) for the above equilibrium.

$$\text{Ans: } K_c = \frac{[\text{NO}]^4}{[\text{NH}_3]^4 [\text{O}_2]^5}$$

4. (a) Derive the relation between K_p and K_c
 (b) Give the relation between K_p and K_c , for the reaction given below.



Ans:(a) Refer notes

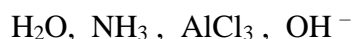
$$(b) K_p = K_c(RT)^{\Delta n} \quad \text{Here } \Delta n = n_{p(\text{g})} - n_{r(\text{g})} = 3 - 2 = 1 \quad \text{So, } K_p = K_c \cdot RT$$

5. Define buffer solutions and write one example for an acidic buffer.

Ans: Solutions which resist the change in pH on dilution or with the addition of small amount of acid or alkali is called Buffer solution.

E.g. A mixture of acetic acid and sodium acetate acts as an acidic buffer

6. According to Lewis theory, classify the following into acids and bases:



Ans : Lewis acids : AlCl_3 Lewis bases : $\text{H}_2\text{O}, \text{NH}_3, \text{OH}^-$

7. Write conjugate acid and conjugate base for H_2O and HSO_4^-

Ans : H_2O - conjugate acid: H_3O^+ conjugate base : OH^-

HSO_4^- - conjugate acid: H_2SO_4 conjugate base : SO_4^{2-}

8. Calculate the pH of 2×10^{-2} molar HCl solution.

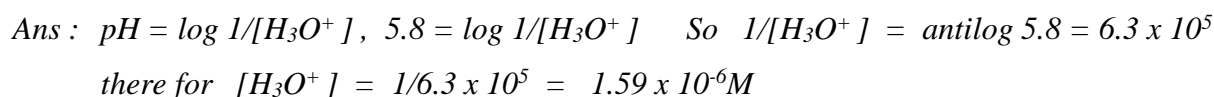


9. (a) What is ionic product of water ?
(b) How it varies when temperature changes?

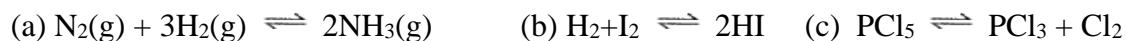
Ans : (a) It is defined as the product of the molar concentration of hydronium ion and hydroxyl ion in water or in any aqueous solution. At room temperature, value of $K_w = 10^{-14}$

(b) Value of K_w increases when temperature is increased.

10. pH of a soft drink is 5.8. Calculate its hydronium ion concentration.



11. In which of the following equilibrium $K_p = K_c$



Ans: $H_2 + I_2 \rightleftharpoons 2HI$ (change in number of moles is zero)

12. Water is amphoteric. Explain with examples

Ans: Water can act both as acid and base. So it is an amphoteric substance.



8 REDOX REACTIONS

ELECTRONIC CONCEPT OF OXIDATION AND REDUCTION

Oxidation: Oxidation is the process involving loss of electrons.

Reduction: Reduction is the process involving gain of electrons.

Oxidising Agent: An oxidising agent is a substance whose atoms gain electrons.

Reducing Agent: A reducing agent is a substance whose atoms lose electrons.

Redox Reaction: A chemical reaction in which both oxidation and reduction reactions occur simultaneously is called a redox reaction.

Oxidation Number or Oxidation State: Oxidation number is defined as the charge that an atom would have if both the electrons in each bond were assigned to the more electronegative element.

Rules for assigning oxidation numbers: Oxidation number of an element in the free or uncombined state is zero.

The sum of the oxidation numbers of all the atoms in a neutral molecule is zero.

The oxidation number of mono atomic ion is equal to the charge on it.

For polyatomic ions, sum of the oxidation numbers of all the atoms in it is equal to the charge on it.

Oxidation number of fluorine is -1 in all its compounds.

Oxidation number of hydrogen is $+1$ in all its compounds

But in ionic hydrides the oxidation number is -1 .

Oxidation number of oxygen is -2 .

In OF_2 , oxidation number of oxygen is $+2$

In peroxides it is -1 and in super oxides it is $-1/2$

Oxidation number of alkali metals is $+1$

Oxidation number of alkaline earth metals is $+2$.

Oxidation number of halogens is -1 .

OXIDATION AND REDUCTION IN TERMS OF OXIDATION NUMBERS

Oxidation: A chemical change in which there is an increase in oxidation number.

Reduction: A chemical change in which there is a decrease in oxidation number.

Oxidising Agent

A substance which undergoes a decrease in oxidation number.

Reducing Agent

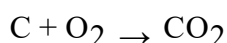
A substance which undergoes an increase in oxidation number.

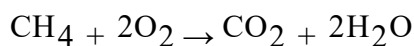
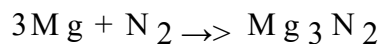
TYPES OF REDOX REACTIONS

1. Combination Reactions

A combination reaction may be represented as $A + B \rightarrow C$.

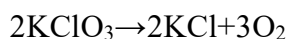
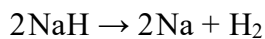
Either A or B or both A and B must be in the elemental form.



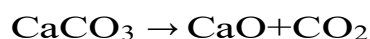


2. Decomposition Reaction

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.



All decomposition reactions are not redox reactions



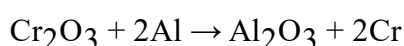
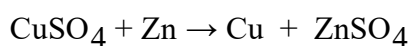
3. Displacement reaction

In a displacement reaction, an ion or an atom in a compound is replaced by an ion or atom of another element.

It may be denoted as $X + YZ \rightarrow XZ + Y$.

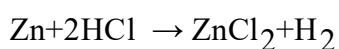
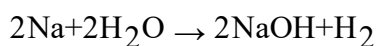
a) Metal Displacement

A metal in a compound can be displaced by another metal in the uncombined state.



b) Non metal Displacement

The non metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement.



4. Disproportionation Reaction

In this reaction, an element in one oxidation state is simultaneously oxidized and reduced

BALANCING OF REDOX REACTIONS

Ion Electron Method or Half Reaction Method

The various steps involved in this method are

Write the skeletal equation represents the chemical change.

Indicate the oxidation numbers of all atoms involved in the reaction.

Find the elements whose oxidation numbers are changed.

Separate the redox reaction into half reactions. i.e., oxidation half and reduction half reactions.

Balance all atoms other than hydrogen and oxygen.

Calculate the oxidation number on the left and on the right. Add electrons to whichever side is necessary, to make up for the difference.

Balance half reaction so that both sides will have the same charge.

Add water molecules to complete the balancing of the equation.

Add the two balanced half equations.

QUESTIONS

1. Given below is a redox reaction $\text{CuO}_{(s)} + \text{H}_{2(g)} \rightarrow \text{Cu}_{(s)} + \text{H}_2\text{O}_{(g)}$

a) Identify the species which undergo reduction and which undergo oxidation.

Ans: CuO undergoes reduction and H₂ undergoes oxidation.

b) Identify the reductant and oxidant in the above reaction.

Ans: H₂ is reductant and CuO is oxidant.

2. Find out the oxidiser and reducer in the following reaction on the basis of the electronic concept.

$2\text{Na}_{(s)} + \text{Cl}_{2(g)} \rightarrow 2\text{NaCl}_{(s)}$ *Ans: Oxidiser: Cl₂*

Reducer: Na

3. Fluorine reacts with ice as given below:

$\text{H}_2\text{O}_{(s)} + \text{F}_{2(g)} \rightarrow \text{HF}_{(g)} + \text{HOF}_{(g)}$. Justify that this is a redox reaction

Ans: Oxidation number of fluorine decreases in HF while the oxidation number of fluorine increases in HOF. So it is a redox reaction.

4. In the reaction

$\text{Pb}_{(s)} + \text{PbO}_{2(s)} + 2\text{H}_2\text{SO}_{4(aq)} \rightarrow 2\text{PbSO}_{4(s)} + 2\text{H}_2\text{O}_{(l)}$.

Identify the following:

- | | |
|-----------------------|----------------------|
| i) Substance oxidised | ii) Substance |
| reduced | iii) Oxidising agent |
| iv) Reducing agent | |

Ans: Substance oxidised: Pb

Substance reduced: PbO₂

Reducing agent: Pb

Oxidising agent: PbO₂

5. During a group discussion, one of your friends argues that thermal decomposition of KClO₃ is a redox reaction while that of CaCO₃ is not a redox reaction. Give your opinion and substantiate.

Ans: The argument is correct. In the decomposition of KClO₃, oxidation and reduction takes place and hence it is a redox reaction. But in the decomposition of CaCO₃, there is no change in the oxidation number and it is not a redox reaction.

6. In disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced. Identify the element undergoing disproportionation in the following reaction:



Ans: Phosphorous

7. Fill in the blanks.

a) The oxidation state of Cl in HClO₄ is.

Ans: +7

b) A reducing agent is a substance which electrons in a chemical reaction.

Ans: loses

c) Among the elements Fluorine and Iodine, exhibit both positive and negative oxidation states.

Ans: Iodine

8. a) Both HCl and NaH contain H, but the oxidation states of H in them are different. What is the oxidation state of H in each compound?

Ans: The oxidation state of H is +1 in HCl and -1 in NaH.

b) What is the oxidation state of 'S' in

SO₄²⁻? *Ans: +6*

9. a) NO and HNO₃ are two compounds of nitrogen. In which of them N is more oxidised?

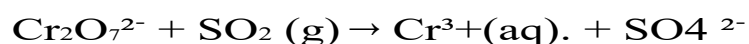
Ans: In NO, N atom is in +2 oxidation state and in HNO₃, N atom is in +5 oxidation state.

10. The concept of oxidation number helps us to understand transfer of electrons in chemical reactions. Consider Cs, Ne, I and F. Identify

- the element shows negative oxidation state
- the element shows positive oxidation state
- the element shows both positive and negative oxidation state

Ans: a) F (b)Cs (c) I

11. Balance the following equation in acid medium (half reaction method)



12. What are Disproportionation reactions?

13. Assign oxidation number

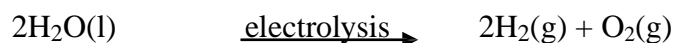
- carbon in Acetic acid
- Phosphorus in H₄P₂O₇

9 HYDROGEN

Commercial production of Hydrogen

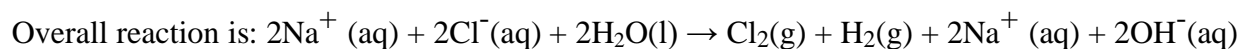
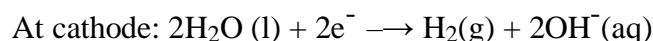
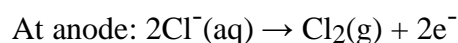
Commercially Hydrogen is prepared by the following methods:

1. Electrolysis of acidified water using platinum electrodes



2. High purity dihydrogen is obtained by the electrolysis of warm aqueous Ba(OH)₂ solution using nickel electrodes.

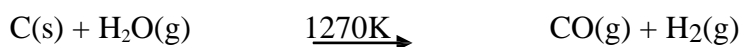
3. By the electrolysis of brine solution (NaCl solution). Here H₂ gas is obtained at the cathode.



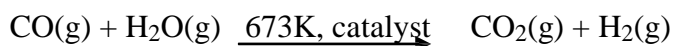
4. By the reaction of steam on hydrocarbons or coke at high temperature in the presence of catalyst. CH₄(g) + H₂O(g) → CO(g) + H₂(g)

The mixture of CO and H₂ is called water gas. Since it is used for the synthesis of methanol and large number hydrocarbons, it is also called *synthesis gas or syn gas*.

Now syngas is also produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called '*coal gasification*'.



The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst. This is called *water-gas shift reaction*.



Hydrides

The binary compounds of hydrogen with other elements are called Hydrides. They are classified into three:

1. Ionic or saline or salt-like hydrides:

These are hydrides formed by s-block elements. They are crystalline, non-volatile and stoichiometric solids. They are non-conductors in the solid state but conduct electricity in the molten state or in aqueous solution state.

e.g. NaH, KH, CaH₂, BaH₂ etc.

2. Covalent or Molecular Hydrides:

These are the hydrides of p-block elements. Examples are CH₄, NH₃, H₂O and HF. Being covalent, they are volatile compounds. Molecular hydrides are further classified into three.

(i) *electron-deficient*, (ii) *electron-precise* (iii) *electron-rich hydrides*.

An electron-deficient hydride has very few electrons for writing its Lewis structure. E.g. Diborane (B₂H₆). All elements of group 13 will form electron-deficient compounds. They act as Lewis acids (i.e. they accept electron pairs).

Electron-precise compounds have the required number of electrons to write their Lewis structures. All elements of group 14 form such compounds (e.g., CH₄, SiH₄ etc.)

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15 to 17 form such compounds. They behave as Lewis bases (i.e., electron donors).

3. Metallic Hydrides:

These are formed by d and f-block elements [Except the elements of group 7, 8 and 9]. Being deficient in hydrogen, they are almost non-stoichiometric. They conduct heat and electricity.

e.g. LaH_{2.87}, YbH_{2.55}, TiH_{1.5–1.8}, ZrH_{1.3–1.75}, VH_{0.56}, NiH_{0.6–0.7}, PdH_{0.6–0.8} etc.

In these hydrides the hydrogen atom is occupied in the metal lattice. So they are also called *interstitial*

hydrides. Due to the property of absorption of hydrogen on interstitial sites, they are widely used as hydrogenation catalysts.

Hard and soft water

Water which does not easily form lather with soap is called hard water. It is due to the presence of calcium and magnesium salts in the form chlorides, sulphates and bicarbonates.

Water free from soluble salts of calcium and magnesium is called soft water. It easily forms lather with soap.

Soaps are sodium or potassium salts of fatty acids like palmitic acid, stearic acid oleic acid etc.

They react with calcium or magnesium salts presenting in hard water and form precipitates.

There are two types of hardness of water – temporary hardness and permanent hardness.

Disadvantages of Hardness of water:

1. It results in wastage of soap.
2. It results in scale formation in boilers which ultimately results in boiler explosion.

Removal of temporary hardness:

- Boiling
- Clark's method

Removal of permanent hardness:

- Treatment with a washing soda
- Calgon's method
- Ion- exchange method (zerolite –permutit method)
- Synthetic resin method

HYDROGEN PEROXIDE (H₂O₂)

Hydrogen peroxide is an important chemical used in pollution control treatment.

Storage

H₂O₂ decomposes slowly on exposure to light.



In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalyzed. It is, therefore, stored in wax-lined glass or plastic vessels in dark. Urea can be added as a stabilizer. It is kept away from dust because dust can induce explosive decomposition of the compound.

10 THE S-BLOCK ELEMENTS

ALKALI METALS

- Group 1 elements: lithium, sodium, potassium, rubidium, cesium, and francium
- Called alkali metals because their hydroxides are alkaline in nature

Electronic Configuration

- General outer electronic configuration is ns^1 .

Atomic and Ionic Radii

- Increase with increase in atomic number (i.e., on moving down the group)

Ionization Enthalpy

- Low
- Decreases on moving down the group, which is because of the following reasons:
 - Increase in size
 - Increase in screening of outermost electrons from the nuclear charge

Hydration Enthalpy

- Decreases on moving down the group

Physical Properties

- **Flame test;** They and their salts impart characteristic color to an oxidizing flame. Reason: after getting heat from the flame, the valence electrons get excited to higher energy level. Then they come back to ground state by emitting radiation in the visible region.

Chemical Properties

- Highly reactive because of
 - **large size**
 - **low ionization enthalpy**
- Reactivity increases down the group.
- Reaction with air:
 - Tarnish in dry air – Reason: formation of oxides and then hydroxides with moisture
 - **Kept in kerosene oil – Reason: highly reactive towards air and water**
- Reducing nature
 - Strong reducing agent
 - Li is the strongest and Na is the weakest.
- **Solutions in liquid ammonia**

- Dissolve in liquid ammonia to give conducting deep blue solution



- Reason for blue colour – The ammoniated electron absorbs energy in the visible region of light.
- The solution is paramagnetic in nature and liberates hydrogen to form amide

Uses

- In making useful alloys
 - Li – in making ‘white metal’ bearings for motor engines, Al – in making aircraft parts, Mg – in making armor plates, which are used in thermonuclear reaction, Cs is used in devising photoelectric cells.

- Reasons for anomalous behavior of lithium:

- The Li atom and ion are exceptionally small in size.
- Li has high polarizing power. [charge to radius ratio (charge/ radius)]

- **Points of difference between lithium and alkali metals**

- Li is harder and has high melting and boiling points.
- Strongest reducing agent, forms Li_2O and Li_3N by reacting with air
- LiCl is deliquescent and crystallizes as a hydrate, $\text{LiCl} \cdot 2\text{H}_2\text{O}$.
- LiHCO_3 does not exist as solid.

- Li shows diagonal relationship to Mg.

- **Points of similarities between Li and Mg**

- Both are harder and lighter than the other elements in the respective groups.
- Both react slowly with water; oxides of both are less soluble in water; hydroxides of both decompose on heating.
- Both form nitrides (Li_3N and Mg_3N_2) by directly reacting with nitrogen.
- Both do not form superoxide.

- Reason for similarities between Li and Mg – **Similar size**

Some Important Compounds of Sodium

Washing Soda or Sodium Carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)

- **Preparation**

- Solvay process



○

Solvay process is not applied to manufacture K_2CO_3 .

Reason – $KHCO_3$ is soluble in water and hence, cannot be precipitated.

Backing Soda or Sodium Hydrogen Carbonates ($NaHCO_3$)

- **Called Baking Soda**

- Reason – It decomposes, producing bubbles of CO_2 on heating. This is the reason why holes are formed in cakes or pastries and as a result, they are light and fluffy.

- **Preparation**



Alkaline earth metals

- Group 2 elements: Beryllium, magnesium, calcium, strontium, barium and radium.
- They are called alkaline earth metals because their oxides and hydroxides are alkaline in nature, and their oxides are found in earth's crust.

Anomalous Properties of Beryllium

- Exceptionally small size of the atom and the cation
- Forms covalent compounds (due to small size and high ionisation enthalpy)
- Highest coordination number is four while other members exhibit six.
- Reason: Be has four orbitals in its valence shell while other members can use *d*-orbitals
- Unlike other elements, the oxides and hydroxides of Be are amphoteric in nature.

Diagonal Relationship Between Be and Al

- Reason: Same charge/radius ratio
- Similarities:
 - Like Al, it is not readily attacked by acids; (Reason – presence of an oxide film on the surface of the metal)
 - Both dissolve in excess of alkali, giving beryllate ion $[Be(OH)_4]^{2-}$ and aluminate ion $[Al(OH)_4]^-$.

○ Like Al_2Cl_6 , BeCl_2 has a Cl^- bridged polymeric structure. Both these compounds are Lewis acids, and are soluble in organic solvents.

○ Both form fluoro complex ions, $[\text{BeF}_4]^{2-}$, $[\text{AlF}_6]^{3-}$

Some Important Compounds of Calcium

Quick Lime or Calcium Oxide (CaO)

- **Preparation:**



- For the completion of the reaction, CO_2 is removed as soon as it is produced.

- **Slaking of lime** – the process of breaking lump of lime by adding a limited amount of water

- When slaked with soda, it gives solid soda lime

- **Uses:**

- **For manufacturing** cement, sodium carbonate from caustic soda, dye stuffs, For purifying sugar

Slaked Lime or Calcium Hydroxide [$\text{Ca}(\text{OH})_2$]

- **Preparation:**

By adding water to quick lime



- **Properties:**

- **Lime water** – clear aqueous solution of $\text{Ca}(\text{OH})_2$

- **Milk of lime** – suspension of slaked lime in water

- With chlorine, slaked lime gives **bleaching powder**



- **On passing carbon dioxide through lime water, it turns milky due to the formation of calcium carbonate (CaCO_3)**



- **On passing excess of CO_2 , calcium carbonate (CaCO_3) dissolves, forming calcium hydrogen carbonate**



Calcium Carbonate (CaCO_3)

- **Naturally Occurs As Limestone, Chalk, Marble**

- **Preparation:**

- By passing CO_2 through slaked lime

On passing excess of CO_2 , CaCO_3 dissolves to form water-soluble calcium hydrogen carbonate.



- By adding aqueous solution of sodium carbonate to calcium chloride




Plaster Of Paris or Calcium Sulphate

- **Hemihydrate of Calcium Sulphate**

- **Preparation:**

By heating gypsum to 393 K



- 
$$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$$
- Above 393 K, water is liberated to form anhydrous calcium sulphate (CaSO_4), known as 'dead burnt plaster'.

- **Property:**

- On mixing with water, it forms a plastic mass which sets into a hard solid in 5 – 15 minutes.

- **Uses:**

- As plaster and as building material, In surgical bandages, for setting broken and fractured bones For making statues, busts, and in ornamental work

Cement

- Also called Portland cement
- Reason: Resembles the natural limestone extracted in the Isle of Portland, England
- Composition of cement:
 - $\text{CaO} = 50 - 60\%$, $\text{SiO}_2 = 20 - 25\%$, $\text{Al}_2\text{O}_3 = 5 - 10\%$, $\text{MgO} = 2 - 3\%$, $\text{Fe}_2\text{O}_3 = 1 - 2\%$
- For a good-quality cement:
 - The ratio of SiO_2 : $\text{Al}_2\text{O}_3 = 2.5$ to 4

- The ratio of CaO: $(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) = 2$
- Manufacture of cement:
 - Raw materials – limestone and clay

On strong heating, clay and lime fuse and react to form 'Cement clinker'

'Cement clinker' is mixed with 2 – 3% by weight of gypsum to form cement.

Setting of cement: On mixing with water, cement sets to give a hard solid

Reason – hydration of the molecules of the constituents and their rearrangement

- **Reason for adding gypsum** – to slow down the process of setting of the cement; this results in sufficient hardening of the cement

Questions

1. Give reasons for the anomalous behavior of Li. Write any four points of similarities between Li and Mg.

Ans: Li shows some anomalous properties due to; its small size and high polarizing power.

. Similarities between Li and Mg:

- *Both Li and Mg are harder but lighter than other elements of the respective group. They do not form superoxide.*

Their bicarbonates are stable only in solution.

2. Name the commercial process used to prepare sodium carbonate and write the chemical equations of the steps involved in it.

Ans: Solvay Process.

3. Account for the following:

- a) Blue colored solutions are obtained when alkali metals are dissolved in liquid ammonia.
- b) 'Li' and 'Mg' show similar properties.
- c) Aqueous solution of Na_2CO_3 is alkaline.
- d) BeSO_4 and MgSO_4 are readily soluble in water.

Ans: a) It is due to the formation of ammoniated electrons.

b) Due to their similar size and same electronegativity.

c) Carbonate part of sodium carbonate gets hydrolyzed to form OH^- ion. So the aqueous solution of Na_2CO_3 is alkaline.

d) This is due to the greater hydration enthalpy of Be^{2+} and Mg^{2+} ions.

4. a) Alkali metals dissolve in liquid ammonia to give blue colored solutions. Why?

b) Plaster of Paris is an important compound of calcium. i) Give the chemical formula of plaster of Paris.

ii) Identify the property of plaster of Paris which helps in plastering of broken bones.

Ans: a) Alkali metals dissolve in liquid ammonia and form ammoniated electron, which absorbs energy in the visible region and gives blue color to the solution.

b) i) $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$

ii) during Setting of plaster of Paris it expands.

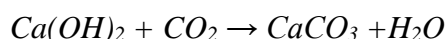
5. a) Fill in the blanks: i) The suspension of a magnesium compound in water is used as an antacid. The compound is (1) ii) A mixture of calcium oxide (Quick lime) and caustic soda (NaOH) is called (1)

b) When CO_2 is passed through lime water it turns milky. On passing excess of CO_2 , the milky colour disappears.

6. Give the chemical reactions involved in these processes.

Ans: a) i) $\text{Mg}(\text{OH})_2$ ii) Soda lime

b) It is due to the formation of CaCO_3 . On passing CO_2 continuously, the solution becomes clear due to the formation of soluble calcium bicarbonate [$\text{Ca}(\text{HCO}_3)_2$]

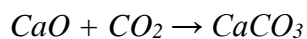


6. a) How will you prepare $\text{Ca}(\text{OH})_2$ and CaCO_3 from quick lime (CaO)?

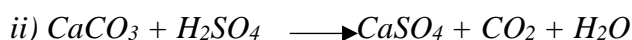
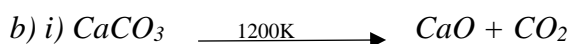
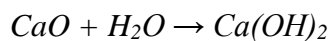
b) Complete the following reactions:



Ans: a) When CO_2 is passed through quick lime, CaCO_3 is formed.



When water is added to CaO, we get $\text{Ca}(\text{OH})_2$



11 THE P BLOCK ELEMENTS

These are elements in which the last electron enters in the outermost **p-subshell**.

There are six groups of p-block elements in the periodic table numbering from 13 to 18. (except He). Their valence shell electronic configuration is $ns^2 np^{1-6}$

They include metals, non metals and metalloids.

Compounds of boron

Diborane: The simplest boron hydride is diborane (B_2H_6)

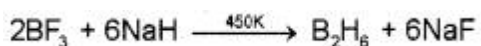
Preparation

Diborane can be prepared by treating BF_3 with **lithium aluminium hydride** in ether.

laboratory method is oxidation of **sodium boron hydride** with **iodine**.



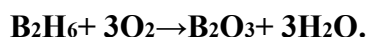
On a commercial scale, diborane is produced by the action of BF_3 on sodium hydride.



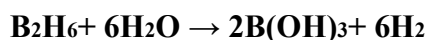
Properties

Diborane is a colourless toxic gas.

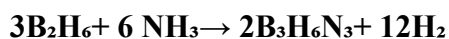
It catches fire on exposure to air releasing large amount of energy and form B_2O_3



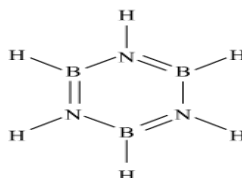
It readily **hydrolysed** by water to give **boric acid**.



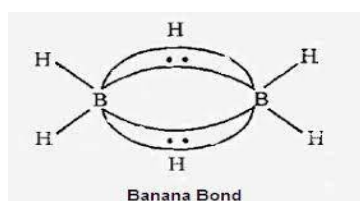
Ammonia reacts with **diborane** to form **Borazine** ($B_3N_3H_3$) commonly known as **inorganic benzene**



structure of borazine



Structure of diborane



In this structure, there are 2 types of Hydrogen atoms.

- 4 terminal Hydrogen and 2 bridged Hydrogen atoms.
- The 4 terminal Hydrogen are bonded by normal covalent bond
- 2 bridged Hydrogen atoms are bonded by **3 centre 2 electron pair bonds**.
- It is also called **banana bond**.

Diborane is an electron deficient bond

Allotropes of Carbon

The phenomenon by which an element can exist in more than one physical state is called allotropy.

The allotropes of carbon can be either amorphous or crystalline.

The important crystalline allotropes of carbon are Diamond, Graphite and fullerenes.

Diamond

In diamond, each carbon atom undergoes sp^3 hybridisation, Each carbon is linked to four other carbon atoms in tetrahedral fashion.

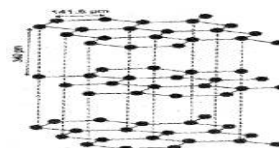
It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth.

Rigid three- dimensional network of carbon atoms

it has very high melting point

It is used as an abrasive for sharpening hard tools.

Graphite



Graphite has a layered structure.

Each Carbon atom is sp^2 hybridised structure.

Each layer is composed of hexagonal rings of C-atoms.

The electrons are delocalised over the whole sheet.

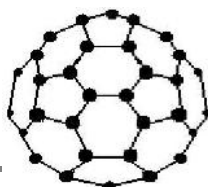
Electrons are mobile and, therefore, graphite conducts electricity along the sheet.

Graphite cleaves easily between the layers and, therefore, it is very soft and slippery.

For this reason graphite is used as a dry lubricant in machines running at high temperature.

It is the thermodynamically most stable form of carbon.

Fullerens



The C_{60} molecule used in smart materials

The general name fullerene refers to the family of spheroidal carbon-cage molecules.

Fullerenes are prepared by heating graphite in an electric arc in the presence of helium or argon.

C₆₀ molecules is named as Buckminster fullerene.

The carbon atoms are sp² hybridized.

Spherical fullerenes are also called bucky balls.

Amorphous forms of carbon

Amorphous forms of Carbon are coal, coke, charcoal and carbon black

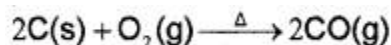
Carbon black is obtained by burning hydrocarbons in limited supply of air.

Charcoal and coke are obtained by heating wood or coal respectively at high temperature in the absence of air.

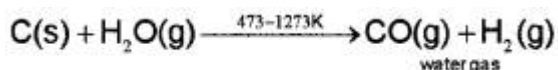
Carbon Monoxide(CO)

Properties

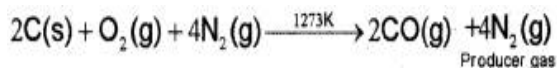
Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.



On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H₂ thus produced is known as water gas or synthesis gas.



When air is used instead of steam, a mixture of CO and N₂ is produced, which is called producer gas.



Water gas and producer gas are very important industrial fuels.

CO is a colourless, odourless poisonous gas.

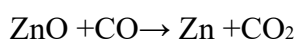
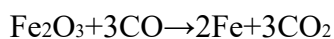
It is insoluble in water

It forms stable complex with haemoglobin called carboxy haemoglobin.

Which is 300 times more stable than oxygen-haemoglobin complex.

It prevents haemoglobin from carrying Oxygen and ultimately results in death.

CO is powerful reducing agent. It reduces all metal oxides



Silicones

They are polymeric organosilicon compounds containing Si—O—Si linkages and Si—C bonds.

They are very stable, because of the presence of strong silicon-oxygen and silicon-carbon bonds repeating unit is **(R₂SiO)**

where R is alkyl or aryl group.

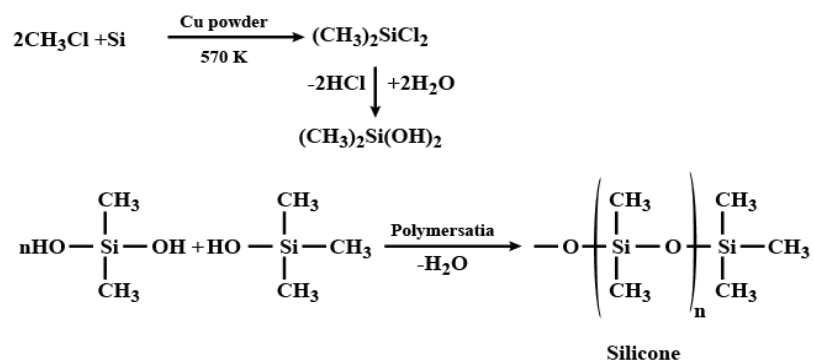
Silicones may be linear, cyclic, or cross-linked polymers

Preparation

When **methyl chloride** reacts with silicon in the presence of copper as a catalyst at a temperature 570K, various types of methyl substituted Chloro silanes are formed.

Hydrolysis of dimethyl dichloro silane i. e., (CH₃)₂SiCl₂ followed by condensation polymerisation forms straight chain polymer i. e., silicone.

Properties



They are water repelling in nature.

They have high thermal stability

high electric strength

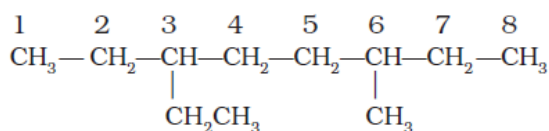
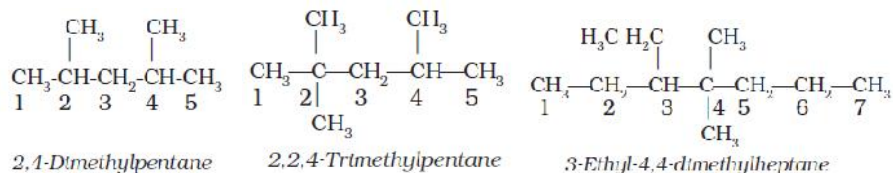
resistance to oxidation and chemicals.

So they are used as sealant, greases, electrical insulators and for water proofing of fabrics.

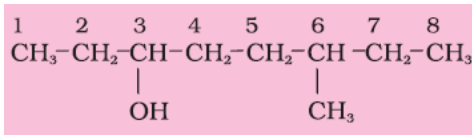
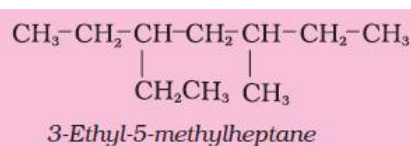
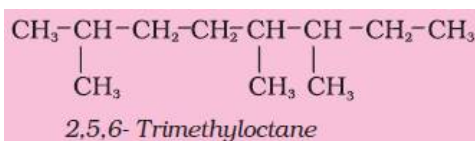
Being biocompatible they are also used in surgical and cosmetic plants.

12 ORGANIC CHEMISTRY : SOME BASIC PRINCIPLES AND TECHNIQUES

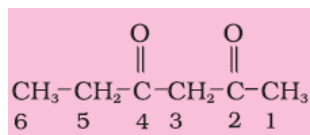
NOMENCLATURE OF ORGANIC COMPOUNDS



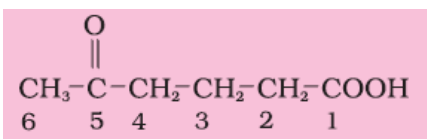
3-Ethyl-6-methyloctane



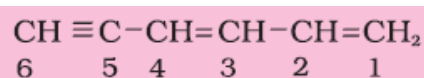
6-Methyloctan-3-ol.



Hexane-2,4-dione.



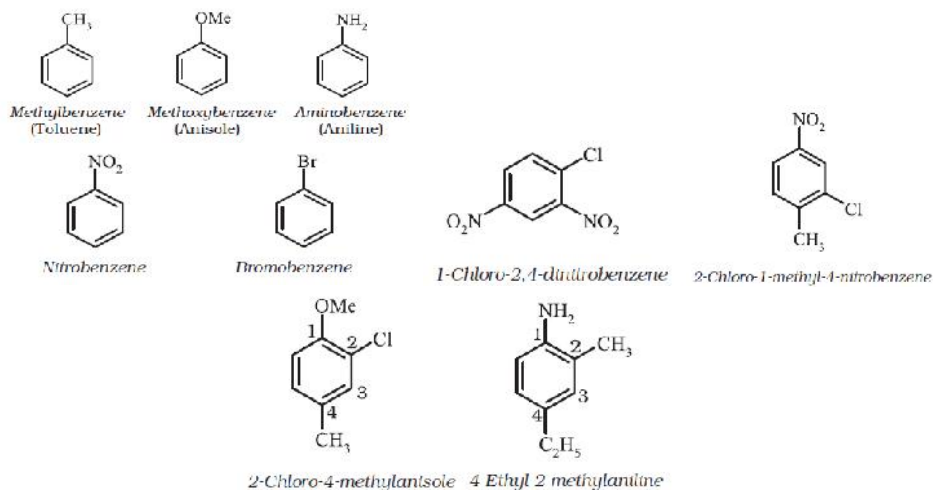
5-Oxohexanoic acid



Hexa-1,3-dien-5-yne.

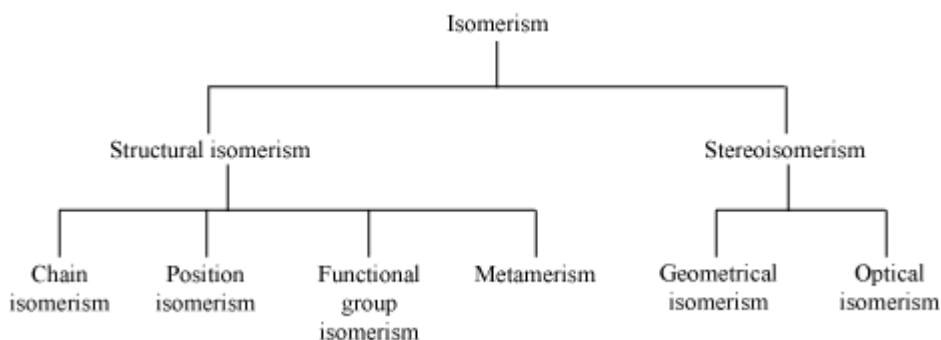
Compound	IUPAC Name
$\text{CH}_3\text{-CH}_2\text{-CH=CH}_2$	1-Butene or, But-1-ene
$\text{CH}_3\text{-CH=CH-CH}_3$	2-Butene or, But-2-ene
$\text{CH}_3\text{-CH}_2\text{-C}\equiv\text{C-CH}_3$	2-Pentyne or Pent-2-yne
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-C}\equiv\text{CH}$	1-Heptyne or Hept-1-yne
$\text{CH}_3\text{-CH}_2\text{-OH}$	Ethanol
$\text{CH}_3\text{-CH}_2\text{-CHOH-CH}_2\text{-CH}_2\text{-CH}_3$	3-Hexanol or Hexan-3-ol
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CHO}$	1-Butanal or Butanal
HCHO	Methanal
$\text{CH}_3\text{-CO-CH}_3$	Propanone
$\text{CH}_3\text{-CO-CH}_2\text{-CH}_2\text{-CH}_3$	2-Pentanone or Pentan-2-one
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	4-Octanone or Octan-4-one
HCOOH	Methanoic acid
$\text{CH}_3\text{-COOH}$	Ethanoic acid
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH}$	1-Butanoic acid or butanoic acid
$\text{CH}_3\text{-CH}_2\text{-Cl}$	1-Chloroethane or Chloroethane
$\text{CH}_3\text{-CH}_2\text{-CHBr-CH}_3$	2-Bromobutane

Compound	IUPAC Name
$\text{CH}_3\text{-CHOH-CH}_2\text{-CO-CH}_3$	4-Hydroxy-2-pentanone
$\text{CH}_2\text{Cl-CH}_2\text{-CHBr-CH}_2\text{-CH}_2\text{OH}$	3-Bromo-5-chloropentan-1-ol or, 3-Bromo-5-chloro-1-pentanol
$\text{CH}_3\text{-CH}_2\text{-CO-CH}_2\text{-CH}_2\text{-CHO}$	4-Oxohexanal
$\text{CH}_3\text{-CHNH}_2\text{-CH}_2\text{-COOH}$	3-Aminobutanoic acid
$\text{CH}_3\text{-CH}_2\text{-CHCl-CH}_2\text{-CO-CH}_2\text{-COOH}$	5-Chloro-3-oxo-heptanoic acid



Isomerism

Two or more compounds having the same molecular formula, but different properties are called isomers, and the phenomenon is called isomerism.



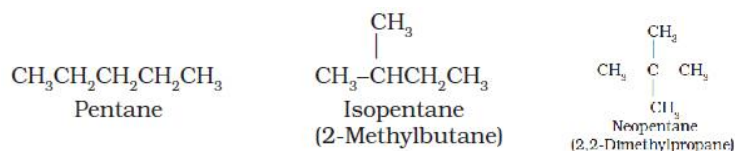
Structural Isomerism

Compounds having the same molecular formula, but different structures are called structural isomers.

- Chain isomerism:**

Two or more compounds having the same molecular formula, but different carbon skeletons are referred to as **chain isomers**, and the phenomenon is called chain isomerism.

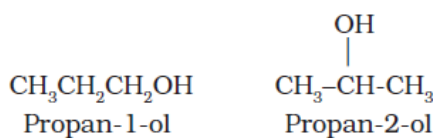
Example



- Position isomerism:**

Two or more compounds differing in the position of functional group on the carbon skeleton are called **position isomers**, and the phenomenon is called position isomerism.

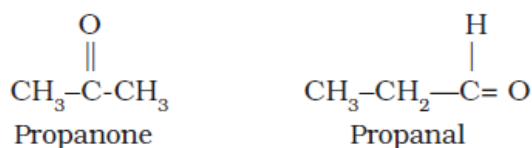
Example –



- Functional group isomerism:**

Two or more compounds having the same molecular formula, but different functional groups are called **functional isomers** and the phenomenon is called functional isomerism.

Example – propanone (ketone) and propanal (aldehyde); both have the same molecular formula $\text{C}_3\text{H}_6\text{O}$, but different functional groups



Another example –



- Metamerism:**

Two or more compounds arising due to different alkyl chains on either side of the functional group in a molecule are called **metamers**, and the phenomenon is called metamerism.

- Example –



- Both have the same molecular formula $C_4H_{10}O$, but have different alkyl chains on either side of the functional group (ether).

Stereoisomerism

- Compounds having the same molecular formula and structural formula but differing in relative positions of their atoms or groups in space are called **stereoisomers**. The phenomenon is called stereoisomerism.
- It can be classified as geometrical and optical isomerism.

Qualitative Analysis of Compounds

Detection of Carbon and Hydrogen

- Detected by heating a compound with copper (II) oxide
- Carbon present in the compound gets oxidised to CO_2 , which is then tested with lime water (lime water turns milky)

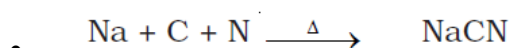


- Hydrogen present in the compound is oxidised to water, which is then tested with anhydrous copper sulphate (anhydrous copper sulphate turns blue)



Detection of Nitrogen

- Nitrogen present in an organic compound is detected by “Lassaigne’s test”. Here the organic compound is fused with metallic sodium in a fusion tube, so that N in the compound is converted to cyanide.



- It is then extracted by boiling with distilled water and then filtered. The filtrate is known as sodium **fusion extract**.
- To a little of the sodium fusion extract, add freshly prepared ferrous sulphate ($FeSO_4$) solution, heated to boiling, cooled and acidified with dil. H_2SO_4 .
- Formation of Prussian blue colour confirms the presence of nitrogen



Quantitative Analysis Carbon and Hydrogen

- Organic compound of known mass is burnt in the presence of excess of oxygen and copper (II) oxide

Carbon and hydrogen (present in the compound) gets oxidised to CO_2 and water respectively.



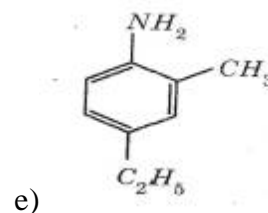
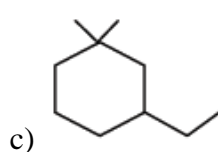
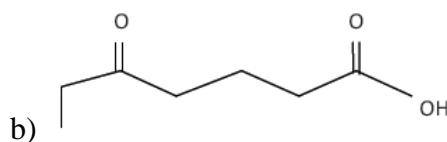
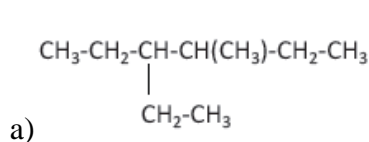
- [Eg ; $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$]
- The mass of water produced can be determined by passing the mixture through a weighed U-tube containing anhydrous CaCl_2 .
- U-tube containing concentrated solution of KOH absorbs CO_2 .
- The increase in the mass of CaCl_2 and KOH gives the amounts of water and CO_2 , from which the percentages of C and H can be calculated as follows:
- Mass of the organic compound = m g
- Mass of H_2O = m_1 g
- Mass of CO_2 = m_2 g

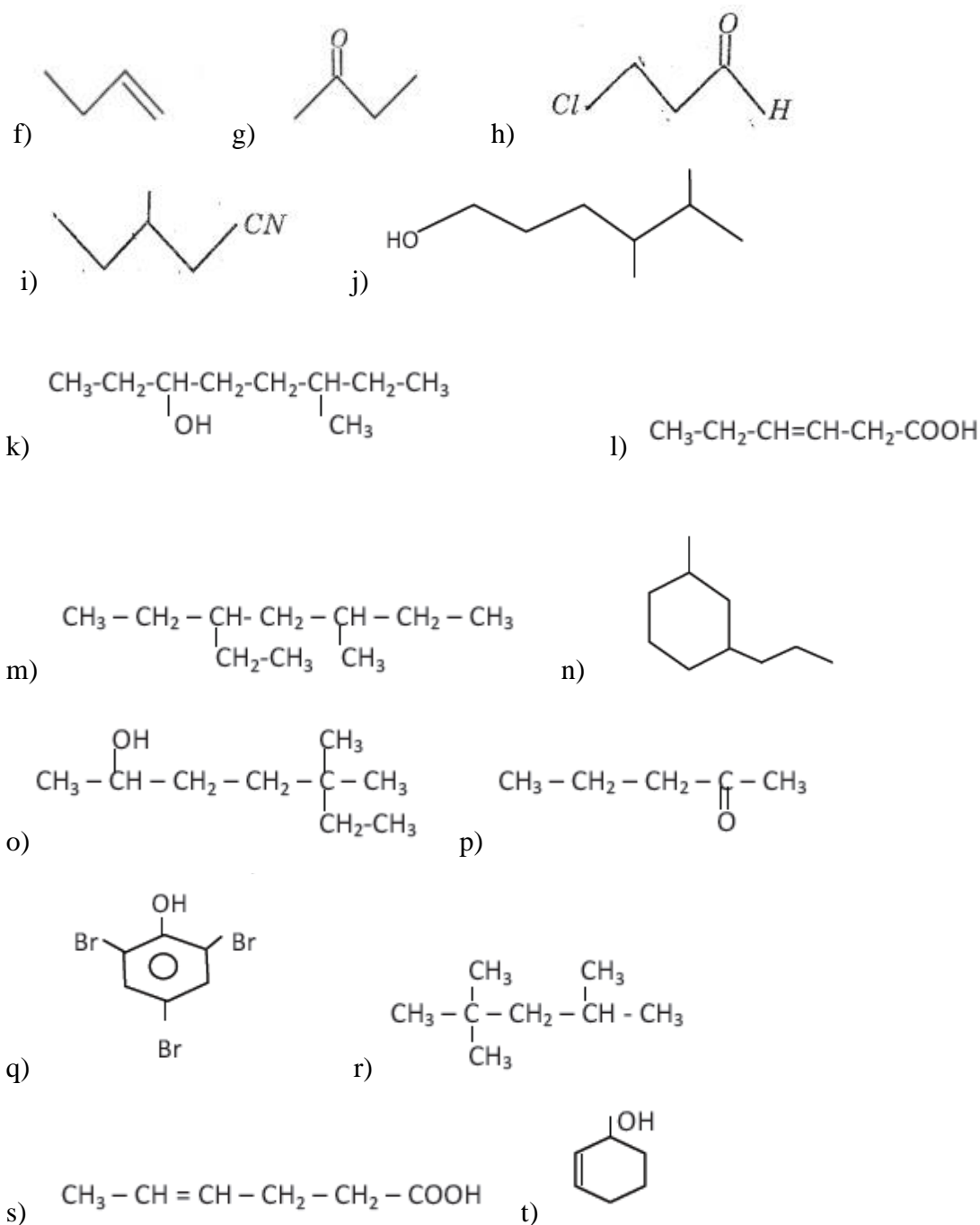
$$\text{Percentage of carbon} = \frac{12 \times m_2 \times 100}{44 \times m}$$

$$\text{Percentage of hydrogen} = \frac{2 \times m_1 \times 100}{18 \times m}$$

Questions

- Write the IUPAC names of the following compounds





Answers

- | | |
|------------------------------------|---------------------------------|
| a) 3-Ethyl-4-methylhexane | b) 5-Oxoheptanoic acid |
| c) 3-Ethyl-1,1-dimethylcyclohexane | d) 3-Bromo-3-chloroheptane |
| e) 4-Ethyl-2-methylaniline | f) But-1-ene |
| g) Butanone | h) 3-chloropropanal |
| i) 3-methylpentanenitrile | j) 4,5-Dimethylhexan-1-ol |
| k) 6-Methyloctan-3-ol | l) Hex-3-enoic acid |
| m) 3-Ethyl-5-methylheptane | n) 1-Methyl-3-propylcyclohexane |

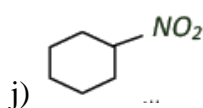
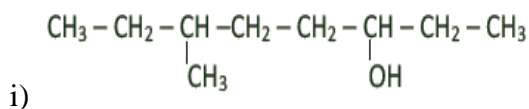
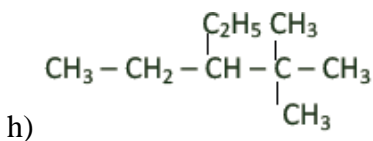
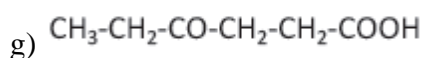
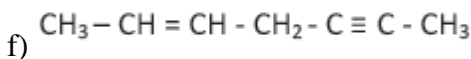
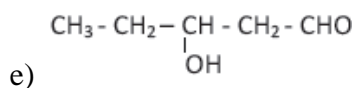
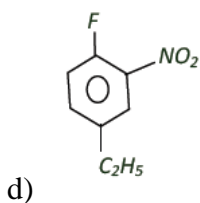
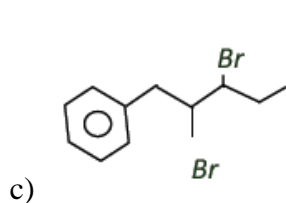
- o) 5,5-Dimethylheptan-2-ol
 q) 2,4,6-Tribromophenol
 s) Hex-4- enoicacid
- p) Pentan-2-one
 r) 2,2,4-trimethylpentane
 t) Cyclohex-2-en-1-ol

2. Give the structural formula of the following compounds

- a) Pent-4-en-2-ol
 c) 2,3-Dibromo-1-phenylpentane
 e) 3-Hydroxypentanal
 g) 4-Oxohexanoic acid
 i) 6-Methyloctan-3-ol
- b) 6-Hydroxyheptanal
 d) 4-Ethyl-1-fluoro-2-nitrobenzene
 f) Hept-2-en-5-yne
 h) 3-Ethyl-2,2-dimethylpentane
 j) Nitrocyclohexane

Answers

- a) $CH_2 = CH - CH_2 - CH(OH) - CH_3$ b) $CH_3 - CH(OH) - CH_2 - CH_2 - CH_2 - CH_2 - CHO$



3. Briefly explain the different types of structural isomerism shown by organic compounds with suitable examples.

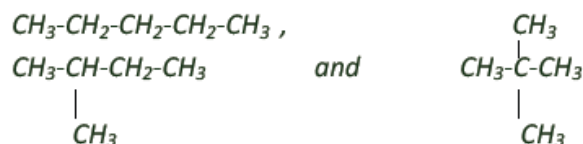
[refer notes]

4. What is metamerism? Write the metamers of $C_4H_{10}O$.

[Isomers which differ in the carbon chain (alkyl groups) around the functional group are called metamers and the phenomenon is called metamerism.

The metamers of $C_4H_{10}O$ are $CH_3 - O - CH_2 - CH_2 - CH_3$ and $CH_3 - CH_2 - O - CH_2 - CH_3$.

5. Write all the possible chain isomers of the compound with molecular formula C_5H_{12} .



6. How the presence of carbon and hydrogen in organic compounds are detected?

[refer notes]

7. What is 'sodium fusion extract'? How the presence of Nitrogen in organic compound is detected?

[refer notes]

8. On complete combustion, 0.246g of an organic compound gave 0.198g of CO₂ and 0.1014g of H₂O. Determine the percentage composition of carbon and hydrogen in the compound.

$$i) \text{ Mass of organic compound (m) = 0.246 g}$$

$$\text{Mass of CO}_2 \text{ formed (m}_1\text{) = 0.198 g}$$

$$\text{Percentage of carbon} = \frac{12 \times m_1 \times 100}{44 \times m} = \frac{12 \times 0.198 \times 100}{44 \times 0.246} = 21.95\%$$

$$\text{Mass of water formed (m}_2\text{) = 0.1014 g}$$

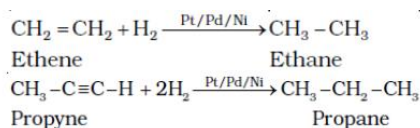
$$\text{Percentage of hydrogen} = \frac{2 \times m_2 \times 100}{18 \times m} = \frac{2 \times 0.1014 \times 100}{18 \times 0.246} = 4.58\%$$

13 HYDROCARBONS

ALKANES

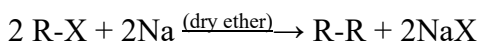
Preparation of alkanes

1. From unsaturated hydrocarbons (hydrogenation): Alkenes and alkynes add Hydrogen in presence of finely divided catalysts like Ni, Pd or Pt to form alkanes..

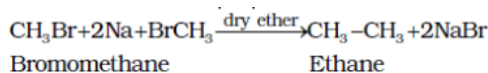


2. From alkyl halides (Wurtz reaction)

Alkyl halides react with metallic sodium in dry ether to form alkanes.



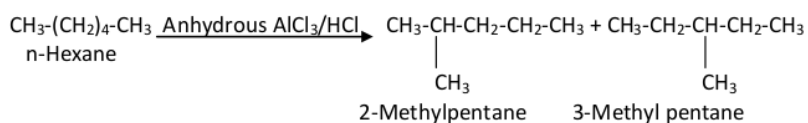
(Alkane formed contains double the number of C atoms than that present in the alkyl halide. So this method is used for the preparation of alkanes with even number of carbon atoms)



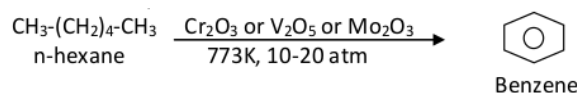
(When two different alkyl halides are used, we get a mixture of alkanes)

Chemical Properties of alkanes

1. **Isomerisation:** n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.



2. **Aromatization:** n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atm pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina, we get aromatic compounds.



Conformations of Alkanes

Different spatial arrangements of atoms arising due to free rotation around a C-C single bond are called conformations or conformers or rotamers.

Conformations of ethane

Ethane contains a C-C σ bond and each carbon atom contains three hydrogen atoms. Due to free rotation of C atoms around the single bond, the spatial arrangement of hydrogen atoms attached to the C atoms change. Thus ethane can show *eclipsed and staggered conformations*.

In eclipsed conformation, the hydrogen atoms of the 2nd carbon atoms are exactly behind that of the first.

In staggered conformation, the hydrogen atoms are far apart as possible.

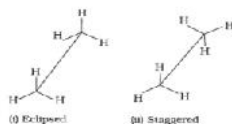
Any conformations between eclipsed and staggered conformations are called skew conformations. Staggered conformation is stabler than eclipsed form because in staggered form, the electron clouds of carbon-hydrogen bonds are very far apart. (Minimum repulsive forces, minimum energy and maximum stability)

Torsional strain: The repulsive interaction between the adjacent bonds in conformations.

Eclipsed and staggered conformations can be represented by Sawhorse and Newman projection formulas.

1. Sawhorse projections:

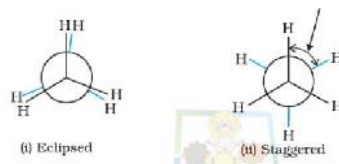
Sawhorse projections of eclipsed and staggered conformations of ethane



Here the molecule is viewed along the molecular axis. C-C bond is denoted by a longer straight line.

2. Newman projections:

The Newman's projections for eclipsed and staggered conformations of ethane



ALKENES

Preparation of alkenes

1. From Alkyl halides:(dehydrohalogenation / β -elimination reaction)

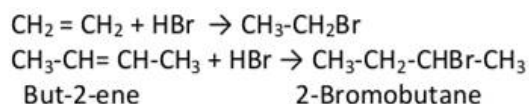
Alkyl halides (R-X) on heating with alcoholic potash, eliminate one molecule of hydrogen halide to form alkenes. (*hydrogen atom is eliminated from the β carbon atom*)



Chemical Properties of Alkenes

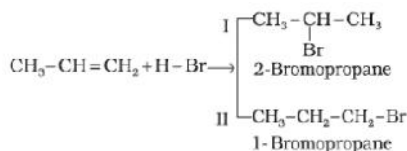
1. Addition of hydrogen halides:

Alkenes add hydrogen halide to form alkyl halides.

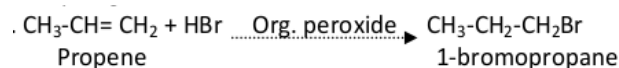


In the case of unsymmetrical alkenes, the addition takes place according to **Markovnikov's Rule** (*When an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the addendum (adding molecule) gets attached to the carbon containing lesser number of hydrogen atoms*).

When HBr is added to propene, we get 2 products – 1-bromopropane(minor) and 2-bromopropane (major).



In presence of peroxide, addition of HBr to unsymmetrical alkenes takes place against Markovnikov rule. This is known as **peroxide or Kharash effect or anti-Markovnikov addition reaction** (*the negative part goes to more hydrogenated carbon atom*)

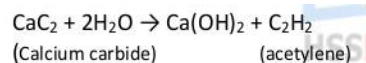
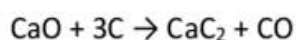
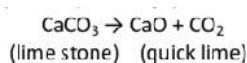


ALKYNES

Preparation of alkynes

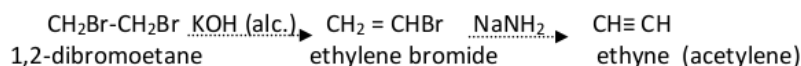
1. From Calcium carbide: **(dehydrohalogenation / β -elimination reaction)**

On large scale, ethyne is prepared by treating calcium carbide with water.



2. From vicinal dihalides **(dehydrohalogenation):**

Vicinal dihalides undergo dehydrohalogenation on treatment with alcoholic KOH to form alkenes.



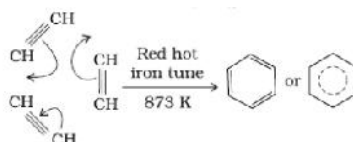
Chemical Properties of Alkynes

1. Addition of water:

On warming with water, alkynes add one molecule of water in presence of dil. H_2SO_4 and mercuric sulphate at 333K to form aldehydes or ketones.



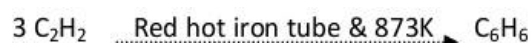
2. **Cyclic polymerisation:** Ethyne (acetylene) on passing through red hot iron tube at 873K, undergoes cyclic polymerisation to form benzene.



AROMATIC HYDROCARBONS (ARENES)

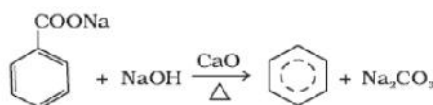
Preparation of Benzene

1. Cyclic polymerisation of ethyne (acetylene):



2. Decarboxylation of aromatic acids:

Sodium salt of benzoic acid on heating with sodalime gives benzene.



3. Reduction of phenol:

Phenol is reduced to benzene by passing its vapours over heated zinc dust.

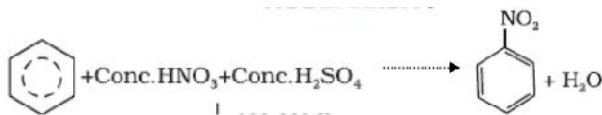


Chemical Properties

Electrophilic Substitution Reactions (weak electrophile is replaced by a strong electrophile)

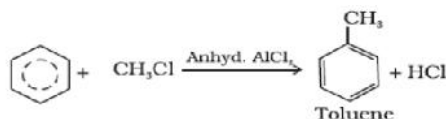
The important electrophilic substitution reactions are *Nitration, Sulphonation, Halogenation and Friedel-Crafts alkylation and acylation.*

1. Nitration: Benzene is heated with a mixture of conc. HNO_3 and conc. H_2SO_4 (nitrating mixture).



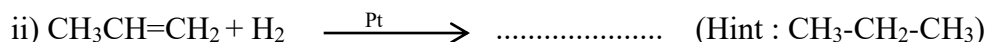
2. Friedel-Craft's Alkylation reaction:

Benzene is treated with alkyl halide in presence of anhydrous AlCl_3 .



Questions (2 Marks)

1. Complete the following reactions



2. Draw the sawhorse representations of the eclipsed and staggered conformations of ethane?

(Hint: eclipsed & staggered structure)

3. Write the chemical equation for the conversion of sodium benzoate to benzene?

(Hint: NaOH in presence of CaO)

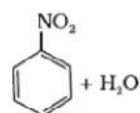
Questions (3 Marks)

1. i) Name the product formed when acetylene is passed through red hot iron tube? (1 mark each)

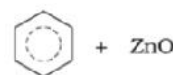
ii) Identify the product in the following reactions.



Hint: i) Benzene, ii, a) Nitro benzene,

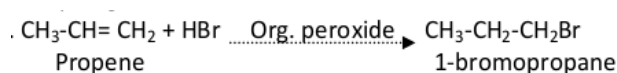


b) benzene,



2. Explain Kharash effect with suitable example.

Hint: Explanation



3. a) Give chemical equation for the conversion of Bromomethane to Ethane?,

b) Name the reaction.

14 ENVIRONMENTAL CHEMISTRY

1. **Global Warming** :- Higher concentration of carbon dioxide in the atmosphere increases the planet temperature known as Global warming.

Adverse effect of global warming :- It causes flood, drought, heat waves

2. **Green House Effect**:- It is the natural process that warms the Earth's surface.

Green house gases :- Methane (CH₄), Carbon dioxide(CO₂), water vapour, CFC, Ozone(O₃)

3. **Acid Rain** :- The P^H of rain water drops below 5.6 due to the presence of H⁺ ion formed by the reaction of rain water with CO₂,SO₂,NO₂.

Adverse effect of acid rain:- It damages buildings and structures made by stones and metals.

4. **Biochemical Oxygen Demand (BOD)**:- It is the amount of oxygen required by bacteria to break down the organic matter present in a certain volume of water.

5. **Green Chemistry** :- It indicate the utilization of existing knowledge for reducing the chemical hazards along with the developmental activities.

Green chemistry in day-to-day life

(i) **Dry cleaning of clothes** :- In earlier time the solvent used for dry cleaning is tetrachloro ethane, which contaminate the ground water and are carcinogenic. Now liquid CO₂ or H₂O₂ (hydrogen peroxide) are used for bleaching clothes.

(ii) **Bleaching of paper**:- In earlier time, chlorine gas was used for bleaching paper. Now H₂O₂ is used for bleaching paper in the presence of catalyst.

Model Questions

1. Write any two applications of green chemistry in day-to-day life.

2. Acid rain causes extensive damage to aquatic life.

(i). What do you mean by acid rain?

(ii). Name the chemical responsible for acid rain

(iii). Which gases are responsible for green house effect?

3. Define the term Biochemical Oxygen Demand .

4. The Taj Mahal in India has been affected by 'acid rain'. Explain the causes and harmful effects of acid rain.

5. Explain the cause of 'Greenhouse effect'.

6. The phenomenon of global warming is due to greenhouse effect.

(i). What is greenhouse effect?

(ii). What are the consequence of greenhouse effect.

7. How the Green Chemistry is useful in bleaching of paper?
8. Atmospheric pollution increases the global average temperature and the phenomenon is called Global warming.
 - (i). What are the major gases which contribute towards global warming?.
 - (ii). What can we do to reduce global warming?.

Answer key

1. Dry cleaning of clothes, Bleaching of paper
 2. (i). pH of rain water below 5.6
(ii). CO_2 , SO_2
(iii). CH_4 , CO_2 , CFC, O_3
 3. Amount of oxygen required by bacteria to break down the organic matter present in a certain volume of water.
 4. Cause: H^+ ion formed by the reaction of rain water with CO_2 , SO_2 , NO_2
Harmful effect: Damage buildings made by stones and metals.
 5. Green house gases present in the atmosphere absorbed and re radiate the Sun's energy.
 6. (ii). Melting of glacial masses, flood, desertification of fertile area.
 7. Hydrogen peroxide with suitable catalyst is a greener alternative to chlorine gas which is used for the bleaching of paper.
 8. (i). CO_2 , CH_4 , CFC, water vapour
(ii). Reduce the production of greenhouse gases, Plant tree, use biofuels .
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