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UG TRB
CHEMISTRY
2023-2024

UNIT-1

ATOMIC STRUCTURE AND PERIODIC CLASSIFICATION & CHEMICAL BONDING

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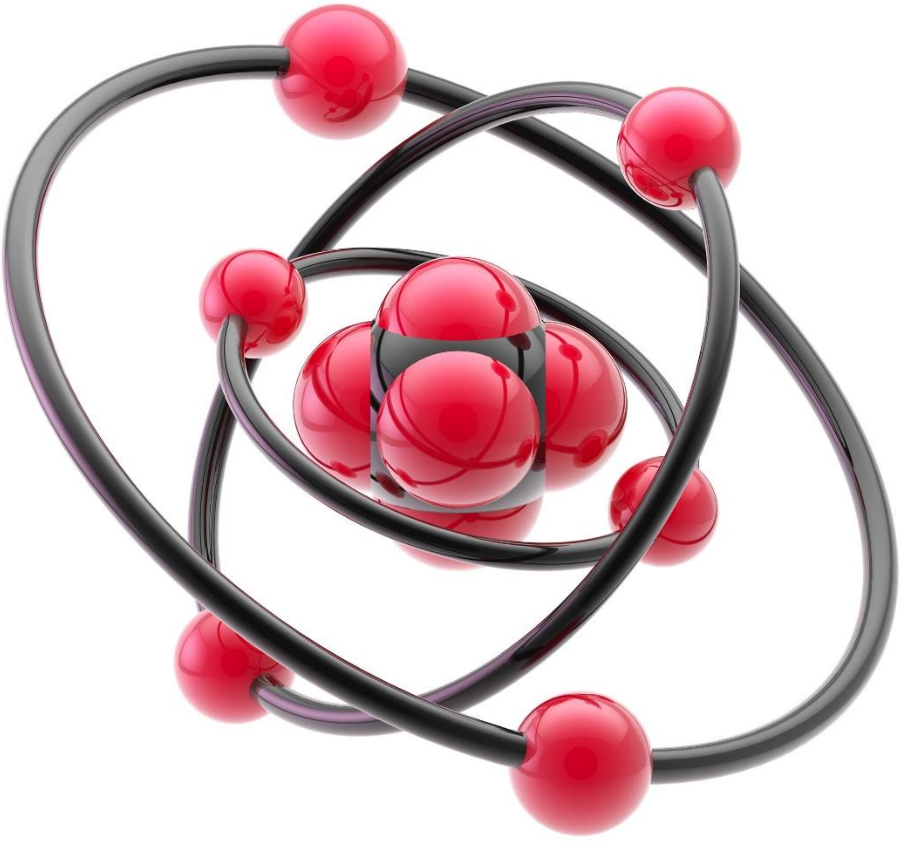
CHEMISTRY

UNIT 1 – ATOMIC STRUCTURE



COMPETITIVE EXAM

For

UG TRB – 2023-24

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UG TRB – CHEMISTRY – 2023-24

UNIT 1

INORGNIC CHEMISTRY

ATOMIC STRUCTURE & PERIODIC CLASSIFICATION

1.1. INTRODUCTION

Atom is the Basic Component Some Basic Term About Atom is Given Below:

- The particles constituting an atom are the electron, the proton, and the neutron.
- An atom is composed of two regions: the nucleus, which is in the center of the atom and contains protons and neutrons, and the outer region of the atom, which holds its electrons in orbit around the nucleus.
- Protons and neutrons have approximately the same mass, about 1.67×10^{-24} grams, which scientists define as one atomic mass unit (amu) or one Dalton.
- Each electron has a negative charge (-1) equal to the positive charge of a proton (+1).
- Neutrons are uncharged particles found within the nucleus.
- The periodic table is a table that logically organizes all the known elements.
- Each row is named "period" where all of the elements have the same number of atomic orbitals.
- Each column is called "group" where the elements have the same number of electrons in the outer orbital.
- In this chapter will see more information about atomic structure and periodic classification

- Atoms are the extremely small particles that are the basic building blocks of ordinary matter.
- Atoms can join together to form molecules, which make up most objects. Different elements (e.g. oxygen, carbon, uranium) are made up of different types of atoms. An atom is the smallest unit of an element that will behave as that element.

1.1.1. Different Kinds of Atoms:

- Atoms, once thought to be the smallest building blocks of nature, are in fact made of smaller particles. Most often these particles are in balance, and as such the atom is stable and lasts nearly forever. Some atoms are out of balance. This can make them radioactive.
- Atoms are made of tiny particles called protons, neutrons and electrons. Protons and neutrons clump together to form a central nucleus. The electrons move in a cloud-like region around the nucleus.
- Stable: Most atoms are stable. Their protons, neutrons and electrons balance. Barring outside forces, a stable atom will stay the same indefinitely.
- Isotopes: Every atom is a chemical element, like hydrogen, iron or chlorine. Every element has cousins called isotopes. These have a different number of neutrons, but are otherwise the same. Having excess neutrons may make isotopes radioactive.
- Radioactive: Some atoms have too many neutrons in the nucleus, which makes them unstable. They're radioactive, giving off particles until they become stable.
- Ions: Atoms with extra or missing electrons are called ions. They have a positive or negative electric charge and are responsible for many chemical reactions.
- Antimatter: Every atomic particle has a twin anti-particle, with an opposite electric charge. Antimatter hydrogen atoms have been formed in the laboratory, containing an anti-proton and anti-electron. Antimatter is very rare and fragile.
- Atoms consist of an extremely small, positively charged nucleus surrounded by a cloud of negatively charged electrons. Although typically the nucleus is less than one ten-thousandth the size of the atom, the nucleus contains more that 99.9% of the mass of the atom. Nuclei are made of positively charged protons and electrically neutral neutrons held together by a nuclear force. This force is much stronger than the electrostatic force that binds electrons to the nucleus, but its range is limited to distances of the order of 1 x 10-15 meters. It is shown in the **Figure 1**.

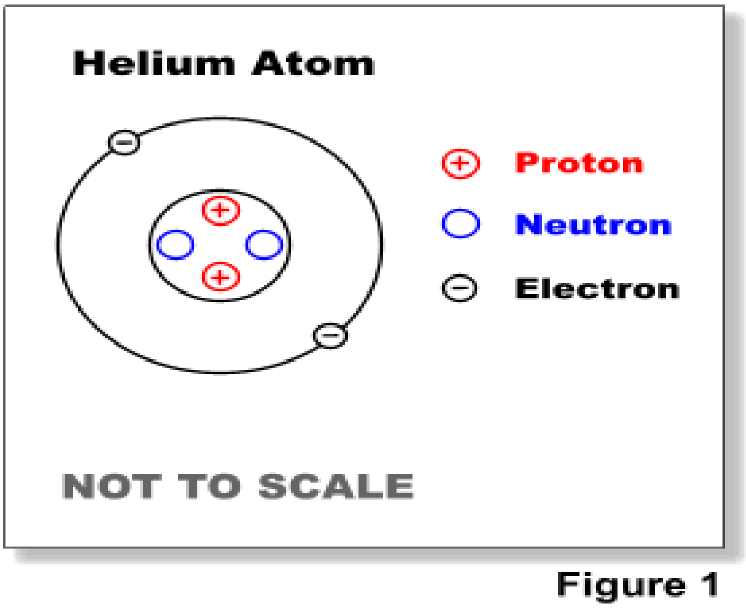

Figure 1: Representation of Helium atom

- The number of protons in the nucleus is called the atomic number (Z), the atomic number defines the element. The number of neutrons in the nucleus is denoted by N. The mass number (A) of the nucleus is equal to Z + N is shown in the **Figure 2**. The mass of the nucleus in atomic mass units (amu) is usually slightly different from the mass number.

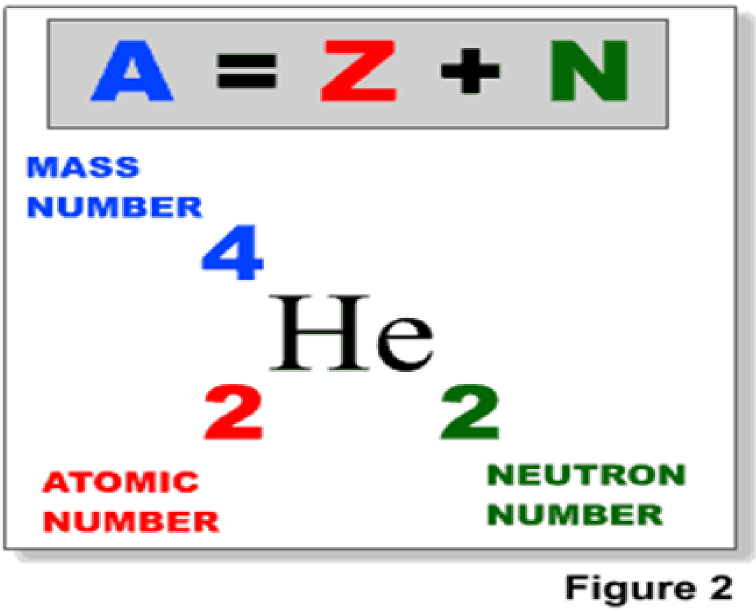

Figure 2: Pictorial representation of Mass Number

- Atoms of the same element can have different number of neutrons and they are called isotopes of that element. As an example, hydrogen has three (3) isotopes: hydrogen-1 (hydrogen), hydrogen-2 (deuterium) and hydrogen-3 (tritium) is shown in the **Figure 3.**

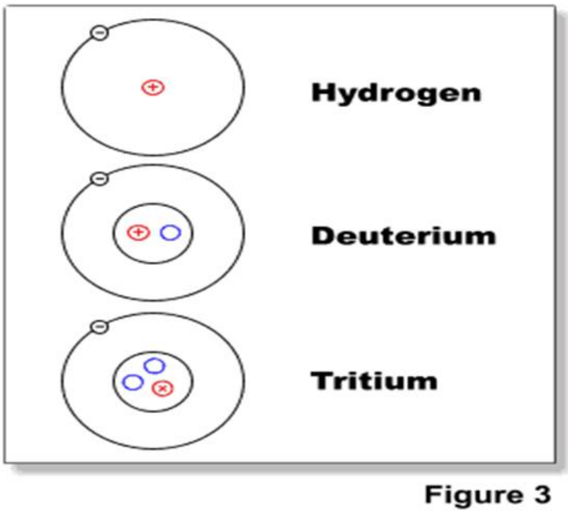

Figure 3: Indication of isotopes of Hydrogen

- At present there are 118 known elements which are typically displayed on the periodic table of the elements. Elements with atomic numbers 1 – 98 have all been shown to exist in nature while elements with atomic number 99 – 118 have only ever been produced artificially.
- Nuclides are often identified using the name of the element and the mass number (total number of protons and neutrons), i.e. lithiu-7, uranium-238, etc. **(Figure 4).**When referring to nuclides of the same element they are generally term isotopes i.e. uranium-238 & uranium-235. Radioactive nuclides or isotopes are called radionuclides or radioisotopes.

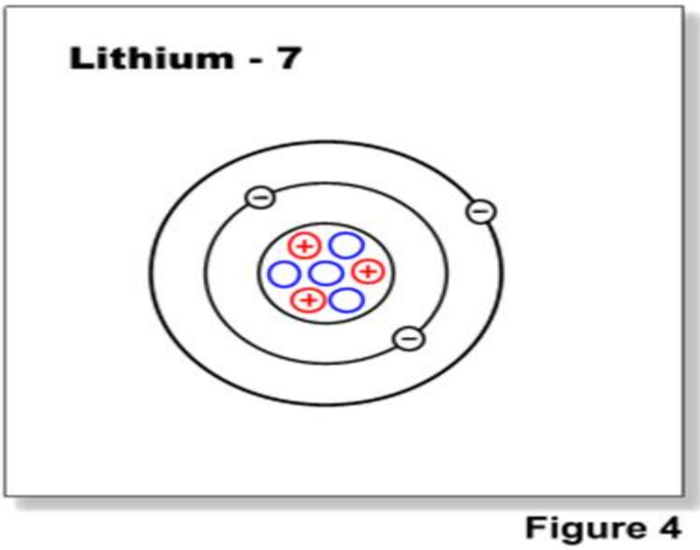

Figure 4: Indication of Lithium

- Among the elements there are 253 stable nuclides, and more than 3000 radioisotopes. The majority of the radioisotopes (>2400) are artificially produced and not presently found in nature.

1.2. ATOMIC STRUCTURE

- Atomic structure refers to the structure of an atom comprising a nucleus (centre) in which the protons (positively charged) and neutrons (neutral) are present. The negatively charged particles called electrons revolve around the centre of the nucleus is shown in the **Figure 5.**
- The history of atomic structure and quantum mechanics dates back to the times of Democritus, the man who first proposed that matter is composed of atoms. The study about the structure of an atom gives a great insight into the entire class of chemical reactions, bonds and their physical properties. The first scientific theory of atomic structure was proposed by John Dalton in the 1800s.
- The advances in atomic structure and quantum mechanics have led to the discovery of other fundamental particles.
- The discovery of subatomic particles has been the base for many other discoveries and inventions.
- The atomic structure of an element refers to the constitution of its nucleus and the arrangement of the electrons around it. Primarily, the atomic structure of matter is made up of protons, electrons and neutrons.
- The protons and neutrons make up the nucleus of the atom, which is surrounded by the electrons belonging to the atom. The atomic number of an element describes the total number of protons in its nucleus.

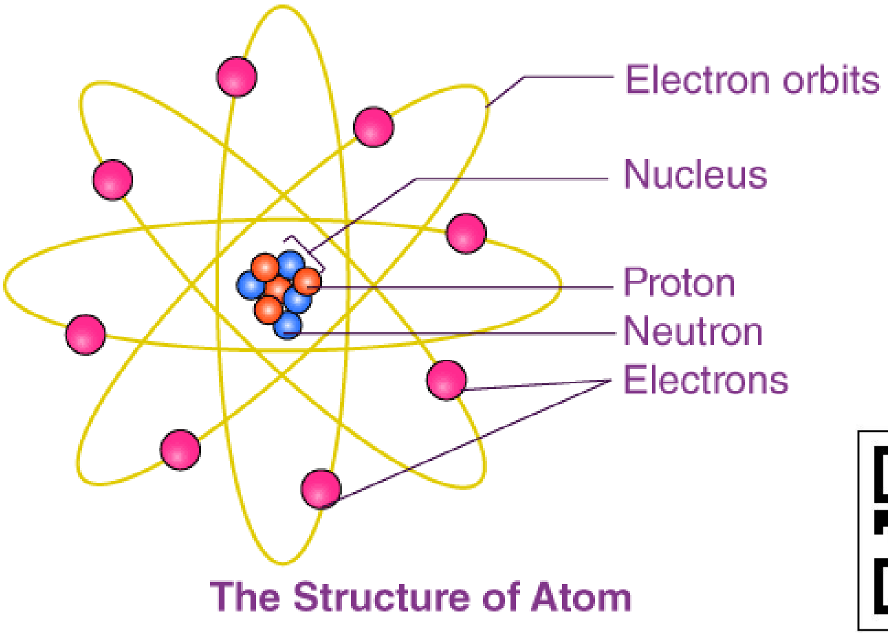

Figure 5: Pictorial representation of Structure of Atom

- The electron is by far the smallest: At 9.11 x 10-31 kg. It carries a negative electrical charge. Usually, it is bound to the positively charged nucleus due to the attraction created from the opposite electric charges. If the electrons carried by an atom are more or fewer than its atomic number, then the atom becomes respectively negatively or positively charged. A charged atom is known as an ion.
- Most of the mass of the atom comes from the protons and neutrons themselves, whereas electrons are almost 1/1837th times the weight of a proton or neutron. Protons and neutrons are both composed of other particles called quarks and gluons.
- The atomic number is the number of protons (equal to the number of electrons in a neutral atom) in the atom and the atomic mass number is the sum of the number of protons and neutrons in the atom.
- The atomic number (Z) is defined as the number of units of positive charges (protons) in the nucleus. It is the number of protons in the nucleus that determines the chemical properties of an atom.
- An atom may gain a positive or negative charge by either losing or gaining electrons respectively. Atoms may attach themselves to each other (of the same type or different type) to some atoms, the nucleus can change naturally. Such an atom is radioactive. In nature, there are some elements that are radioactive, like uranium or radium. In labs, scientists can produce radioactivity by bombarding atoms with smaller particles.
- The molecular mass of a substance is the sum of the atomic masses of all the atoms in a molecule of the substance. It is therefore the relative mass of molecule expressed in atomic mass units (u).
- Isotopes are atoms in a chemical element having different numbers of neutrons than protons and electrons. The atoms in a particular element have the same number of protons and electrons, but can carry varying numbers of neutrons.
- As instance, Hydrogen's atomic number is 1, i.e. its nucleus contains 1 proton. It also has one electron. The Hydrogen atom is neutral since it contains the same number of protons and electrons (as the positive and negative charges cancel each other out).
- However, approximately, one hydrogen atom out of 6000 contains a neutron in its nucleus. These atoms are still Hydrogen because they have one proton and one electron; they simply have a neutron that most hydrogen atoms do not carry. Hence, these atoms are called Isotopes.

- There's also an isotope of hydrogen that contains two neutrons. It's called Tritium, it doesn't occur naturally on earth, but it can easily be created.rm molecules of different compounds, to form matter.

1.3. HISTORY OF THE PERIODIC LAW

- The early years of the 19th century witnessed a rapid development in analytical chemistry—the art of distinguishing different chemical substances—and the consequent building up of a vast body of knowledge of the chemical and physical properties of both elements and compounds.

- This rapid expansion of chemical knowledge soon necessitated classification, for on the classification of chemical knowledge are based not only the systematized literature of chemistry but also the laboratory arts by which chemistry is passed on as a living science from one generation of chemists to another. Relationships were discerned more readily among the compounds than among the elements; it thus occurred that the classification of elements lagged many years behind that of compounds. In fact, no general agreement had been reached among chemists as to the classification of elements for nearly half a century after the systems of classification of compounds had become established in general use.

- J.W. Döbereiner in 1817 showed that the combining weight, meaning atomic weight, of strontium lies midway between those of calcium and barium, and some years later he showed that other such "triads" exist (chlorine, bromine, and iodine [halogens] and lithium, sodium, and potassium [alkali metals]).

- J.-B.-A. Dumas, L. Gmelin, E. Lenssen, Max von Pettenkofer, and J.P. Cooke expanded Döbereiner's suggestions between 1827 and 1858 by showing that similar relationships extended further than the triads of elements, fluorine being added to the halogens and magnesium to the alkaline-earth metals, while oxygen, sulfur, selenium, and tellurium were classed as one family and nitrogen, phosphorus, arsenic, antimony, and bismuth as another family of elements.

- Attempts were later made to show that the atomic weights of the elements could be expressed by an arithmetic function, and in 1862 A.-E.-B. de Chancourtois proposed a classification of the elements based on the new values of atomic weights given by Stanislao Cannizzaro's system of 1858. De Chancourtois plotted the atomic weights on the surface of a cylinder with a circumference of 16 units, corresponding to the approximate atomic weight of oxygen. The resulting helical curve brought closely related elements onto corresponding points above or below one another on the cylinder, and he suggested in consequence that "the properties of the elements are the properties of numbers," a remarkable prediction in the light of modern knowledge.

1.4. CLASSIFICATION OF THE ELEMENTS

- In 1864, J.A.R. Newlands proposed classifying the elements in the order of increasing atomic weights, the elements being assigned ordinal numbers from unity upward and divided into seven groups having properties closely related to the first seven of the elements then known: hydrogen, lithium, beryllium, boron, carbon, nitrogen, and oxygen. This relationship was termed the law of octaves, by analogy with the seven intervals of the musical scale.
- Then in 1869, as a result of an extensive correlation of the properties and the atomic weights of the elements, with special attention to valency (that is, the number of single bonds the element can form), Mendeleyev proposed the periodic law, by which "the elements arranged according to the magnitude of atomic weights show a periodic change of properties." Lothar Meyer had independently reached a similar conclusion, published after the appearance of Mendeleyev's paper.

1.5. THE FIRST PERIODIC TABLE

- Mendeleyev's periodic table of 1869 contained 17 columns, with two nearly complete periods (sequences) of elements, from potassium to bromine and rubidium to iodine, preceded by two partial periods of seven elements each (lithium to fluorine and sodium to chlorine), and followed by three incomplete periods. In an 1871 paper Mendeleyev presented a revision of the 17-group table, the principal improvement being the correct repositioning of 17 elements. He, as well as Lothar Meyer, also proposed a table with eight columns obtained by splitting each of the long periods into a period of seven, an eighth group containing the three central elements (such as iron, cobalt, nickel; Mendeleyev also included copper, instead of placing it in Group I), and a second period of seven. The first and second periods of seven were later distinguished by use of the letters "a" and "b" attached to the group symbols, which were the Roman numerals.
- With the discovery of the noble gases helium, neon, argon, krypton, radon, and xenon by Lord Rayleigh (John William Strutt) and Sir William Ramsay in 1894 and the following years, Mendeleyev and others proposed that a new "zero" group to accommodate them be added to the periodic table. The "short-period" form of the periodic table, with Groups 0, I, II,III, IV, V, VI, VII VIII, became popular and remained in general use until about 1930.

UNIT I- Inorganic Chemistry and Chemical Bonding

1.54. Important Multiple-Choice Question:

1. The element having tetra atomic atomicity is

A) Helium B) Nitrogen C) Phosphorous D) Chlorine

2. Who was the first to propose Atomic theory?

A) J J Thomson B) Ruther ford C) John Dalton D) Neils Bohr

3. What is common among Lithium, Sodium and Potassium?

A) These have one electron in their outermost shell

B) There are alkaline earth metals

C) These cannot form oxides

D) These are inert elements

4. Which of the following statements does not form a part of Bohr's model of hydrogen atom?

A) Energy of the electrons in the orbit is quantized

B) The electron in the orbit nearest the nucleus has the lowest energy

C) Electrons revolve in different orbits around the nucleus

D) The position and velocity of the electrons in the orbit cannot be determined simultaneously

5. Identify the wrong statement in the following

A) The atomic radius of the elements increases as one moves down the first group of the periodic table

B) The atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table

C) Amongst isoelectronic species, the smaller the positive charge on the cation, the smaller is the ionic radius

D) Amongst isoelectronic species, the greater the negative charge on the anion, larger is the ionic radius

6. Which of the following properties of atom could be explained correctly by Thomson Model of atom?

A) Overall neutrality of atom

B) Spectra of hydrogen atom

C) Position of electrons, protons and neutrons in atom

D) Stability of atom

7. The energy of an electron in first Bohr orbit of H-atom is –13.6 eV. The possible energy value of electron in the excited state of Li^{2+} is

A) – 122.4 eV B) 30.6 eV C) – 30.6 eV D) 13.6 eV

8. Electronic configuration of the outer shell of the element Gd with atomic number 64 is

A) $4f^4\ 5d^5\ 6s^1$ B) $4f^3\ 5d^5\ 6s^2$ C) $4f^5\ 5d^4\ 6s^1$ D) $4f^7\ 5d^1\ 6s^2$

9. If both the K and L shells are full, what would be the atomic number of that element?

A) 20 B) 14 C) 10 D) 16

10. Which of the following statements about the electron is incorrect?

A) It is a constituent of cathode rays

B) The mass of an electron is equal to the mass of a neutron

C) It is a basic constituent of all atoms

D) It is a negatively charged particle

11. The ratio of the amplitude of the magnetic field to the amplitude of the electric field for electromagnetic wave propagation in a vacuum is equal to

A) Unity

B) Speed of light in vacuum

C) Reciprocal of the speed of light in vacuum

D) The ratio of magnetic permeability to electrical susceptibility in a vacuum.

12. Which properties amount the following is false about electromagnetic waves?

A) The energy in an electromagnetic wave is divided equally between electric and magnetic vectors.

B) Both electric and magnetic field vectors are parallel to each other and perpendicular to the direction of propagation of the wave.

C) These waves do not require any material medium for propagation

D) Both electric and magnetic field vectors attain the maxima and minima at the same place and the same time

13.To which part of the spectrum does an EM wave belong if the energy of the wave is of the order of 15 KeV.

A) X rays B) Infrared rays C) Ultraviolet rays D) Gamma rays

14. The ultra-high frequency band of radio waves in the electromagnetic wave is used as in

A) Television B) Cellular phone communication

C) Commercial FM radio D) Both a and b

15. Good absorber of heat is good radiator of heat also is

A) Stefan's law B) Kirchhoff's law C) Planck's law D) Wien's law

16. A man with dark skin, in comparison with a man with white skin, will experience

A) Less heat and less cold B) Less heat and more cold

C) More heat and less cold D) More heat and more cold

17. Each object emits radiation. The radiation energy is proportional to what power of temperature?

A) T B) T^2 C) T^3 D)T^4

18. A polished metal plate has a rough and black spot. It is heated to 1400K and brought immediately in a dark room. Which of the following is true?

A) The spot will appear brighter than the plate

B) The spot will appear darker than the plate

C) The spot and plate will appear equally bright

D) The spot and the plate will not be visible in the dark room

19. A black body is at a temperature of 500K.It emits energy at a which is proportional to

A) $(500)^4$K B) $(500)^3$ K C) $(500)^2$ K D) (500) K

20. Electromagnetic wave theory of light could not explain Black Body radiations.

A) True B) False

C) Sometimes true sometimes false D) Neither true nor false

21. **Assertion:** Photoelectric effect demonstrates the wave nature of light.

Reason: The number of photoelectrons is proportional to the frequency of light

A) If both assertion and reason are true and the reason is the correct explanation of the assertion

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CHEMISTRY

UNIT 1

ATOMIC STRUCTURE

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UNIT-2

p-BLOCK ELEMENTSs, d-BLOCK & f-BLOCK ELEMENTS

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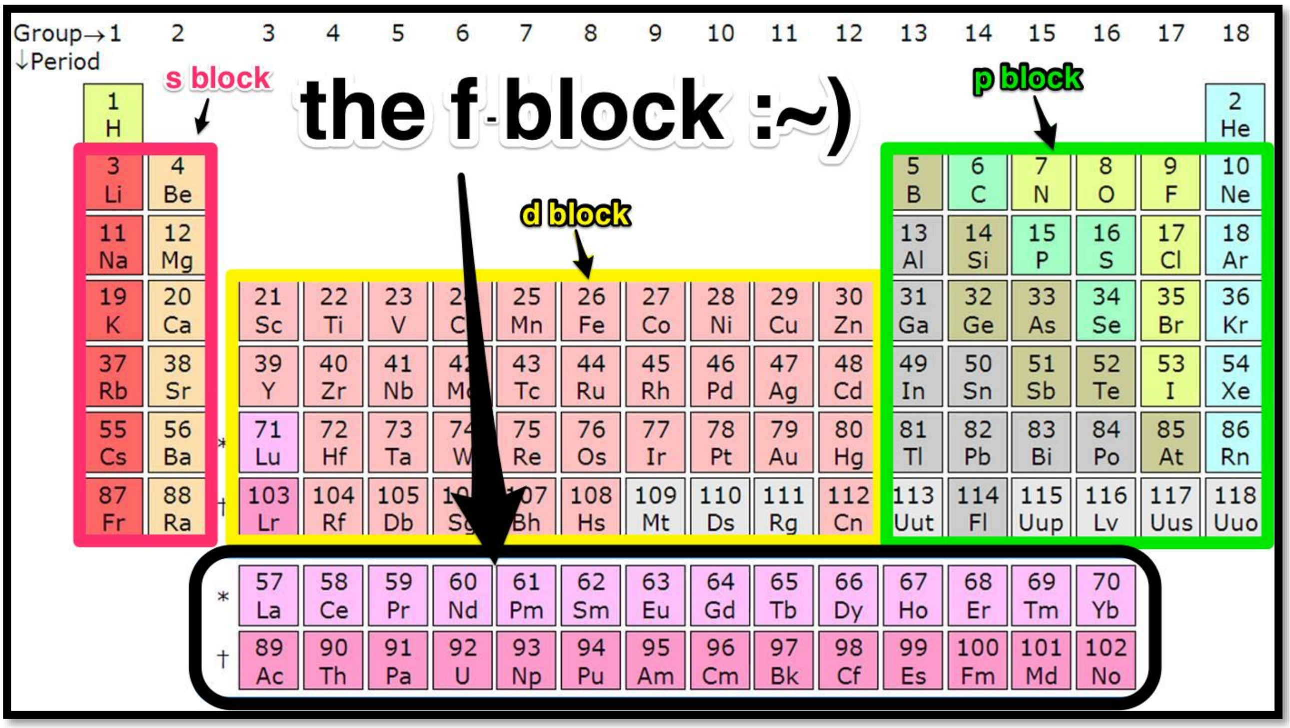
CHEMISTRY

UNIT - 2 – p, d & f Block Elements



Group→1 ↓Period	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																		2 He
3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca		21 Sc	22 Ti	23 V	2 C	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 M	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	†	103 Lr	104 Rf	105 Db	10 S	07 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
		*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
		†	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

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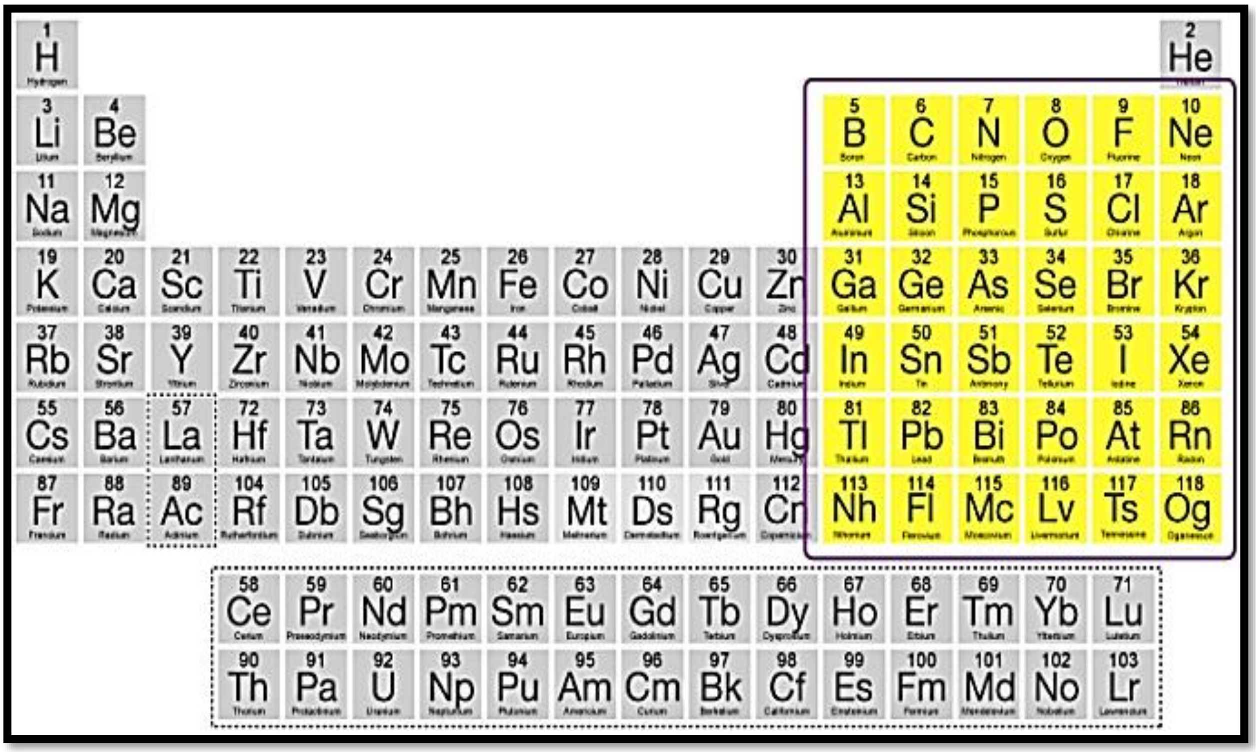
INORGNIC CHEMISTRY - UNIT 2

'p, d and f' Block Elements

2.1. p- Block Elements:

- p- block elements are those in which the last electron enters any of the three p-orbitals of their respective shells. Since a p-subshell has three degenerate p-orbitals each of which can accommodate two electrons, therefore in all there are six groups of p-block elements.
- p-block elements are shiny and usually a good conductor of electricity and heat as they have a tendency to lose an electron. You will find some amazing properties of elements in a p-block element like gallium. It's a metal that can melt in the palm of your hand. Silicon is also one of the most important metalloids of the p-block group as it is an important component of glass.
- p- block elements are nothing but the element in which the last electron enters the outermost p-subshell. P block starts from the 13th group and goes till the 18th group in the periodic table is shown in the **Figure 1.**
- Coal is used in villages to cook food. It is nothing but a p-block element i.e., carbon. diamonds used for making beautiful ornaments are also made up of carbon. Aluminium foil made up of aluminium is also made up of the p-block element.
- The p-block is the region of the periodic table that includes columns IIIA to column VIIIA and does not include helium. There are 35 p-block elements, all of which are in p orbital with valence electrons. The p-block elements are a group of very diverse elements with a wide range of properties.



- The elements p-block are so-called because their valence electrons are filled in an orbital p. These are often called Standard Components, in order to differentiate them from the sequence of transformation and internal transformation.
- Non-metals are on the extreme right side of the periodic table, except for hydrogen, found in the upper left corner. The 17 non-metal elements are: Hydrogen, Helium, Carbon, Nitrogen, Oxygen, Fluorine, Neon, Phosphorus, Sulphur, Chlorine, Argon, Selenium, Bromine, Krypton, Iodine, Xenon, and Radon.
- Usually non-metal is brittle when it is solid and typically has low thermal conductivity and electrical conductivity. Chemically, non-metals tend to have relatively high energy from ionization, contact with electrons, and electron negativity. As they react with other elements and chemical compounds, they receive or exchange the electrons.
- The general electronic external configuration for p-block components is $ns^2\ np^{(1-6)}$.
- The property of p-block element that gives it the ability to form covalent bonds with other atoms of same element (resulting in the formation of a chain of atoms) is called catenation. Carbon exhibits the property of catenation to a great extent. For example, carbon atoms can combine to each other to form long chains, branched chains and closed rings.
- In p-block elements, a lot of variation in properties of elements in a group is observed. Because, difference in inner core of electronic configuration greatly influences the physical and chemical properties of elements.

2.1.1. Occurrence of the p-Block Elements:

- Some elements occur free as well as in the combined state in nature. For example, elements such as oxygen, nitrogen, carbon, sulphur occur in both the form. Noble gases occur in free state only. All other elements usually occur in combined state.

2.1.2. General characteristics of p-block Elements:

2.1.2.1. Electronic Configuration:

The general electronic configuration of p-block elements is $ns^2 np^{1-6}$.

1) These elements include metals and non-metals with a few semi metals (Metalloids).
2) Most of them form covalent compounds.
3) These elements possess relatively higher ionization energy and the value tends to increase along the period but decrease down the group.
4) Most of the elements show negative (except some metals) as well as positive oxidation states (except Fluorine).
5) One of the familiar characteristics of p-block elements is to show inert pair effect i.e. the tendency of being less availability for ns electron in bonding. The inert pair effect increases down the group with the increase in atomic number.

2.1.2.2. Group 13 Elements - The Boron Family:

The group 13(IIIA) elements are Boron, aluminium, gallium, indium and thallium.

1) Boron is a relatively rare element, accounting for only about 0.001% of the earth's crust by mass.
2) Aluminium is the most important of 13th group elements.
3) Gallium is remarkable for its unusually low melting point (29.7^{o}C) and therefore generally exist as a liquid at room temperature. Its most important use is in making gallium arsenide. This is a semi conductor material employed in the manufacture of diode lasers for laser printers, compact -disc players and fibre optic communication devices.
4) Indium is also used in making semi-conductor devices, such as transistors and electrical resistance thermometers called thermistors.
5) Thallium is extremely toxic and has no commercial use.

i) Boron:

- It has Atomic Number of 5 and the Electronic Configuration is given as: [He] $2s^2 2p^1$. It belongs to Group Number: 13 and Period Number: 2

ii) Aluminium:

- It has Atomic Number of 13 and the Electronic Configuration is given as [Ne] 3s2 3p1. It belongs to Group Number: 13 and Period Number: 3

iii) Gallium:

- It has Atomic Number of 31 and the Electronic Configuration is given as [Ar] $3d^{10}$ $4s^2$ $4p^1$. It belongs to Group Number: 13 and Period Number: 4

iv) Indium:

- It has Atomic Number of 49 Electronic Configuration is given as [Kr] $4d^{10}$ $5s^2$ $5p^1$. It belongs to Group Number: 13 and Period Number: 5

v) Thallium:

- It has Atomic Number: 81 and the Electronic Configuration is given as [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^1$. It belongs to Group Number: 13 and Period Number: 6

2.2. Some Important Special Characteristics of p-block Elements:

1. Boron, carbon, nitrogen, oxygen, fluorine and neon head these groups of p block elements. Their valence shell electronic configuration is ns2 np1-6 where n= 2-7.
2. The maximum oxidation state shown by a p block element is equal to the sum of the valence electrons or the group number minus 10. This is called group oxidation state. Beside group oxidation state, p block elements show a number of other oxidation states.
3. In boron, carbon and nitrogen families, the group oxidation state is the most stable for the lighter elements in the group. A lower oxidation state which is 2 units less than the group oxidation state becomes progressively more stable for the heavier elements in each group.
4. The group oxidation state of group 13 elements is +3 but +1 oxidation state is most stable for thallium. The group oxidation state for group 14 elements is +4 but +2 oxidation state is most stable for lead.

Trend of occurrence of oxidation state two units less than the group oxidation state is called inert pair effect and becomes more prominent as we move down the group.

2.2.1. Chemical Behaviour:

1. p-block is the only one which contains metals, non-metals and metalloids. The common metal among p block elements is: aluminium, gallium, indium and thallium (group 13), tin and lead (group 14) and bismuth (group 15). The common metalloids are silicon, germanium, arsenic, antimony and tellurium while all the remaining elements are non-metals.

2. Non-metals have higher ionization enthalpies and higher electronegativity than those of metals. Therefore, non-metals readily form anions.
3. The compounds formed by the union of highly reactive metals with non-metals are generally ionic because of large differences in their electro negativities.

- Compounds formed by the union of non-metals themselves are largely covalent in character due to small differences in their electronegativities. Oxides of non-metals are either acidic or neutral; the oxides of metals are always basic in nature.
- More electropositive the metal, the more basic is its oxide and more electronegative the non-metal, more acidic is its oxides. Among p-block elements, the acidic character of the oxides increases or basic character decreases along a period. The basic character of oxide increases or the acidic character decreases down the group.
- First member of each group of p block elements differ from its exceeding members of their respective group.

The two main reasons for the differences are:

1. Size and other properties which depends upon size.
2. Absence of d orbital in their valence shell.

2.2.2. Size and other Properties Which Depend Upon Size:

- Due to small size, high electronegativity and high ionization enthalpy, the first element of each group of p-block elements differs from rest of the members of the respective groups.

2.2.3. Absence of d-Orbital:

- The absence of d-orbitals in the elements of 2nd period and the presence of d orbital in the heavier elements.

a) Maximum Covalency of Four:

- The first member of each group has 4 orbitals in the valence shell for bonding and hence can accommodate at the maximum 4 pairs or 8 electrons. These elements show a maximum covalency of four. Elements of 3rd period of p-block elements have vacant 3d orbitals lying between 3p and 4s level of energy. Using these d-orbitals, the elements of 3rd period can accommodate more electrons and hence can expand their covalency beyond 4.

1) Boron forms only $[BF_4]^-$ or $[BH_4]^-$ ion while Al gives $[AlF_6]^{3-}$ ion.

2)Carbon forms only tetrahalides whereas other members form hexahalides, i.e. $[SiF_6]^{2-}$, $[GeCl_6]^{2-}$, $[SnCl_6]^{2-}$.

3) Nitrogen forms only NF_3 while phosphorus forms both trihalides i.e., PF_3, PCl_3 and pentahalides i.e., PF_5 and PCl_5.

4) Fluorine does not form FCl_3 having 10 valence electrons while chlorine forms ClF_3.

b) Reactivity:

- Due to presence of d orbital, the elements of 3rd period are more reactive than elements of 2nd period which do not contain d-orbitals.
- Tetrahalides of carbon are not hydrolyzed by water while tetrahalides of other elements of group 14 are readily hydrolyzed. This hydrolysis involves the nucleophilic attack by water molecules and the pair of electrons provided by water is accommodated in the vacant d-orbitals.

c) Tendency to form Multiple Bonds:

1. The presence of d-orbitals also influences the chemistry of heavier elements in a number of other ways.
2. The combined effect of size and availability of d-orbital affects the ability of these elements to form π-bonds.
3. The first member of each group differs from the heavier elements in its ability to form pπ-pπ multiple bonds either with itself or with the other elements of the second period. This type of π-bonding is not strong in case of heavier p-block elements. The heavier elements also form π-bonds but this involves d-orbitals.

- For Example: In SO_2, one of the two π-bonds between S and O involves dπ-pπ bonding while the other involves pπ-pπ bonding. In SO_3 two of the three π-bonds involved dπ-pπ bonding while the third one involves pπ-pπ bonding. In these dπ-pπ bonds, a half filled 3d orbital of sulphur overlaps with the half-filled 2p orbitals of oxygen.
- Since d -orbitals are of higher energy then p-orbitals; therefore, they contribute less towards the overall stability of the molecule as compared to pπ-pπ bonding

between elements of 2nd period. But at the same time, such type of bonding may increase the coordination number in species of heavier elements in the same oxidation state.

2.3. Position of p-block Elements in the Periodic Table:

- In the elements of p-block, the last electron enters the furthest p orbital. They have 3 to 8 electrons in the peripheral shell. As we realize that the quantity of p orbitals is three and, therefore, the most extreme number of electrons that can be obliged in an arrangement of p orbitals is six. Consequently, there are six groups of p-block elements in the periodic table numbering from 13 to 18.

  I. First group: group IIIA called as Boron group
  II. Second group: group IVA called as Carbon group
  III. Third group: group VA called as Nitrogen group
  IV. Fourth group: group VIA called as Chalcogens
  V. Fifth group: group VIIA called as Halogens
  VI. Sixth group: zero group or group 18 called as Inert or Noble gasses group.

- In the p-block, all the three sorts of elements are available, i.e. the Metals, Non-Metals, and Metalloids. The crisscross line in the p-block isolates every one of the elements that are metals from those that are non-metals. Metals are found on the left of the line, and non-metals are those on the right. Along the line, we discover the metalloids. Because of the nearness of a wide range of elements, the p-block demonstrates a great deal of variety in properties.
- You must have seen that coal is used in villages to cook food. It is nothing but a P-block element i.e., carbon. Diamonds used for making beautiful ornaments are also made up of carbon. Aluminium foil made up of aluminium is also made up of the p block element.

2.3.1. Electronic Configuration of p-Block Elements:

- The general electronic configuration of p-block elements is ns^2np^{1-6}(except He). Whereas the inner core electronic configuration may differ. Just because of this difference in the inner core, there are changes in both physical and chemical properties of the elements.

- The general electronic configuration appeared by elements from group13 to 18 of p-block is as given underneath: -
  - Group 13 (Boron family):- $ns^2\ np^1$
  - Group 14 (Carbon family):- $ns^2\ np^2$
  - Group 15 (Nitrogen family):- $ns^2\ np^3$
  - Group 16 (Oxygen family):- $ns^2\ np^4$
  - Group 17 (Halogen family):- $ns^2\ np^5$
  - Group 18 (Noble gases):- $ns^2\ np^6$ (except Helium)
- The general electronic configuration of Helium is $1s^2$. Because of their particular electronic configuration p-block elements demonstrate a great deal of variety in properties.
- The oxidation state of elements in p – block is maximum when it is equal to a total number of valence electrons i.e., the sum of S and P electrons. One of the most interesting facts about the p-block elements is that it contains both non-metals and metalloids.

2.4. Silicones - Structure and Uses:

- The silicones are a group of organosilicon polymers. They have a wide variety of commercial uses.
- The complete hydrolysis of $SiCl_4$ yields silica SiO_2, which has a very stable three-dimensional structure. The fundamental research of F.S. Kipping on the hydrolysis of alkyl-substituted chlorosilanes led, not to the expected silicon compound analogous to a ketone, but to long-chain polymers called silicones is shown in the **Figure 2.**

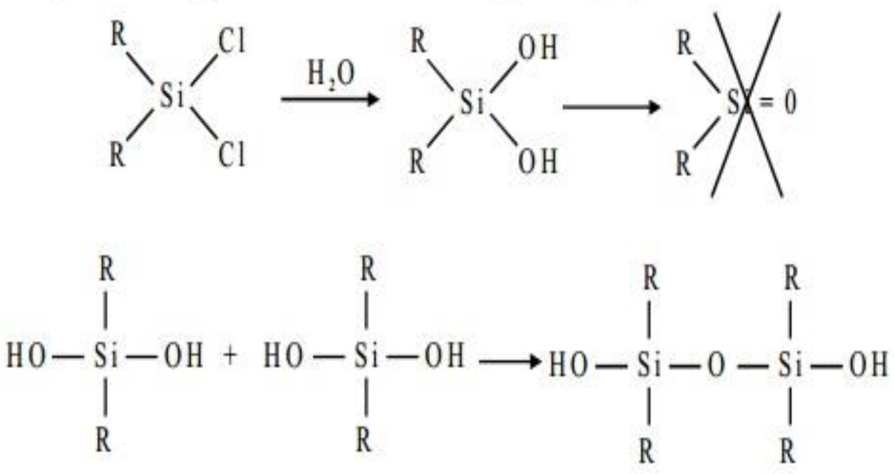


Figure 2: Structure of silicones

- The starting materials for the manufacture of silicones are alkyl-substituted chlorosilanes. Thus, the hydrolysis of trialkylmonochlorosilane R_3SiCl yields hexa- alkyl siloxane is shown in the **Figure 3.**

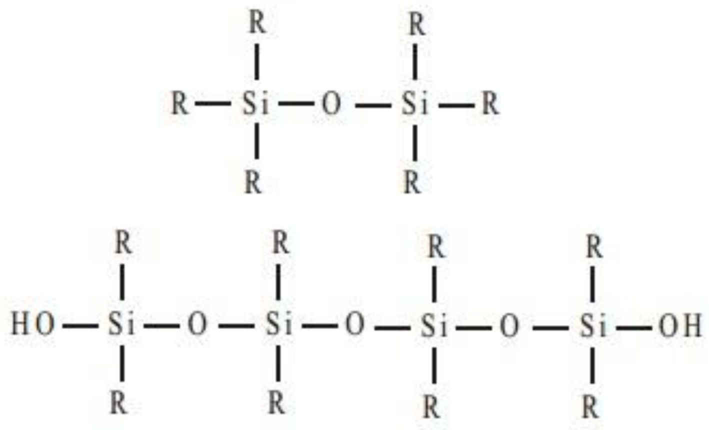


Figure 3: Structure of hexa-alkyl siloxane

- The dialkyldichlorosilane R_2SiCl_2 on hydrolysis gives rise to straight chain polymers and, since an active OH group is left at each end of the chain, polymerization continues and the chain increases in length.
- The hydrolysis of alkyl trichlorosilane $RSiCl_3$ gives a very complex cross- linked polymer. Illustration of cross-linked polymer is given in the **Figure 4.**

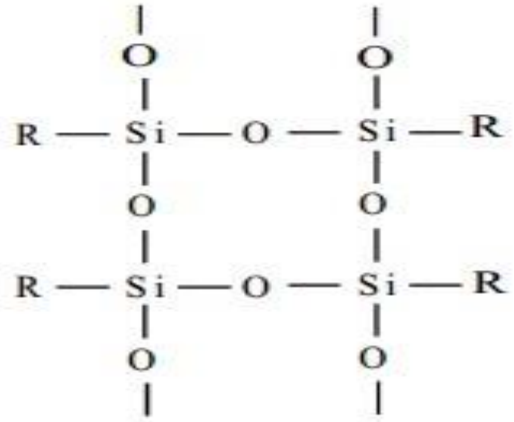


Figure 4: Illustration of cross-linked polymer

2.5. Anomalous Nature of Fluorine:

- Fluorine is the most reactive element among halogen. This is due to the minimum value of F-F bond dissociation energy.Fluorine decomposes cold dilute alkalis liberating OF_2 and with conc. alkali, O_2 is liberated. Under similar conditions, the other halogens will give rise tothe hypohalites and halates respectively.

2.38. UNIT II (p-block elements) – Important Multiple-Choice Questions:

1. What is the correct order of electron affinity among O, F and Cl?

A) O < Cl < F B) O < F < Cl C) F < O < Cl D) Cl < O < F

2. A yellow precipitate is formed upon the addition of aqueous silver nitrate to a solution of?

A) Orthophosphate B) Metaphosphate

C) Pyrophosphate D) Phosphite

3. Which among these has the highest bond angle?

A) NH_3 B) NF_3 C) BF_3 D) PH_3

4. How many S-S bonds are there in tetrathionate ion?

A) 2 B) 3 C) 4 D) 5

5. H_2S is more acidic than H_2O because

A) Oxygen is more electronegative than sulphur

B) Atomic number of sulphur is higher than oxygen

C) H — S bond dissociation energy is less as compared to H — O bond

D) H — O bond dissociation energy is less also compared to H — S bond

6. Helium is preferred to be used in balloons instead of hydrogen because it is

A) Incombustible B) Lighter than hydrogen

C) More abundant than hydrogen D) Non-polarizable

7. Among the 15th group elements, as we move from nitrogen to bismuth, the pentavalency becomes less pronounced and trivalency becomes more pronounced due to

A) Nonmetallic character B) Inert pair effect

C) High electronegativity D) Large ionization energy

8. **Assertion:** In p-block elements, a lot of variation in properties of elements in a group isobserved.

Reason: Difference in inner core of electronic configuration greatly influence the physical and chemical properties of elements

A) Both assertion and reason are correct and the reason is the correct explanation of the assertion

B) Both assertion and reason are correct and the reason is not the correct explanation of the assertion

C) Assertion is correct but the reason is incorrect

D) Both assertion and reason are incorrect

9. Ionic radii (in Å) of As^{3+}, Sb^{3+} and Bi^{3+} follow the order

A) $As^{3+} > Sb^{3+} > Bi^{3+}$

B) $Sb^{3+} > Bi^{3+} > As^{3+}$

C) $Bi^{3+} > As^{3+} > Sb^{3+}$

D) $Bi^{3+} > Sb^{3+} > As^{3+}$

10. Nitrogen is relatively inactive element because

A) Its atom has a stable electronic configuration

B) It has low atomic radius

C) Its electronegativity is fairly high

D) Dissociation energy of its molecule is fairly high

11. Pick out the wrong statement.

A) Nitrogen has the ability to form pπ-pπ bonds with itself

B) Bismuth forms metallic bonds in elemental state

C) Catenation tendency is higher in nitrogen when compared with other elements of the same group

D) Nitrogen has higher first ionisation enthalpy when compared with other elements of the same group

12. The type of hybridization of boron in diborane is?

A) sp^3 hybridization

B) sp^2 hybridization

C) sp hybridization

D) sp^3d^2 hybridization

13. AlF_3 is soluble in HF only in presence of KF. It is due to the formation of?

A) $K_3[AlF_3H_3]$

B) $K_3[AlF_6]$

C) AlH_3

D) $K_3[AlF_3H]$

14. Boron compounds behave as Lewis acids, because of their

A) Ionization property

B) Electron deficient nature

C) Acidic nature

D) Covalent nature

15. Collectively the elements of group 15 are called –

A) Pnicogens

B) Pnicopens

C) Nicopen

D) None of these

16. Boric acid is an acid because its molecule

A) Contains replaceable H^+ ion

B) Gives up a proton

C) Accepts OH^- from water releasing proton

D) Combines with proton from water molecule

17. Which of the following structure is similar to graphite?

A) B_4C
B) B_2H_6
C) BN
D) B

18. **Assertion (A):** When diborane is heated with NH_3 200^0 C, borazole is obtained.

Reason (R): Borazole is known as inorganic benzene.

A) Both A and R is true and R is correct

B) Both A and R is true and R is not correct

C) A is true but R is false

D) a is false but R is true

19. Alum results in early sedimentation true or false?

A) True

B) False

C) Sometimes true sometimes false

D) Neither true nor false

20. Which of the following is not a common property of aluminium alloys?

A) Low strength

B) Heat treatable

C) Easy for machining

D) Readily joined b welding

21. Why has the aluminium association established a system of designating aluminium alloys?

A) To create employment

B) To remove confusion

C) To encourage research

D) To ensure availability

22. Aluminium alloys also have a system that indicates temper.

A) True

B) False

C) Sometimes true sometimes false

D) Neither true nor false

23. Which of the following is the chemical formula of fullerenes?

A) C_0
B) C_6
C) C
D) C_{60}

24. Stainless steel is very useful material for our life. In stainless steel, iron is mixed with

A) Ni and Cr
B) Cu and Cr
C) Ni and Cu
D) Cu and Ni

Teacher's Care Academy

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CHEMISTRY

UNIT - 2

p, d & f Block Elements

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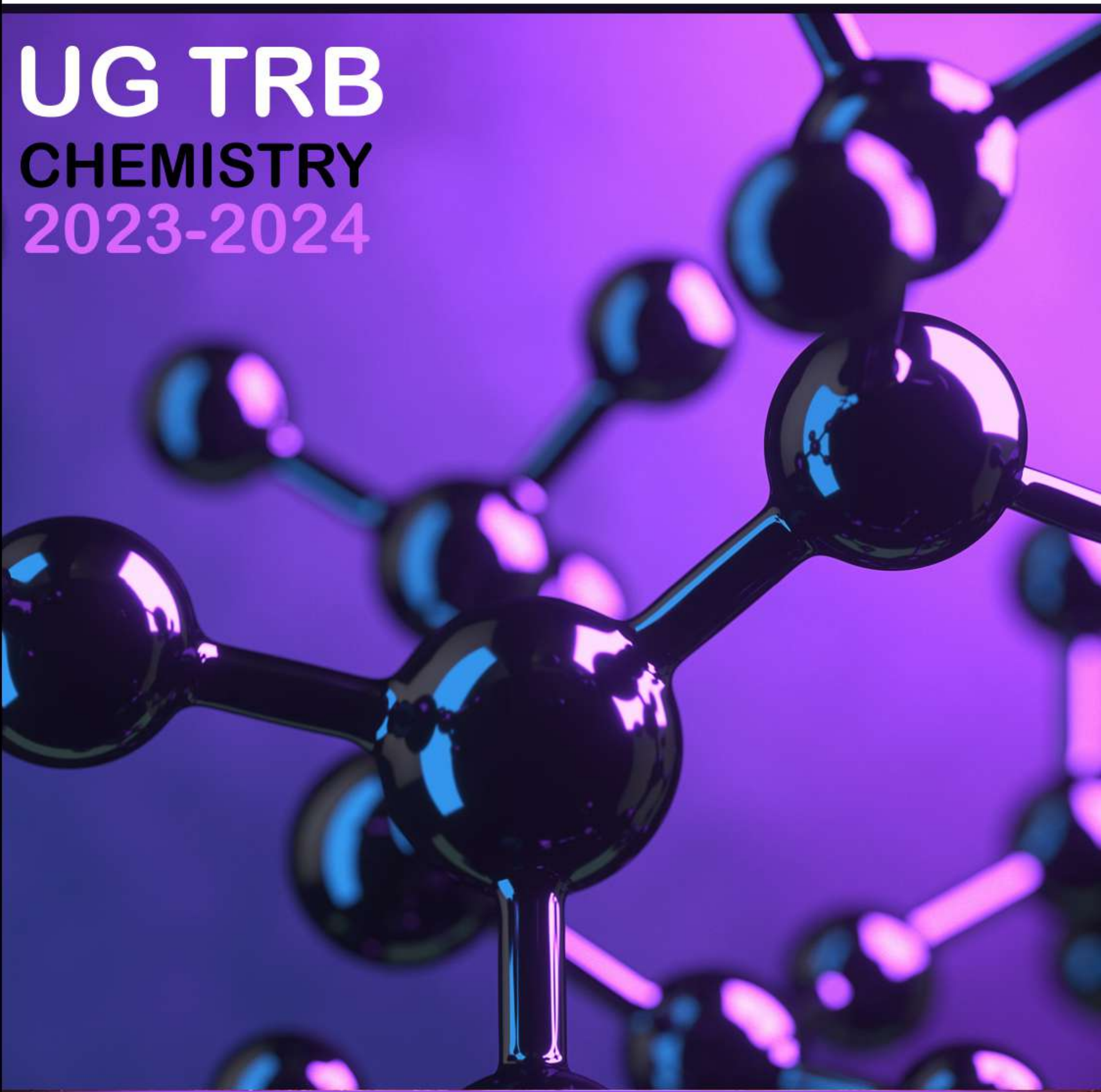

UNIT-4
GASEOUS STATE & SOLID STATE

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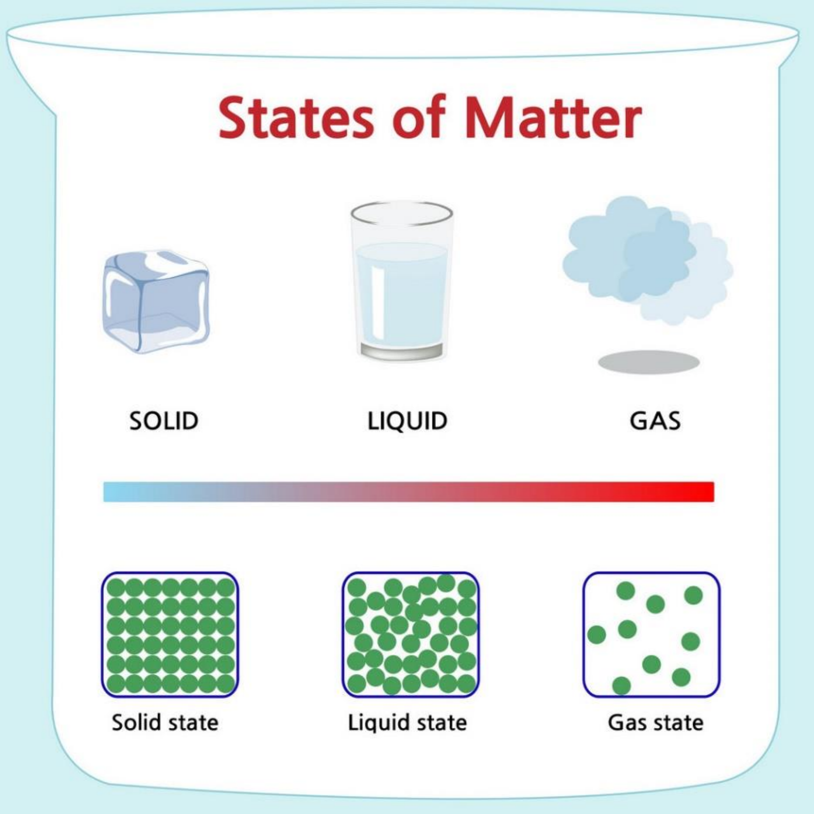
KANCHIPURAM

CHEMISTRY

UNIT - 4 - GASEOUS STATE & SOLID STATE



COMPETITIVE EXAM

For

UG TRB – 2023-24

INDEX - UNIT 4

4.1. GASEOUS STATE

4.2. SOLID STATE

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UG TRB – CHEMISTRY – 2023-24

PHYSICAL CHEMISTRY - UNIT 4

GASEOUS STATE & SOLID STATE

4.1. GASEOUS STATE

4.1.1. Gas laws:

- All matters exist in three states gas, liquid and solid.
  - A **Solids** have a definite shape and definite volume. This is because in solids the ions are closely packed in certain order in fixed positions in the crystal lattice, the particle in a solid are not free to move about but vibrate in their fixed position, so the intermolecular force of attraction is greater.
  - A **Liquids** have no definite shape but have definite volume. In liquids, the intermolecular force of attraction is smaller than that in solids. So the particles do not have a fixed position.
  - A **Gases** have no definite shape and volume. Here the particles are far apart and hence they have no force of attraction. A gas consist of molecules separated wide apart in empty space, the molecules are free to move about throughout the container.

Comparison between the Three States of Matter:

Properties	Solid State	Liquid State	Gaseous State
Shape an volume	Have definite shape and volume	No definite shape but have definite volume	Have no definite shape and volume
Inter molecular force of attraction	Strong	In between solids and gases	Very small
Arrangement of particles	Closely packed	Loosely packed	Far apart
K.E of particles	Very low	In between solids and gases	Very high
Diffusability	Very low	In between solids and gases	Very high
Compressibility	Very low	In between solids and gases	Very high

General characteristics of Gases:

- Gas has limitless expansibility. They expand to fill the entire vessel they are placed in
- Gases are easily compressed by application of pressure to a movable piston fitted in the container.
- Gases can diffuse rapidly through each other to form a homogeneous mixture.
- Gases exert pressure on the walls of the containers in all directions.
- When a gas confined in a vessel is heated, its pressure increased. Upon heating in a vessel fitted with a piston, volume of the gas increases.
- Pressure. Gases exert pressure on the walls of the container in all direction. You can site the example of a gas balloon.

Parameters of a Gas:

- A gas sample can be described in terms of four parameters
- the volume, V of the gas
- it's pressure, **P**

- it's temperature, **T**
- the number of moles, n, of gas in the container

Volume:

- The volume of the container is the volume of the gas sample. It's is usually given in litre or millilitres
  - 1 litre (l) = 1000ml and $1\ ml = 10^{-3} l$

Pressure:

- The pressure of a gas is defined as the force exerted by the impact of its molecules per unit surface area in contact.
- The pressure of a gas sample can be measured with the help of a **mercury manometer**.
- The atmospheric pressure can be determined with a **mercury barometer**.
  - 1 atm = 760 mm Hg = 760 torr $= 1.013 \times 10^5 Pa$.

Temperature:

- The temperature of a gas may be measured in centigrade degrees $\left(^\circ C\right)$ or celsius degrees. The SI unit of temperature is Kelvin (K)
  - $K = ^\circ C + 273$

The Moles of a Gas Sample, n:

- The number of moles, n, of a sample of a gas in a container can be found the mass, m of the sample by dividing the molar mass, M
  - Moles of a gas (n) = mass of gas sample (m)/ molecular mass of gas(M)

Measurable Properties of Gases:

- **Mass:** The mass of gas is generally used in the form of number of moles which is related as

(i) $no.of\ moles = \frac{wt.in.gm}{Molecular\ mass\ of\ gases}\left(n = \frac{w}{M}\right)$

(ii) $number\ of\ moles = \frac{no.\ of\ molecules\ of\ given\ gas}{Avogadro's\ number\ of\ molecules}\left(n = \frac{N}{N_A}\right)$

(iii) $no.\ \text{of}\ moles\ = \dfrac{volume\ of\ given\ gas\ in\ litters\ at\ STP}{22.4L}$

Volume :

- Volume of gas is volume of the container in which it is present, i.e space which the gas molecules can occupy.

Relation Between Different Units of Volume :

- $1m^3 = 10^3 dm^3 = 10^3 litre = 10^6 cm^3 = 10^6 ml = 10^9 mm^3$

Temperature:

Degree of Hotness or Coldness of a Body is Measured by Temperature:

- $\dfrac{C}{100} = \dfrac{K-273}{100} = \dfrac{F-32}{180}$
- **C-Celsius scale , K – Kelvin scale, F- Fahrenheit scale**

Note:

- In all the problem of gaseous state (i.e . in all gas law equations), temperature must be expressed in Kelvin scale i.e.. $t^\circ C + 273.15 = TK$

Pressure:

- Pressure of gas is defined as the force excreted by the on the walls of it's container It is often assumed that pressure is isotropic, i.e it is the same in all the three directions.

4.1.2. The Gas Laws:

- These are some relationships connecting the measurable properties of gases like pressure (P), temperature (T), volume (V) and number of moles (n). These are some relationships connecting the measurable properties of gases like pressure (P), temperature (T), volume (V) and number of moles (n).

Postulates of Kinetic Theory of Gases:

1. Every gas consists of large number of tiny particles called point masses i.e. the actual volume of molecules is negligible when compared to the total volume of the gas. For the same gas, all molecules are of same size and mass.

2. The gas molecules are always in a state of rapid zig-zag motion in all directions. These molecules collide with each other and with the walls of the containing vessel.

3. A molecule moves in a straight line with uniform velocity between two collisions.

4. The molecular collisions are perfectly elastic so that there is no net loss of energy when the gas molecules collide with one another or against the walls of the vessel. Suppose two molecules collide having same mass m. Before collision the velocity of one molecule is υ_1 and velocity of other molecule is υ_2 and after collision the velocity of the molecule's changes from $\upsilon1$to υ_1' and from υ_2 to υ_2' then if the collisions are elastic there is no loss of kinetic energy. This can be expressed as follows.

Total kinetic energy of two molecules before collision is

$$\frac{1}{2}m_1\upsilon_1^2 + \frac{1}{2}m_2\upsilon_2^2$$

And after collision total kinetic energy of both the molecules is

$$\frac{1}{2}m_1\upsilon_1'^2 + \frac{1}{2}m_2\upsilon_2'^2$$

If $\frac{1}{2}m_1\upsilon_1^2 + \frac{1}{2}m_2\upsilon_2^2 = \frac{1}{2}m_1\upsilon_1'^2 + \frac{1}{2}m_2\upsilon_2'^2$

i.e. total kinetic energy before collision is equal to total kinetic energy after collision then the collision is said to be an elastic collision.

5. There are no attractive forces operating between molecules or between molecules and the walls of the vessel in which the gas has been contained. The molecule move independently of one another.

6. The pressure of the gas is the hits recorded by the molecules on the walls of the container in which the gas is contained.

7. The average kinetic energy of gas molecules is directly proportional to absolute temperature. This means that the average kinetic energy of molecules is the same at a given temperature. This must be clear to you that all the above postulates are applicable to ideal gases only i.e. the gas which obey Boyle's and Charle's law under all conditions of temperature and pressure. These are only approximately valid for real gases.

Derivation of Kinetic Gas Equation:

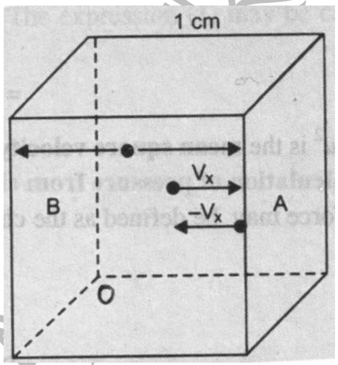
- Suppose a volume of gas enclosed in a cubical vessel at a fixed temperature
- Suppose that:
  - The length of each side of cube = *l* cm

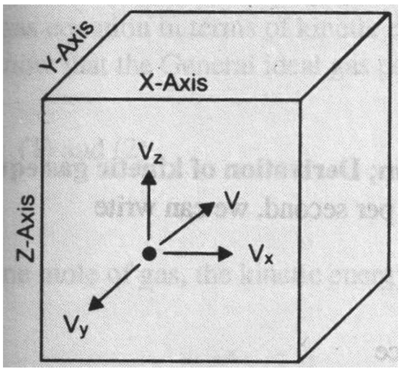
- the number of gas molecules = n
- the mass of one molecule = m
- the velocity of a molecule = υ

- Let us consider one single molecule of a gas can be evaluated by calculating the momentum during collisions.
- According to kinetic model the molecules of the gas are moving in straight lines in all possible directions.
- They collide with one another frequently as also with the walls of the container. Since their mutual collisions are perfectly elastic and do not involve the loss of energy, these may be neglected. Here we will, therefore, assume that gas molecules move in all directions but rebound whenever they strike the wall of the container. Now you proceed to derive kinetic gas equation in the following steps According to the kinetic theory, a molecule of a gas can move with velocity in any direction velocity is a vector quantity can be resolved into components *x, y, z* along the X, Y and Z axes. These components are related to velocity υ by the following expression.

$$\upsilon^2 = \upsilon_x{}^2 + \upsilon_y{}^2 + \upsilon_z{}^2$$

- Let us consider a molecule moving in OX direction between opposite faces A and B. It will strike the face A with velocity *x* and rebound with velocity - *x*. To hit the same face again the molecule must travel *l* cm to Collide with opposite face B and then again *l* cm to return to face A. Therefore, time taken between two collisions can be calculated as follows:





- The molecule travels υ_x cm in 1 sec

hence1 cm in $1/\upsilon_x$ sec

And 2*l* cm in $2l/\upsilon_x$ sec

In $2l/\upsilon_x$ sec molecule suffers 1 collision

In 1 sec no of collisions = $\upsilon_x/2l$

Each impact of the molecule on the face A causes a change of momentum which is mass X velocity.

Momentum of the molecule before impact $= m\upsilon_x$

Momentum of the molecule after impact $= -m\upsilon_x$

Hence change of momentum $= m\upsilon x - (-m\upsilon x) = 2m\upsilon x$

But the number of collisions per second on face $A = \upsilon x / 2l$

- Therefore, total change of momentum per second on face A caused by one Molecule

$$= 2m\upsilon x^2 / 2l$$

$$= m\ \upsilon x^2 / l$$

- As there are two faces along x- direction, total change of momentum per second
- Considering both the faces along x-direction will be $2m\upsilon x^2 / l$
- This is change of momentum caused by one molecule along x-direction per second will be $2m\ \upsilon z^2 / l$. The change of momentum caused by one molecule along y-direction per second will be $2m\ \upsilon y^2 / l$ and change of momentum caused by one molecule along z- direction per second will be
- Total change of momentum caused by one molecule considering along three direction will be

$$= 2m\ \upsilon x^2 / l + 2m\ \upsilon y^2 / l + 2m\ \upsilon z^2 / l$$

$$= 2m / l\ \left(\upsilon x^2 + \upsilon y^2 + \upsilon z^2\right)$$

$$= 2m\ \upsilon^2 / l$$

- Since there are n molecules in the vessel then total change of momentum due to n molecules will be $2mn\ \upsilon^2 / l$

$\upsilon^2 =$ mean square velocity

- Since change of momentum per second is force

Hence force $= 2mn\upsilon^2 / l$

Since pressure = Total force/Total area

- Since there are six faces in a cube, area of each cube is l^2. Hence total area is $6l^2$.
- Then pressure $= 2mn\upsilon^2 / lx\ 1/6l^2 = mn\upsilon^2/3l^2$

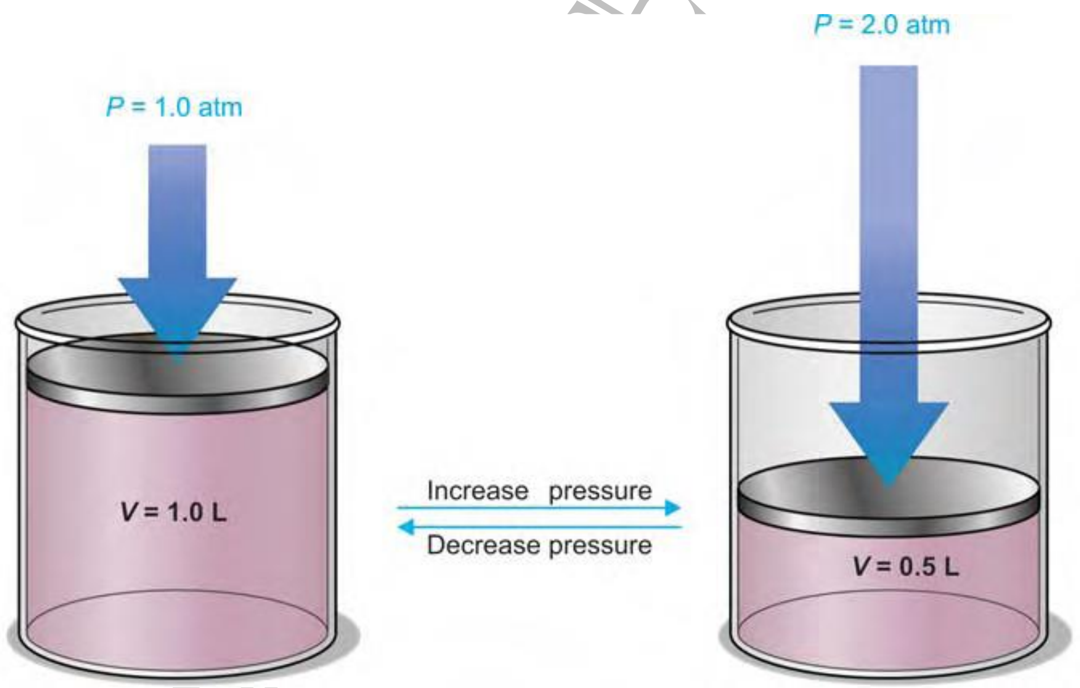
As l^2 = volume V

Hence pressure $P = 1/3\ mn\upsilon^2/V$

(or) $\mathbf{PV = 1/3\ mn\upsilon^2}$

- This is known as **Kinetic Gas Equation**. This equation has been derived for a cubical vessel. It is equally valid for vessel of any shape. The available volume in the vessel may be considered as made up of large number of infinitesimally small cubes, for each of them the equation is valid.

Boyle's Law (Pressure -Volume Relationship):



- It states that at constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure.
- The Boyle law may be express mathematically,

$V \alpha 1/P$

$V = k\,x\,1/P,$

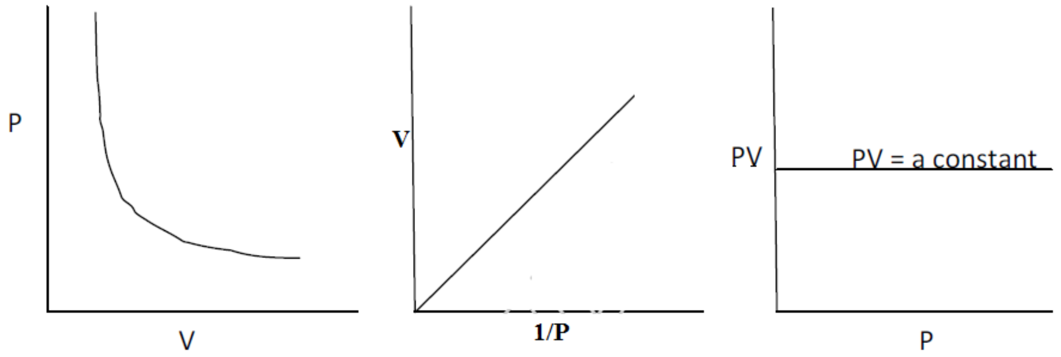
- where *k* is the proportionality constant.

(or) PV = k, a constant

- Consider a fixed amount of gas at constant temperature T. Let V_1 & P_1 are its initial volume and pressure respectively. Let the gas undergoes expansion, so that its final volume and pressure becomes V_2 and P_2.
- Then according to Boyle's law,

$$P_1V_1 = k = P_2V_2 \,;\, P_1V_1 = P_2V_2$$

- If we plot graphs between pressure against volume (hyperbola), volume against 1/pressure (straight line) and PV against P at constant temperature, the graphs obtained are as follows
- These graphs are obtained at constant temperature and are called **isotherms**



Consequence of Boyle,s Law:

- The pressure-density relationship can be derived fromthe boyle,s law as

$P_1V_1 = P_2V_2$ (Boyle,s law)

$$P_1(m/d_1) = P_2(m/d_2)$$

$$\mathbf{P_1 / d_1 = P_2 / d_2}$$

1. A gas is present at a pressure of 2atm. What should be the increase in pressure so that the volume of the gas can be decreased to ¼ th of the initial value if the initial value if the temperature is maintained constant.

Sol : PV = constant for a given mass of gas at constant pressure

$$\Rightarrow P_1V_1 = P_2V_2 \qquad P_1 = 2atm \quad V_1 = V \quad V_2 = V/4 \quad P_2 = ?$$

Now, $2\times V = P_2 = \frac{V}{4}$ $\Rightarrow$ $P_2 = 8atm$ increase

Pressure should be increased from 2 to 8 atm.

Total increase $= 8 - 2 = 6\ atm$

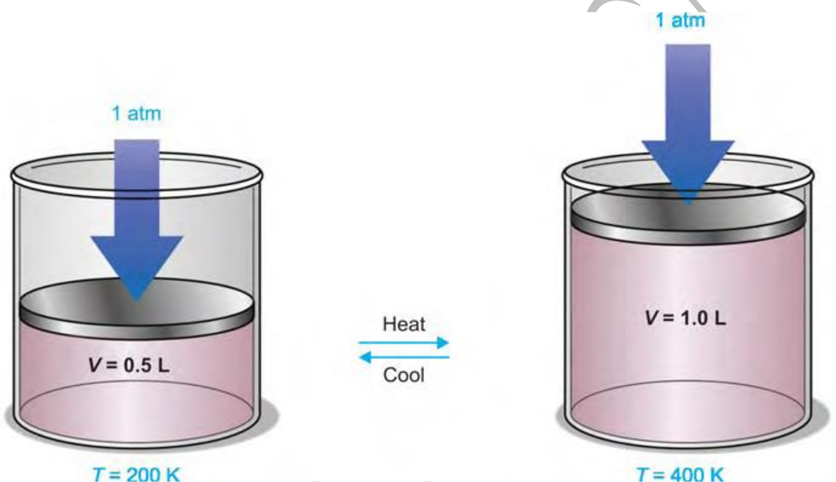
A sample of gas occupies 10 litre under a pressure of 1 atmosphere. What will be its volume if the pressure is increased to 2 atmospheres? Assume that the temperature of the gas sample does not change .

Ans: 5 Litre

4.1.3. Charles' Law (Temperature -Volume Relationship)

- It states that at constant pressure, volume of a fixed mass of gas is directly proportional to its temperature. Mathematically, $V \alpha\ T$

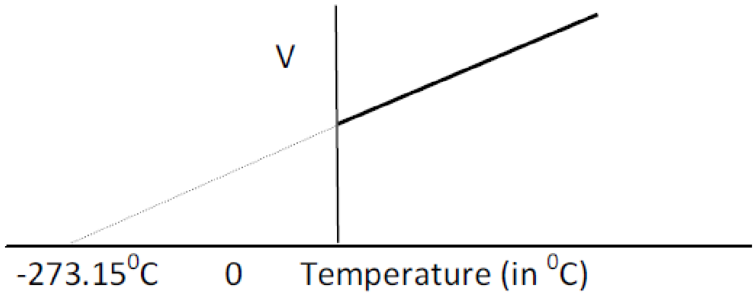
$$V = k\ x\ T; V / T = k, \text{ a constant}$$



- Consider a fixed amount of gas at constant pressure P. Let V_1 be its volume at a temperature T_1 and V_2 be its volume at a temperature T_2 .

Then according to Charle's Law:

- $V_1 / T_1 = V_2 / T_{2;}$ Since the graph is obtained at constant pressure, it is called **isobar**
- If volume is plotted against temperature at constant pressure, the graph obtained is as follows



Since the graph is obtained at constant pressure, it is called **isobar**

A gas occupies a volume of 580 ml at $17^{\circ}C$. It is heated to $100^{\circ}C$ at constant pressure. Calculate the volume of the gas

(A) 746 ml (B) 760ml (C) 773ml (D) 780ml

Ans . A

Sol :

Initial volume $(V_1)=580ml,$

$T_1=17+273=290K$

Find the volume $(V_2)=?$

$T_2=100=273=373K$

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

$$\therefore V_2=T_2\times\frac{V_1}{T_1}=373\times\frac{580}{290}=746ml$$

A gas occupies 3 litters at and one atmospheric . hat volume will it occupy if the temperature is changed , the pressure remaining constant-

(A) 2.91 litres (B) 2.86 litres (C) 2.30 litres (D) none of these

Ans : (b) 2.86 litres

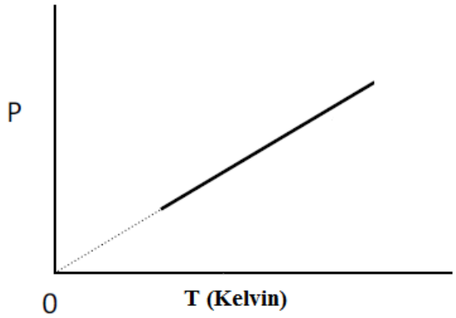
4.1.4. Gay Lussac's Law (Pressure-Temperature Relationship):

- It states that at constant volume, the pressure of a fixed amount of a gas is directly proportional to the kelvin temperature.
- Mathematically,

$P \alpha T$

(or) P = a constant $\times T$

(or), P/T = a constant



- If we plot a graph between pressure and temperature of a fixed mass of gas at constant volume, the graph obtained is as follows.
- The above is obtained at constant volume and is termed as an **isochore.**

4.1.5. Avogadro Law (Volume-no. of Moles or Amount Relationship):

- It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of moles or molecules. This means that at constant temperature and pressure, the volume of a gas is directly proportional to its number of moles (n) or molecules (N).

$V \alpha n,$2the number of moles

$V = k \times n,$ where k is a constant; $V / n = k;$ for any two gases with volumes V_1, V_2 and moles n_1, n_2 at constant T and $P. V_1 / n_1 = A = V_2 / n_2$

$V_1 = V_2; n_1 = n_2$

- We know that number of moles (n) = mass in gram (m)/molar mass (M)

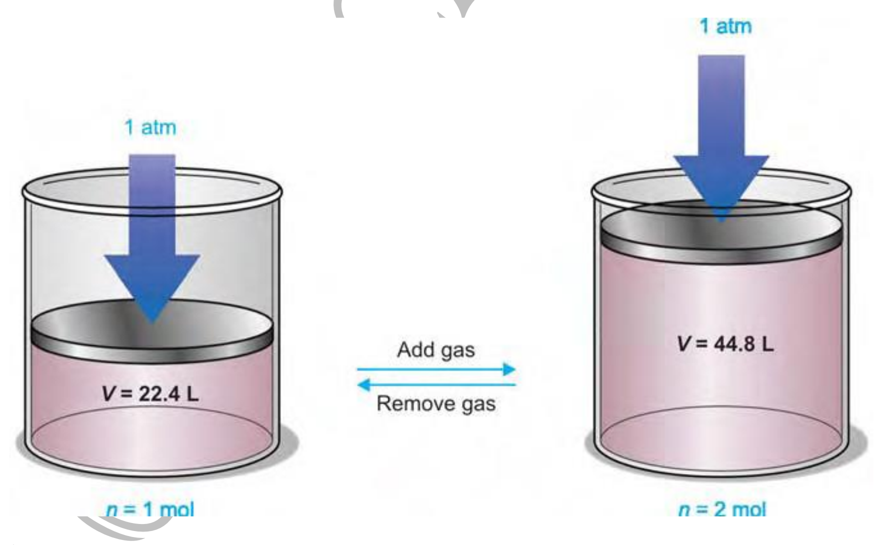
i.e., n = m/M

- So, the above equation becomes:

$V = k\, x\, m / M$

Or, $M = k\, x\, m / V; M = k\, x\, d; M \alpha d$

- The density of a gas is directly proportional to its molar mass.



Molar Gas Volume:

- The molar gas volume its follow as a corollary of Avogadro law that one mole of any gas at a given temperature and pressure has the same fixed volume.It is called the **molar gas volume.**

1 mole of a gas at STP = $22.7109\ litres\ mol^{-1}$

Question for Practice:

1. Which of the following does not express the properties of gases?

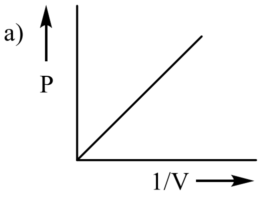
(A) Gases are highly compressible.

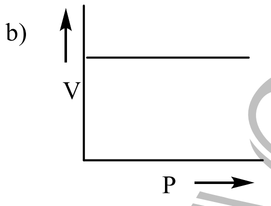
(B) Gases exert pressure equally in all directions.

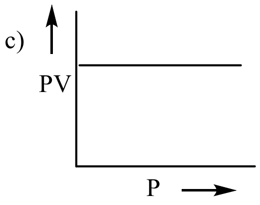
(C) Gases have much higher density than liquids and solids.

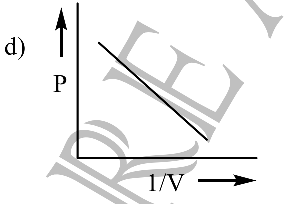
(D) Gases mix evenly and completely in all proportions.

2.Which of the following graphs represents the incorrect Boyles law (correct ansB)









3. A flask of capacity 2L is heated from $35^{o}C$ to $45^{o}C$ what volume of air will escape from the flask?

(A)10 ml (B) 24 ml (C) 65 ml (D) 50 ml

4. Absolute zero can be defined as the temperature at which

(A) pressure becomes zero (B) volume becomes zero

(C) mass becomes zero (D) density becomes zero

5. If we plot volume of a certain mass or volume of gas against temperature at constant pressure. this graph known as

(A) isochore (B) isotherm (C) isotone (D) isobar

6. Mathemtically, Boyles law can be represented as

(A) $V \alpha 1/P$ (B) $V= K/P$ (C) $VP=K$ (D) all of these

7. At constant temperature, the pressure of the gas is reduced to one third, the volume

(A) reduced the one third (B) increased by three times

(C) cannot be predicted (D) remains same

Density $= \dfrac{n \times at.wt}{V \times N_A}$

$$7.2 = \frac{3 \times at.wt}{24 \times 10^{-24} cm^3}$$

6.023×10^{23}

At.wt = 34.69

34.69 g has no.of atoms $= 6.023 \times 10^{23}$

200g has no of atoms $= \dfrac{6.023 \times 10^{23} \times 200}{34.69}$

$= 3.4722 \times 10^{24} atoms$

$= approx.. \, 3.5 \times 10^{24} atoms$

4.3. Multiple Choice Questions

1. Which of the following is not a close packing

   A) hcp B) ccp C) bcc D) fcc

2. Which of the following has HCP structure

   A) Al B) Mg C) Cu D) Ni

3. All Nobel gases crystallise in the ccp structure except

   A) Helium B) Neon C) Argon D) Krypton

4. If the coordination number of an element in its crystal lattice is 8, then packing is

   A) FCC B) HCP

   C) BCC D) None of the above

5. In close packed lattice the number of octahedral sites as compared to tetra ones will be

   A) equal B) Half C) Double D) One fourth

6. A compound contains P and Q element, atoms Q are ccp arrangement While P occupy all tetrahedral sites. Formula of compound is

   A) PQ B) PQ_2 C) P_2Q D) P_3Q

7. The co-ordintion number of Zn^{2+} and S^{2-} ions in the zinc blende (ZnS) type structure is______________

A) 4:4 B) 6:6 C) 8:8 D) 4:8

8. Antifluorite structure is derived from fluorite structure by

A) Heating fluorite crystal lattice

B) Subjecting fluorite structure to high pressure

C) Interchanging the position of positive and negative ions in the lattice

D) All the above

9. At zero Kelvin, most of the ionic crystal posses

A) Frenkel defect B) Schottky defect

C) Metal excess defect D) No defect

10. As a result of schottky defect

A) there is no effect on the density B) density of the crystal increase

C) density of the crystal decreases D) any of the above three can happen

11. Frenkel defect is generally observed in

A) AgBr B) AgI

C) ZnS D) All of these

12. F-centres in an ionic crystal are

A) lattice sites containing electron B) interstitial sites continuing electron

C) lattice sites that are vacant D) interstitial sites containing cations

13. The correct statement regarding F-centre is

A) Electrons are held in the lattice sites of crystal

B) F-centre imparts colour to the crystal

C) Conductivity of the crystal increases due to F-centre

D) All the three above

14. For tetragonal crystal system which of the following is not true

A) $a = b \neq c$ B) $\alpha = \beta = \gamma = 90^o$

C) $a \neq b \neq c$ D) $\alpha = \beta \neq \gamma = 90^o$

15. In an ionic crystal, a cation and an anion leave the lattice to cause two vacancies. This defect is called

A) Schottky defect B) Frenkel defect

C) interstitial defect D) none of these

16. Which of the following defects is generally found in sodium chloride and cesium chloride?

A) Frenkel defect B) interstitial defect

C) Schottky defect D) none of these

17. In a solid lattice, a cation has left a lattice site and is present in interstitial position, the lattice defect is

A) Schottky defect B) Frenkel defect

C) vacancy defect D) interstitial defect

18. In Frenkel defect,

A) some of the lattice sites are vacant

B) an ion occupies interstitial position

C) some of the cations are replaced by foreign ions

D) none of the above

19. A device used to convert light energy into electrical energy is called

A) a semiconductor B) a solar cell

C) an irreversible cell D) an electrochemical cell

20. For an ionic crystal of formula AX, the radius ratio lies between 0.732 and 0.414. Its co-ordination number is

A) 4 B) 6 C) 8 D) 12

21. The radius ratio in an ionic crystal lies between 0.732–1.000, the co-ordination number is

A) 3 B) 4 C) 6 D) 8

22. The number of atoms per unit cell in a simple cubic, fcc and bcc are

A) 1, 2, 4 B) 1, 4, 2 C) 4, 2, 1 D) 2, 4, 1

23. In a crystal, the atoms are located at the positions where potential energy is

A) maximum B) zero C) minimum D) infinite

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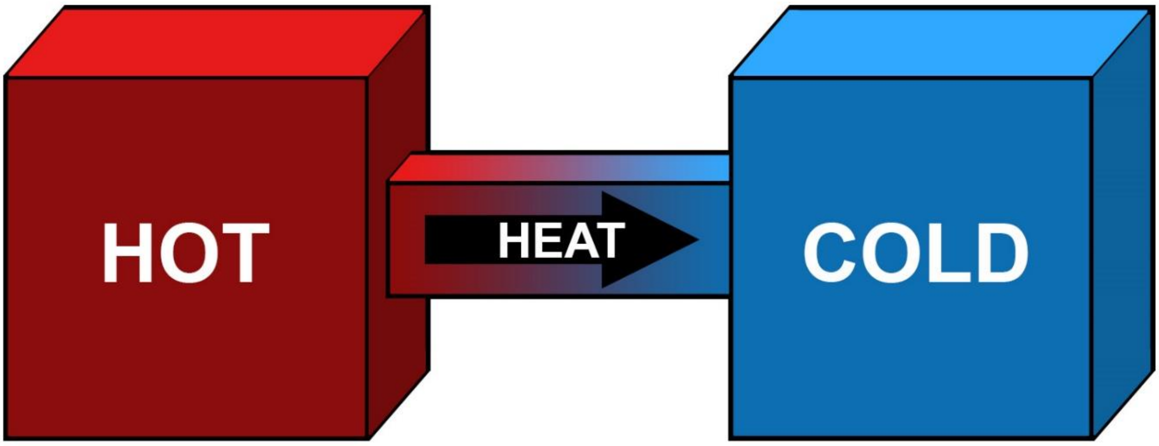

COMPETITIVE EXAM

For

UG TRB – 2023-24

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INORGNIC CHEMISTRY - UNIT 5

THERMODYNAMICS

5.1. INTRODUCTION:

- Thermodynamics, science of the relationship between heat, work, temperature, and energy. In broad terms, thermodynamics deals with the transfer of energy from one place to another and from one form to another.
- The key concept is that heat is a form of energy corresponding to a definite amount of mechanical work.
- Heat was not formally recognized as a form of energy until about 1798, when Count Rumford (Sir Benjamin Thompson), a British military engineer, noticed that limitless amounts of heat could be generated in the boring of cannon barrels and that the amount of heat generated is proportional to the work done in turning a blunt boring tool. Rumford's observation of the proportionality between heat generated and work done lies at the foundation of thermodynamics. Another pioneer was the French military engineer Sadi Carnot, who introduced the concept of the heat-engine cycle and the principle of reversibility in 1824. Carnot's work concerned the limitations on the maximum amount of work that can be obtained from a steam engine operating with a high-temperature heat transfer as its driving force. Later that century, these ideas were developed by Rudolf Clausius, a German mathematician and physicist, into the first and second laws of thermodynamics, respectively.
- Thermodynamics is the study of the relations between heat, work, temperature, and energy. The laws of thermodynamics describe how the energy in a system changes and whether the system can perform useful work on its surroundings. It is represented in the Figure 1.

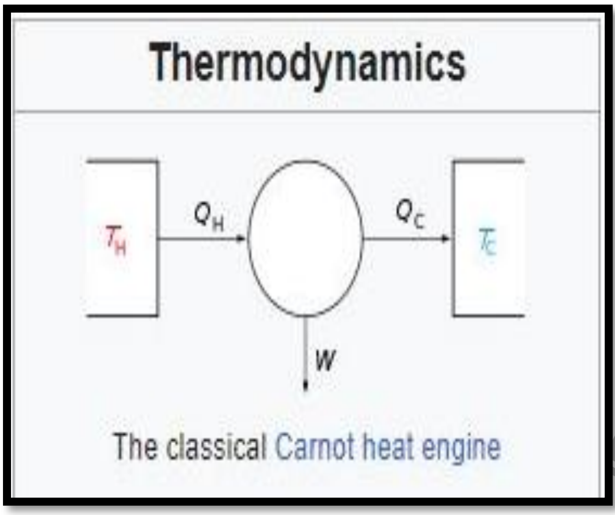


Figure 1: Representation of Flow of heat and Work

- The history of thermodynamics as a scientific discipline generally begins with Otto von Guericke who, in 1650, built and designed the world's first vacuum pump and demonstrated a vacuum using his Magdeburg hemispheres. Guericke was driven to make a vacuum in order to disprove Aristotle's long-held supposition that 'nature abhors a vacuum'. Shortly after Guericke, the Anglo-Irish physicist and chemist Robert Boyle had learned of Guericke's designs and, in 1656, in coordination with English scientist Robert Hooke, built an air pump. Using this pump, Boyle and Hooke noticed a correlation between pressure, temperature, and volume. In time, Boyle's Law was formulated, which states that pressure and volume are inversely proportional. Then, in 1679, based on these concepts, an associate of Boyle's named Denis Papin built a steam digester, which was a closed vessel with a tightly fitting lid that confined steam until a high pressure was generated.
- Later designs implemented a steam release valve that kept the machine from exploding. By watching the valve rhythmically move up and down, Papin conceived of the idea of a piston and a cylinder engine. He did not, however, follow through with his design. Nevertheless, in 1697, based on Papin's designs, engineer Thomas Savery built the first engine, followed by Thomas Newcomen in 1712. Although these early engines were crude and inefficient, they attracted the attention of the leading scientists of the time.
- The fundamental concepts of heat capacity and latent heat, which were necessary for the development of thermodynamics, were developed by Professor Joseph Black at the University of Glasgow, where James Watt was employed as an instrument maker. Black and Watt performed experiments together, but it was Watt who conceived the idea of the external condenser which resulted in a large increase in steam

engine efficiency. Drawing on all the previous work led Sadi Carnot, the "father of thermodynamics", to publish Reflections on the Motive Power of Fire (1824), a discourse on heat, power, energy and engine efficiency. The book outlined the basic energetic relations between the Carnot engine, the Carnot cycle, and motive power. It marked the start of thermodynamics as a modern science.

- The first thermodynamic textbook was written in 1859 by William Rankine, originally trained as a physicist and a civil and mechanical engineering professor at the University of Glasgow. The first and second laws of thermodynamics emerged simultaneously in the 1850s, primarily out of the works of William Rankine, Rudolf Clausius, and William Thomson (Lord Kelvin). The foundations of statistical thermodynamics were set out by physicists such as James Clerk Maxwell, Ludwig Boltzmann, Max Planck, Rudolf Clausius and J. Willard Gibbs.
- Clausius, who first stated the basic ideas of the second law in his paper "On the Moving Force of Heat",published in 1850, and is called "one of the founding fathers of thermodynamics", introduced the concept of entropy in 1865.
- During the years 1873to 1876 the American mathematical physicist Josiah Willard Gibbs published a series of three papers, the most famous being “On the Equilibrium of Heterogeneous Substances”, in which he showed how thermodynamic processes, including chemical reactions, could be graphically analyzed, by studying the energy, entropy, volume, temperature and pressure of the thermodynamic system in such a manner, one can determine if a process would occur spontaneously. Also Pierre Duhem in the 19th century wrote about chemical thermodynamics.
- During the early 20th century, chemists such as Gilbert N. Lewis, Merle Randall, and Guggenheim applied the mathematical methods of Gibbs to the analysis of chemical processes.
- Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, entropy, and the physical properties of matter and radiation.
- The behavior of these quantities is governed by the four laws of thermodynamics which convey a quantitative description using measurable macroscopic physical quantities, but may be explained in terms of microscopic constituents by statistical mechanics.

- Thermodynamics applies to a wide variety of topics in science and engineering, especially physical chemistry, biochemistry, chemical engineering and mechanical engineering, but also in other complex fields such as meteorology.
- Historically, thermodynamics developed out of a desire to increase the efficiency of early steam engines, particularly through the work of French physicist Sadi Carnot (1824) who believed that engine efficiency was the key that could help France win the Wars. Cots-Irish physicist Lord Kelvin was the first to formulate a concise definition of thermodynamics in 1854 which stated, "Thermo-dynamics is the subject of the relation of heat to forces acting between contiguous parts of bodies, and the relation of heat to electrical agency."
- German physicist and mathematician Rudolf Clausius restated Carnot's principle known as the Carnot cycle and gave so the theory of heat a truer and sounder basis. His most important paper, "On the Moving Force of Heat", published in 1850, first stated the second law of thermodynamics. In 1865 he introduced the concept of entropy. In 1870 he introduced the virial theorem, which applied to heat.
- The initial application of thermodynamics to mechanical heat engines was quickly extended to the study of chemical compounds and chemical reactions. Chemical thermodynamics studies the nature of the role of entropy in the process of chemical reactions and has provided the bulk of expansion and knowledge of the field. Other formulations of thermodynamics emerged.
- Statistical thermodynamics, (or) statistical mechanics, concerns itself with statistical predictions of the collective motion of particles from their microscopic behavior. In 1909, ConstantinCarathéodory presented a purely mathematical approach in an axiomatic formulation, a description often referred to as geometrical thermodynamics.
- A description of any thermodynamic system employs the four laws of thermodynamics that form an axiomatic basis. The first law specifies that energy can be transferred between physical systems as heat, as work, and with transfer of matter.
- The second law defines the existence of a quantity called entropy, that describes the direction, thermodynamically, that a system can evolve and quantifies the state of order of a system and that can be used to quantify the useful work that can be extracted from the system.

- In thermodynamics, interactions between large ensembles of objects are studied and categorized. Central to this are the concepts of the thermodynamic system and its surroundings.
- A system is composed of particles, whose average motions define its properties, and those properties are in turn related to one another through equations of state.
- Properties can be combined to express internal energy and thermodynamic potentials, which are useful for determining conditions for equilibrium and spontaneous processes.
- With these tools, thermodynamics can be used to describe how systems respond to changes in their environment. This can be applied to a wide variety of topics in science and engineering, such as engines, phase transitions, chemical reactions, transport phenomena, and even black holes.
- The results of thermodynamics are essential for other fields of physics and for chemistry, chemical engineering, corrosion engineering, aerospace engineering, mechanical engineering, cell biology, biomedical engineering, materials science, and economics, to name a few.

5.1.1. Branches of Thermodynamics:

- The study of thermodynamical systems has developed into several related branches, each using a different fundamental model as a theoretical (or) experimental basis, (or) applying the principles to varying types of systems.

(i) Classical Thermodynamics:

- Classical thermodynamics is the description of the states of thermodynamic systems at near-equilibrium that uses macroscopic, measurable properties. It is used to model exchanges of energy, work and heat based on the laws of thermodynamics. The qualifier classical reflects the fact that it represents the first level of understanding of the subject as it developed in the 19th century and describes the changes of a system in terms of macroscopic empirical (large scale, and measurable) parameters. A microscopic interpretation of these concepts was later provided by the development of statistical mechanics.

(ii) Statistical Mechanics:

- Statistical mechanics, also known as statistical thermodynamics, emerged with the development of atomic and molecular theories in the late 19th century and early 20th century, and supplemented classical thermodynamics with an interpretation of the microscopic interactions between individual particles or quantum-mechanical states. This field relates the microscopic properties of individual atoms and molecules to the macroscopic, bulk properties of materials that can be observed on the human scale, thereby explaining classical thermodynamics as a natural result of statistics, classical mechanics, and quantum theory at the microscopic level.

(iii) Chemical Thermodynamics:

- Chemical thermodynamics is the study of the interrelation of energy with chemical reactions (or) with a physical change of state within the confines of the laws of thermodynamics. The primary objective of chemical thermodynamics is determining the spontaneity of a given transformation.

(iv) Equilibrium Thermodynamics:

- Equilibrium thermodynamics is the study of transfers of matter and energy in systems (or) bodies that, by agencies in their surroundings, can be driven from one state of thermodynamic equilibrium to another. The term 'thermodynamic equilibrium' indicates a state of balance, in which all macroscopic flows are zero, in the case of the simplest systems (or) bodies, their intensive properties are homogeneous, and their pressures are perpendicular to their boundaries. In an equilibrium state there are no unbalanced potentials, (or) driving forces, between macroscopically distinct parts of the system. A central aim in equilibrium thermodynamics is given a system in a well-defined initial equilibrium state, and given its surroundings, and given its constitutive walls, to calculate what will be the final equilibrium state of the system after a specified thermodynamic operation has changed its walls or surroundings.

(v) Non-equilibrium Thermodynamics:

- Non-equilibrium thermodynamics is a branch of thermodynamics that deals with systems that are not in thermodynamic equilibrium. Most systems found in nature are not in thermodynamic equilibrium because they are not in stationary states, and are continuously and discontinuously subject to flux of matter and energy to and from other systems. The thermodynamic study of non-equilibrium systems requires more general concepts than are dealt with by equilibrium thermodynamics. Many natural systems still today remain beyond the scope of currently known macroscopic thermodynamic methods.

5.1.2. The Most Important Laws of Thermodynamics Are:

- Thermodynamics is principally based on a set of four laws which are universally valid when applied to systems that fall within the constraints implied by each. In the various theoretical descriptions of thermodynamics these laws may be expressed in seemingly differing forms, but the most prominent formulations are the following.
- The zeroth law of thermodynamics is defined as when two systems are each in thermal equilibrium with a third system, the first two systems are in thermal equilibrium with each other. This property makes it meaningful to use thermometers as the “third system” and to define a temperature scale.
- If two systems are each in thermal equilibrium with a third, they are also in thermal equilibrium with each other. This statement implies that thermal equilibrium is an equivalence relation on the set of thermodynamic systems under consideration. Systems are said to be in equilibrium if the small, random exchanges between them (e.g. Brownian motion) do not lead to a net change in energy. This law is tacitly assumed in every measurement of temperature. Thus, if one seeks to decide whether two bodies are at the same temperature, it is not necessary to bring them into contact and measure any changes of their observable properties in time. The law provides an empirical definition of temperature, and justification for the construction of practical thermometers.
- The zeroth law was not initially recognized as a separate law of thermodynamics, as its basis in thermodynamical equilibrium was implied in the other laws. The first, second, and third laws had been explicitly stated already, and found common acceptance in the physics community before the importance of the zeroth law for the definition of temperature was realized. As it was impractical to renumber the other laws, it was named the zeroth law, which is illustrated in the **Figure 2.**

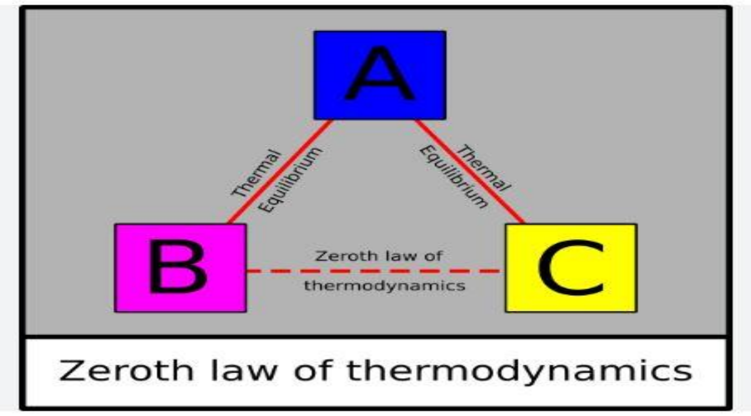


Figure 2: Illustration of Zeroth law of Thermodynamics

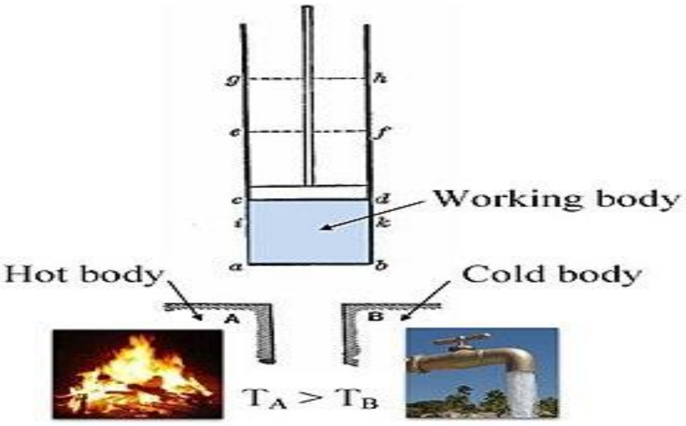


Figure 3: Schematic representation of transformation of heat from hot body, cold body and working body.

- The first law of thermodynamics or the law of conservation of energy is states that the change in a system's internal energy is equal to the difference between heat added to the system from its surroundings and work done by the system on its surroundings.
- In a process without transfer of matter, the change in internal energy, of a thermodynamic system is equal to the energy gained as heat, less the thermodynamic work, done by the system on its surroundings.
- The schematic representation of flow of heat in hot body, cold body and working body is represented in the Figure 3.

5.1.3. First law of Thermodynamics:

- The first law of thermodynamics states that the energy of the universe remains the same. Though it may be exchanged between the system and the surroundings, it can't be created or destroyed. The law basically relates to the changes in energy states due to work and heat transfer are shown in the **Figure 4.**

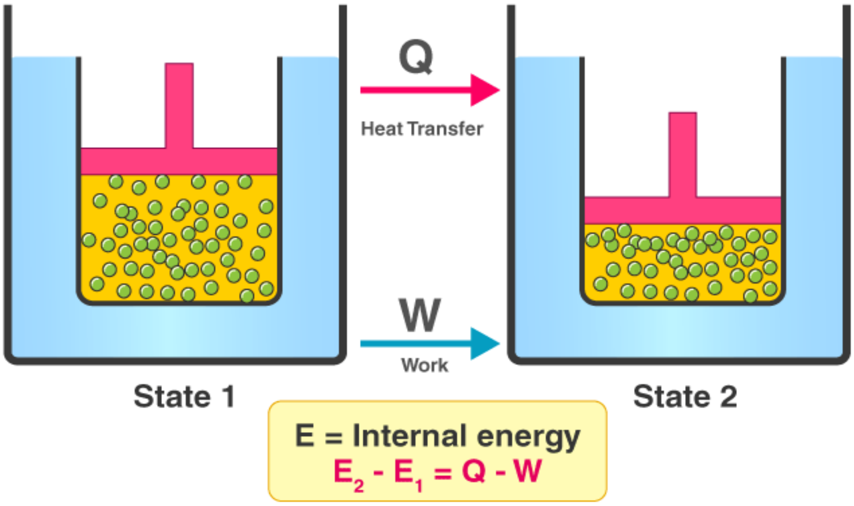
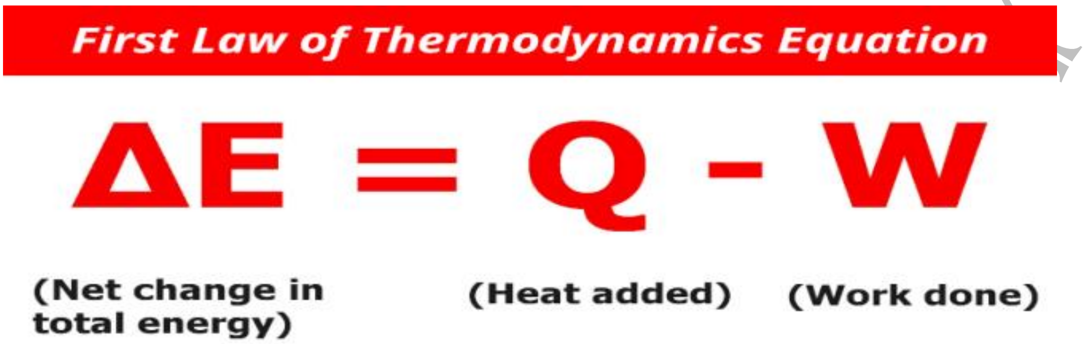


Figure 4: Schematic representation of First law of Thermodynaics

- The first law of thermodynamics can be the conversion of heat energy into work done that can be calculated by the following equation given in the Figure 5.



First Law of Thermodynamics Equation

$$\Delta E = Q - W$$

(Net change in total energy) (Heat added) (Work done)

Figure 5: Indication of first Law of Thermodynamics Equation

- Where denotes the change in the internal energy of a closed system (for which heat (or) work through the system boundary are possible, but matter transfer is not possible), denotes the quantity of energy supplied to the system as heat, and denotes the amount of thermodynamic work done *by* the system on its surroundings. An equivalent statement is that perpetual motion machines of the first kind are impossible, work done by a system on its surrounding requires that the system's internal energy decrease (or) be consumed, so that the amount of internal energy lost by that work must be resupplied as heat by an external energy source or as work by an external machine acting on the system (so that is recovere(d) to make the system work continuously.

- For processes that include transfer of matter, a further statement is needed, With due account of the respective fiducially reference states of the systems, when two systems, which may be of different chemical compositions, initially separated only by an impermeable wall, and otherwise isolated, are combined into a new system by the thermodynamic operation of removal of the wall, then

$$U_0 = U_1 + U_2,$$

- Where U_0 denotes the internal energy of the combined system, and U_1 and U_2 denote the internal energies of the respective separated systems. The internal energy denoted by the term E or U.

- Adapted for thermodynamics, this law is an expression of the principle of conservation of energy, which states that energy can be transformed (changed from one form to another), but cannot be created (or) destroyed.

5.39. Multiple Choice Questions:

1. Which of the following is a branch of thermodynamics?

   A) Equilibrium thermodynamics B) Classical thermodynamics

   C) Chemical thermodynamics D) All of the above mentioned

2. What is the value of the absolute thermodynamic temperature scale?

   A) 3K B) 0K C) 1K D) 4K

3. What is the magnitude of mechanical work?

   A) product of the force and distance travelled perpendicular to the force

   B) product of the force and distance travelled parallel to the force

   C) sum of the force and distance travelled perpendicular to the force

   D) sum of the force and distance travelled parallel to the force

4. Joule was the first to prove that heat is a type of energy, laying the groundwork for the fundamental law of thermodynamics.

   A) False B) True

   C) Sometimes true sometimes false D) Neither true nor false

5. Which of the following is true for a discharging tank?

   A) the process is quasi-static B) the process is adiabatic

   C) dQ=0 D) all of the mentioned

6. The entropy of an isolated system can never ___________________

   A) decrease B) be zero

   C) increase D) none of the mentioned

7. Which of the following properties describe entropy?

   A) point function, intensive property B) point function, extensive property

   C) path function, extensive property D) path function, intensive property

8. When work is dissipated into internal energy, what is the change in the disorderly motion of molecules.

   A) increases B) remains the same

   C) decreases D) none of the mentioned

9. The available energy of a system ________________________ as its temperature or pressure decreases and approaches that of the surroundings.

A) remains constant B) increases

C) decreases D) none of the mentioned

10. Which of the following is true?

A) Q for reversible < Q for irreversible and work for reversible < work for irreversible

B) Q for reversible > Q for irreversible and work for reversible < work for irreversible

C) Q for reversible < Q for irreversible and work for reversible > work for irreversible

D) Q for reversible > Q for irreversible and work for reversible > work for irreversible

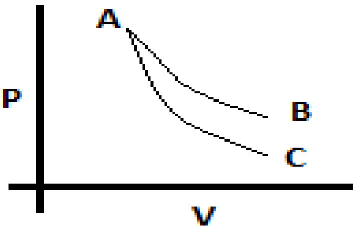
11. The first law of thermodynamics for an adiabatic process is

A) $du = \delta W$ B) du =0 C) $du = -\delta W$ D) $du = \delta H + 2\delta W$

12. A cycle tyres burst suddenly. What is the type of this process?

A) Isothermal B) Adiabatic C) Isochoric D) Isobaric

13. In the given diagram, one process is adiabatic and the other is isothermal. It can be said that process AB is adiabatic. True or False?



A) True B) False

C) Sometime true sometimes false

D) Neither true nor false

14. **Assertion A):** Thermodynamic process in nature is irreversible.

Reason (R) : Dissipative effects cannot be eliminated

A) If both assertion and reason are true but reason is correct explanation for assertion.

B) If both assertion and reason are true but reason is not correct explanation for assertion.

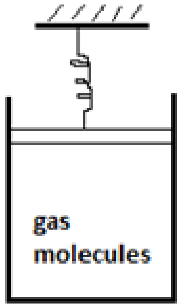
C) If assertion is true but reason is false.

D) If both assertion and reason are false

15. If 315cal of heat is given to the system, and the system does 20cal of work, find the change in internal energy.

A) 295cal B) 335cal C) 0 cal D) 335J

16. In the given system, 20J of heat is supplied to the gas molecules. The spring is initially not elongated or compressed. If the spring gets compressed by 1cm. Calculate the change in internal energy of the system. Spring constant = 200N/m. Assume piston moves slowly.



A) 19J B) -19J C) 21J D) -21J

17. Equilibrium state of a thermodynamic system is described by path variables. True or False?

A) True B) False

C) Sometimes true sometimes false D) Neither true nor false

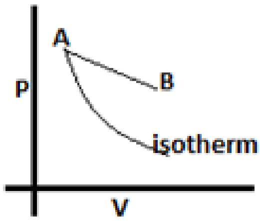
18. In which of the following processes is heat transfer equal to zero?

A) Isentropic B) Isochoric C) Isothermal D) Diathermic

19. Calculate the work done by the gas in an isothermal process from A to B. $P_A = 1Pa, V_A = 3m^3, P_B = 3Pa.$

A) 3.3J B) 3J C) -3.3J D) -4.58J

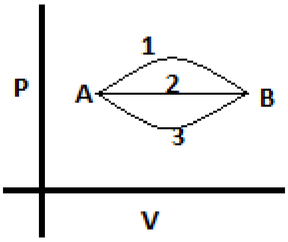
20. When the state changes from A to B, what will happen to internal energy?



A) Increase B) Decrease

C) Remain same D) Depends on value of heat supplied

21. What is the relation between heat supplied in the 3 processes?



A) $Q_1 > Q_2 > Q_3$ B) $Q_1 < Q_2 < Q_3$

C) $Q_1 = Q_2 = Q_3$ D) $Q_1 = Q_3 > Q_2$

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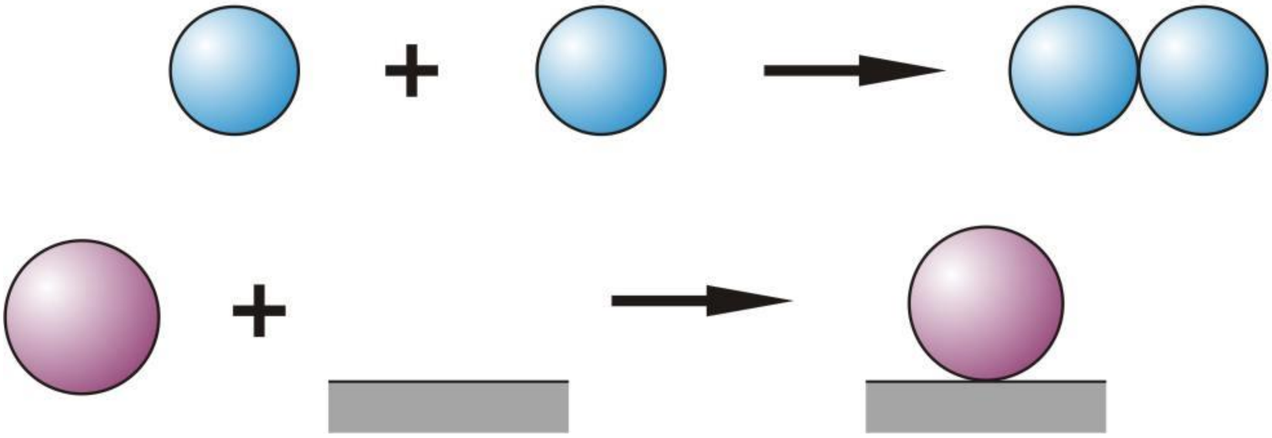

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UG TRB – CHEMISTRY – 2023-24

PHYSICSL CHEMISTRY - UNIT 6

COLLOIDS AND SURFACE CHEMISTRY

6.1. COLLOIDS:

6.1.1. Introduction of Colloids:

- The scientific study of colloids dates from the early 19th century.
- Among the first notable investigations was that of the British botanist **Robert Brown**.
- During the late 1820s Brown discovered, with the aid of a microscope, that minute particles suspended in a liquid are in continual, random motion.

What are colloids:

- A colloid is primarily a heterogeneous mixture in which the minute particles of one substance are dispersed in another substance, called the dispersion medium.
- The minute particles here are 1 to 1000 nanometers in diameter but they still remain suspended and do not settle at the bottom of the mixture.
- They are visible under an optical or an electron (smaller particles) microscope.

Colloids:

- It is a mixture with particle size 1-1000nm

CLASSIFICATION OF COLLOIDS

DISPERSED PHASE	DISPERSION MEDIUM	NAME OF COLLOIDAL SYSTEM	COMMON EXAMPLES
Liquid	Gas	Liquid Aerosol	Mist, clouds, fog
Solid	Gas	Aerosol	Dust, smoke
Gas	Liquid	Foam	Suds, whipped cream
			Cream, milk, mayo
Liquid	Liquid	Emulsion	Paints, jellies, sewage
Solids	Liquid	Sol	
Gas	Solid	Solid foam	Marshmallow
Liquid	Solid	Solid emulsion	Butter, cheese
Solid	Solid	Solid sol	Opals, some alloys

Interaction

lyophilic colloids are solvent	Lyophobic colloids are solvent hating colloids
Thermodynamically stable	Thermodynamically unstable
Precipitation in the lyophilic sol is reversible process	Precipitation in the Lyophobic sol is irreversible process
There is strong attraction force between colloids and the liquid	There is less or no attraction force between colloids and the liquid
Highly viscous	Having the same viscosity as the solvent
From a lyophilic sol	From a Lyophobic sol

Particle size

6.1.2. Classification of Colloids:

- Colloids can be classified into two types by their dispersed phase and medium. They are given below,

  1. Physical state of dispersed phase and dispersion medium.

  2. Natural of interactions between dispersed phase and dispersion medium.

  3. Type of particles of the dispersed phase.

1. Physical state of dispersed phase and dispersion medium.

- Depending upon the physical state of dispersed phase and dispersion medium whether these are solids, liquids or gases, eight types of colloidal systems are possible.

Dispersed phase	Dispersed medium	Type of colloid	Example
Solid	Solid	Solid sol	Some coloured glasses, and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

Depending upon the nature of the dispersion medium, colloidal solutions are sometimes given specific names. For example:

Dispersion Medium	Name of Colloidal Solution
Water	Hydrosols or aquasol
Alcohol	Alcosols
Benzene	Benzosols
Air	Aerosols

Classification based on Nature of Interaction between Dispersed Phase and Dispersion Medium

- Depending upon the nature of interactions between dispersed phase and the dispersion medium, the colloidal solutions can be classified into two types as:

  (i) lyophilic and

  (ii) lyophobic sols.

(i) Lyophilic colloids

- The colloidal solutions in which the particles of the dispersed phase have a great affinity (or love) for the dispersion medium, are called lyophilic colloids.

  a) These solutions are easily formed and the lyophilic colloids are reversible in nature. The reversible. If the dispersion medium is separated from the dispersed phase the sol can be again formed by simply remixing it with the dispersion medium.

  b) These sols are quite stable and cannot be easily coagulated. Examples of lyophilic colloids are gum, gelatine, starch, proteins, rubber, etc.

(ii) Lyophobic colloids

- The colloidal solutions in which there is no affinity between particles of the dispersed phase and the dispersion medium are called lyophobic colloids. Such solutions are formed with difficulty.

  (a) These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking. Therefore, these are not stable.

  (b)Further, once precipitated, they do not form the colloidal sol by simple addition of dispersion medium. Hence, these are irreversible in nature. These sols need some stabilising agents for their preservation.

  (c) In case, the dispersion medium is water, the lyophobic sol. is called **hydrophobic colloid**. For example: the solutions of metals like Ag and Au, hydroxides $Fe(OH)_3$, metal sulphides like AS_2S_3 etc.

S.NO	PROPERTY	LYOPHOBIC SOL (SUSPENSOID)	LYOPHILLIC SOL (EMULSOID)
1	Preparation	Cannot be prepared easily special methods are required	Can be easily prepared by shaking or warming the substance with solvent are more stable
2	Stability	are less stable	are more stable
3	Reversibility	are irreversible	are reversible
4	Viscosity	Viscosity is nearly same as that of the solvent	Viscosity is much higher than that of solvent
5	Surface tension	Surface tension is almost same as that of solvent	Surface tension is usually low.
6	Hydration or salvation	These are less solved as the particles have less affinity for the solvent	These highly solved as the particles have great affinity for solvent
7	Charge	The particles carry a characteristic charge either positive or negative	The particles have little charge or no charge at all.
8	Visibility	Particles can be seen under microscope	Particles cannot be seen under microscope
9	Coagulation or precipitation	Precipited by low concentration of electrolysis	Precipited by high concentration of electrolysis
10	Tyndal effect	More scattering	Less scattering
11	Migration in electric filed	Migrate towards anode or cathode as these participles	Mayor may not migrate carry charge
12	General example	Mostly of inorganic nature	Mostly of organic nature

Classification Based on Type of Particles of Dispersed Phase:

- Depending upon the type of the particles of the dispersed phase, the colloids are classified as:

    1) Multimolecular colloids
    2) Macromolecular colloids
    3) Associated colloids.

1) Multimolecular Colloids:

- When on dissolution, atoms or smaller molecules of substances (having diameter less than 1 nm) aggregate together to form particles of colloidal dimensions, the particles thus formed are called **multimolecular colloids.**
- Therefore, in these sols the dispersed phase consists of aggregates of atoms or molecules with molecular size less than 1 nm.
    - **For example:** sols of gold atoms and sulphur (S_8) molecules.

      In these colloids, the particles are held together by van der Waals forces.

2) Macromolecular Colloids:

- These are the substances having big size molecules (called macro molecules) which on dissolution form solution in which the dispersed phase particles have size in the colloidal range.
- **Naturally occurring macro-molecules** are starch, cellulose, proteins, enzymes, gelatin etc.
- **Artificial macro-molecules** are synthetic polymers such as nylon, polythene, plastics, polystyrene etc.
- Since these macromolecules have large sizes comparable to those of colloidal particles, the solutions of such molecules are called macromolecular colloidal solutions.
- Thus, the common examples of macromolecular colloids are starch, cellulose, proteins, plastics, etc.

3) Associated Colloids:

- These are the substances which when dissolved in a medium behave as normal electrolytes at low concentration but behave as colloidal particles at higher concentration due to the formation of aggregated particles.

- The aggregate particles thus formed are called **micelles**.
  - **For example:** In aqueous solution soap (sodium stearate) ionises as:

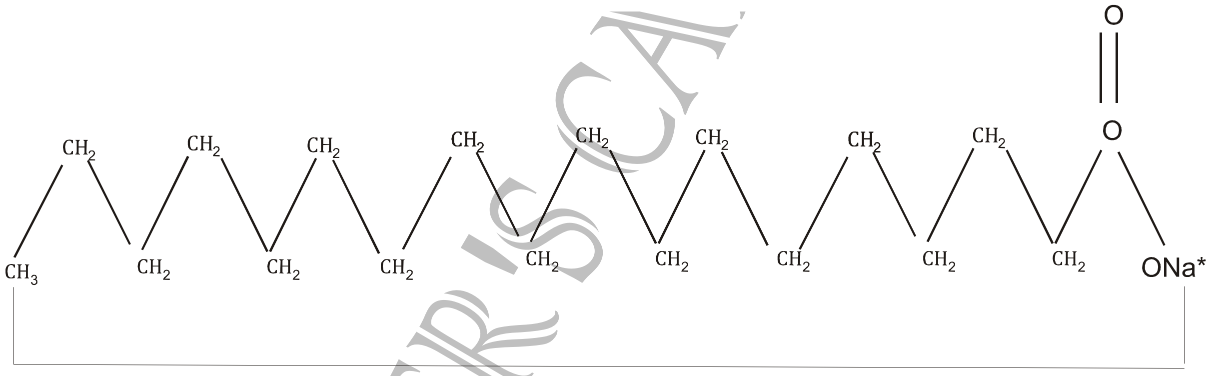
$$C_{17}H_{35}COONa \Leftrightarrow C_{17}H_{35}COO^{-} + Na^{+}$$

- In concentrated solution, these ions get associated to form an aggregate of colloidal size. The colloidal behaviours of such substances is due to the formation of aggregates or clusters in solutions. Such aggregated particles are called **micelles**.
- Thus, micelles are the cluster or aggregated particles formed by association of colloids in solution. The common examples of micelles are soaps and detergents.
- The formation of micelles takes place above a particular temperature called **Kraft** temperature (T_k) and above a particular concentration called **critical** micellization concentration (CMC).
  - **For example:** CMC for soaps is about 10^{-4} to 10^{-3} mol L^{-1}

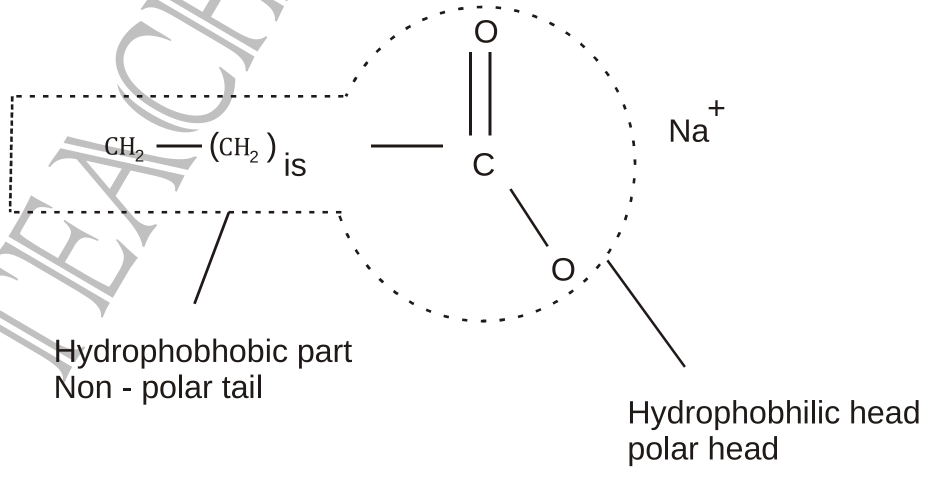
    On dilution, these colloids revert back to individual ions.

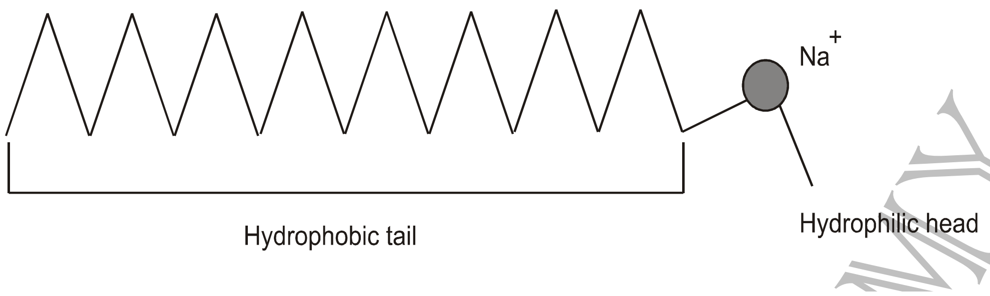
Mechanism of Micelle Formation:

These two parts soaps are represented as:



Sodium stearate of simply as $C_{17}H_{35}COO^{-}Na^{+}$





- Micelles are generally formed by the aggregation of several ions or molecules with lyophobic as well as lyophilic parts. The micelle may contain as many as 100 molecules or more. When sodium stearate is dissolved in water, it gives Na^+ and CH_3COO^- ions.

$$C_{17}H_{35}COONa \Leftrightarrow C_{17}H_{35}COO^- + Na^+$$

- The stearate ions associate to form ionic micelles of colloidal size. The stearate ion, $C_{17}H_{35}COO^-$ consists of two parts:

1) a non-polar part which consists of long chain hydrocarbon part. It is called non-polar tail. This part is insoluble in water but soluble in oil or grease. It is also called water repelling or hydrophobic part.

2) a polar group which consists of carboxylate ion, COO^- . It is called polar-ionic head. It is soluble in water and insoluble in oil or grease. It is water attracting or hydrophilic part.

a) The stearate ions are therefore, present on the surface with their COO^- groups in water and the hydrocarbon tail staying away from it and remains at the surface.

b) Inside water, these molecules have a unique orientation which keeps the hydrocarbon portion out of water.

c) At critical micelle concentration, the anions are pulled into the bulk of the solution and form a cluster of molecules in which the hydrocarbon tails are in the interior of the cluster and ionic ends are at the surface of the cluster. This formation is called **micelle formation** and the aggregate thus formed is known as **ionic micelle.**

Examples of Micelles are:

(i) Sodium palmitate $[C_{15}H_{31}COONa]$

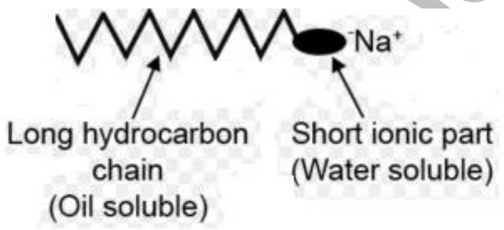
(ii) Cetyl trimethyl ammonium bromide $CH_3(CH_2)_{15}(CH_3)_3N^+Br^-$

(iii) Sodium lauryl sulphate $[CH_3(CH_2)_{11}SO_3O^-Na^+]$

- In case of detergents e.g., sodium lauryl sulphate, $CH_3(CH_2)_{11}OSO_3^-Na^+$, the polar group is SO_4^{2-} along with the long hydrocarbon chain.Therefore, the mechanism of micelle formation is same as that of soaps.

Multimolecular colloids	**Macromolecular colloids**	**Associated colloids**
They consist of aggregates of atoms or molecules which generally have diameter less than 1nm.	They consist of large size molecules	They consist of aggregation of a large number of ions which behave as colloidal size
The atoms of molecules are held by weak van der waal forces	The molecules are flexible and take any shape.	They behave as normal electrolyte at low concentration and behave as colloidal only at high concentration.
Their molecules masses are not very high	They have high molecular masses.	Their molecular masses are generally high.
They have usually lyophillic character	They have usually lyophobic character	Their molecular contain both lyophilic and lyophobic groups.

Cleansing Action of Soap:



1) The cleansing action of soap is due to its tendency to act as micelle and form emulsions.

2) A soap is composed of long chain of alkyl group called tail and a polar part COO^- ion called head.

3) The dirt in the cloth is due to the presence of dust particles in fat or grease which stick to the cloth.

4) When the cloth is dipped in aqueous soap solution, the soap and the dirt come in contact with each other.

- Mitigate against the impacts of heat and chlorides in association with other corrosion-impacting factors
- Use treated and coated wood products if they will be in contact with soils or in waterfront environments
- Use coatings appropriate for the intended use to protect structures
- Apply proper construction and maintenance practices, accompanied by appropriate material selection and surface treatments, to reduce the impacts of ultraviolet degradation on asphaltic materials in pavements and roofs
- Use appropriate concrete cover and coatings to minimize spalling in reinforced concrete structures

Exercise Questions: VI

1. Conductivity (unit Siemen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel then the unit of the constant of proportionality is **[2002]**

(a) $Sm\ mol^{-1}$

(b) $Sm^2\ mol^{-1}$

(c) $S^{-2}m^2\ mol$

(d) $S^2m^2\ mol^{-2}$.

6.5. MULTIPLE CHOICE QUESTIONS

1. Which is not correct regarding the adsorption of a gas on surface of solid?

A) on increasing temperature adsorption increases continuously

B) enthalpy and entropy change is –ve

C) adsorption is more for some specific substance

D) reversible

2. Position of non-polar and polar part in micelles:

A) polar on outer surface and non-polar on inner surface

B) polar on inner surface and non-polar on outer surface

C) distributed over all the surface

D) are present on the surface only

3. Which of the following forms cationic micelles above certain concentration?

A) sodium dodecyl sulphate B) sodium acetate

C) urea D) cetyltrimethyl ammonium bromide

4. The statement not applicable to chemisoption is that it is

A) highly specific B) independent of temperature

C) irreversible D) slow

5. The blue colour of water in the sea is due to

A) scattering of blue light by water molecules

B) reflection of blue sky by sea water

C) refraction of blue light by the impurities in sea water

D) adsorption of other colours, except the blue colour by water molecules

6. Which of the following is correct for lyophilic sol?

A) irreversible sol B) formed from inorganic substances

C) readily coagulated by addition of electrolyte D) self stabilized

7. Rate of physisorption increases with

A) decrease in temperature B) increase in temperature

C) decrease in pressure D) decrease in surface area

8. Milk is a colloid in which

A) liquid is dispersed in liquid B) gas is dispersed in liquid

C) sugar is dispersed in water D) solid is dispersed in liquid

9. Physical adsorption is inversely proportional to

A) temperature B) volume C) concentration D) all of these

10. The migration of colloidal particle under the influence of electric field towards an electrode is known as

A) electrophoresis B) electro-osmosis

C) Tyndall effect D) Brownian movement

11. Butter is a colloidal solution of

A) solid–solid B) liquid–solid C) solid–liquid D) gas–solid

12. How many layers are adsorbed in chemical adsorption?

A) zero B) one C) two D) infinite

13. In the adsorption of oxalic acid on activated charcoal, the activated charcoal is known as

A) adsorber B) adsorbent C) absorber D) adsorbate

14. Adsorbed acetic acid on activated charcoal is

A) adsorbate B) adsorber C) absorber D) absorbent

15. Which one of the following forms micelles in aqueous solution above certain concentration?

A) dodecyl trimethyl ammonium chloride B) glucose

C) urea D) pyridinium chloride

16. What is the name of a phenomenon in which both adsorption and absorption takes place?

A) chemisorption B) physisorption C) desorption D) sorption

17. What is the equation form of Langmuir isotherm under high pressure?

A) x/m = a/b B) x/m = a.p C) x/m = 1/a.p D) x/m = b/a

18. Which of the following is a lyophillic colloidal solution?

A) aqueous starch solution B) aqueous protein solution

C) gold sol

D) polymer solutions in some organic solvents

19. Which one of the following statements is not correct?

A) physical adsorption decreases with increase in the temperature

B) physical adsorption is multilayered

C) activation energy of physical adsorption is very high.

D) enthalpy change of physical adsorption is about $20\ kJ\ mol^{-1}$.

20. Which one of the following is an example of adsorption?

A) ammonia in contact with water B) anhydrous $CaCl_2$ with water

C) silica gel in contact with water vapours D) all of these.

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Branch Office 2 : Vijiyaraghavachariar Memorial Hall (Opp to Sundar Lodge), Salem- 636007.

CONTACT : TRICHY : 76399 67359; SALEM : 93602 68118

UG TRB – 2023-24

CHEMISTRY

PHYSICSL CHEMISTRY

UNIT 6 - COLLOIDS AND SURFACE CHEMISTRY