

Atomic and Molecular Structure

Atomic orbitals (s,p,d,f) orbital shapes, Electronic Configuration, Molecular orbital theory (MOT), bonding and anti-bonding orbitals, Molecular orbital diagrams of Homonuclear and Heteronuclear diatomic molecules: Be₂, O₂, CO, NO their bond order and magnetic properties.

1.1 ATOMIC ORBITAL

In atomic theory and quantum mechanics, an **atomic orbital** is a mathematical function that describes the wave-like behavior of either one electron or a pair of electrons in an atom. This function can be used to calculate the probability of finding any electron of an atom in any specific region around the atom's nucleus. The term **atomic orbital** may also refer to the physical region or space where the electron can be calculated to be present, as defined by the particular mathematical form of the orbital. Each orbital in an atom is characterized by a unique set of values of the three quantum numbers n , ℓ , and m , which respectively correspond to the electron's energy, angular momentum, and an angular momentum vector component (the magnetic quantum number).

Each such orbital can be occupied by a maximum of two electrons, each with its own spin quantum number s . The simple names **s-orbital**, **p-orbital**, **d-orbital** and **f-orbital** refer to orbitals with angular momentum quantum number $\ell = 0, 1, 2$ and 3 respectively. These names, together with the value of n , are used to describe the electron configurations of atoms. They are derived from the description by early spectroscopists of certain series of alkali metal spectroscopic lines as sharp, principal, diffuse, and fundamental. Orbitals for $\ell > 3$ continue alphabetically, omitting j (g, h, i, k, ...) because some languages do not distinguish between the letters "i" and "j".

Example 1.1: How many electrons can **s, p, d, f** orbital hold?

Answer: If ℓ is the angular quantum number of subshell then maximum electrons it can hold is $2(2\ell+1)$

Sub-shell	ℓ	Maximum electrons
s	0	$2(2(0)+1)=2$
p	1	$2(2(1)+1)=6$
d	2	$2(2(2)+1)=10$
f	3	$2(2(3)+1)=14$

i.e. 2, 6, 10, 14 respectively

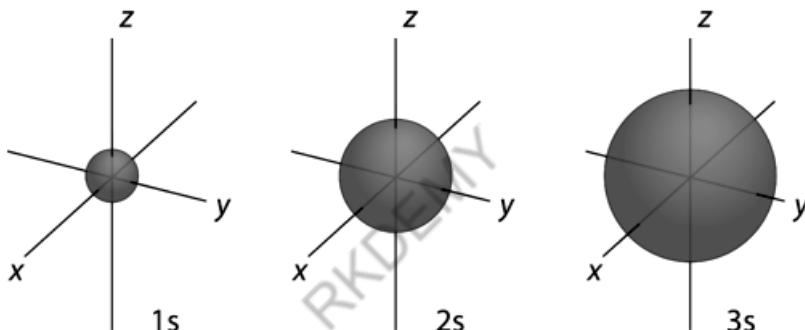
1.1.1 s, p, d, f ORBITALS

Orbitals are the regions of space in which electrons are most likely to be found. Each orbital is denoted by a number and a letter. The number denotes the energy level of the electron in the orbital. Thus 1 refers to the energy level closest to the nucleus; 2 refers to the next energy level further out, and so on.

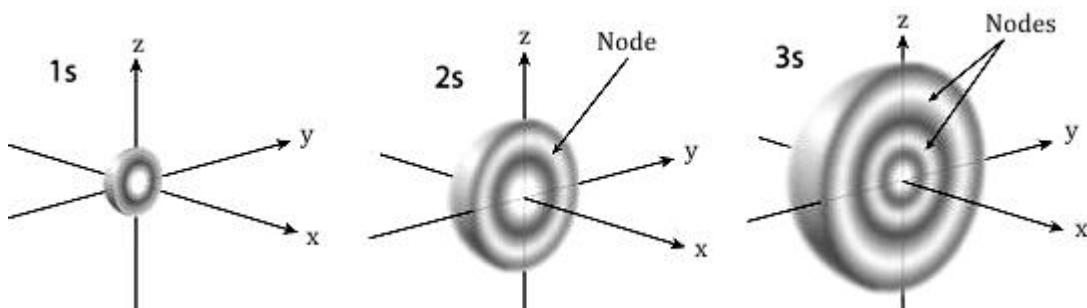
The letter refers to the shape of the orbital. The letters go in the order s, p, d, f, g, h, i, k, etc. Since an electron can theoretically occupy all space, it is impossible to draw an orbital. All we can do is draw a shape that will include the electron most of the time, say 95% of the time. We call this shape the 95% contour.

s-ORBITALS

An s orbital is spherically symmetric around the nucleus of the atom, like a hollow ball made of rather fluffy material with the nucleus at its centre. As the energy levels increase, the electrons are located further from the nucleus, so the orbitals get bigger. The order of size is $1s < 2s < 3s < \dots$, as shown below.



Now, let's look at a cross-section of these orbitals.



If you look carefully, you will notice that a 1s orbital has very little electron density near the nucleus, but it builds up to a maximum as you get further from the nucleus and then decreases beyond the contour. It is sort of like a hollow tennis ball.

A 2s orbital is similar to a 1s orbital, but it has a sphere of electron density inside the outer sphere, like one tennis ball inside another. There is a surface between the two balls where there is zero probability of finding an electron. We call this surface a node or a nodal surface.

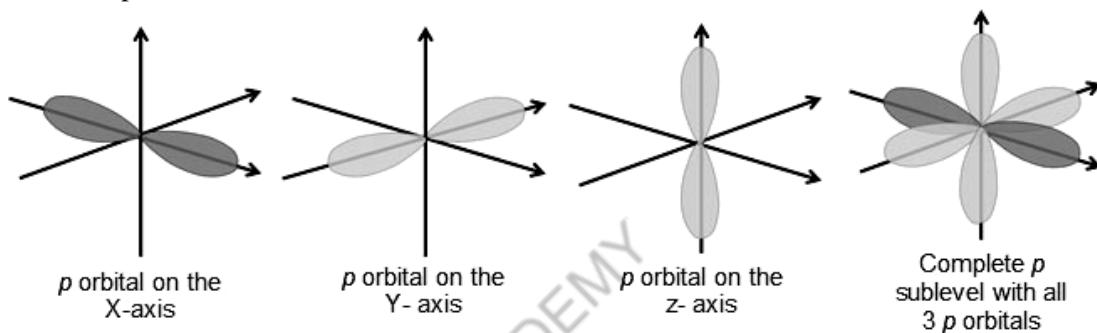
A 3s orbital is even larger, and it has three nodes.

p-ORBITALS

Not all electrons inhabit s orbitals. At the first energy level, the only orbital available to electrons is the 1s orbital. However, at the second level, there are also orbitals called 2p orbitals in addition to the 2s orbital. Unlike an s orbital, a p orbital points in a particular direction.

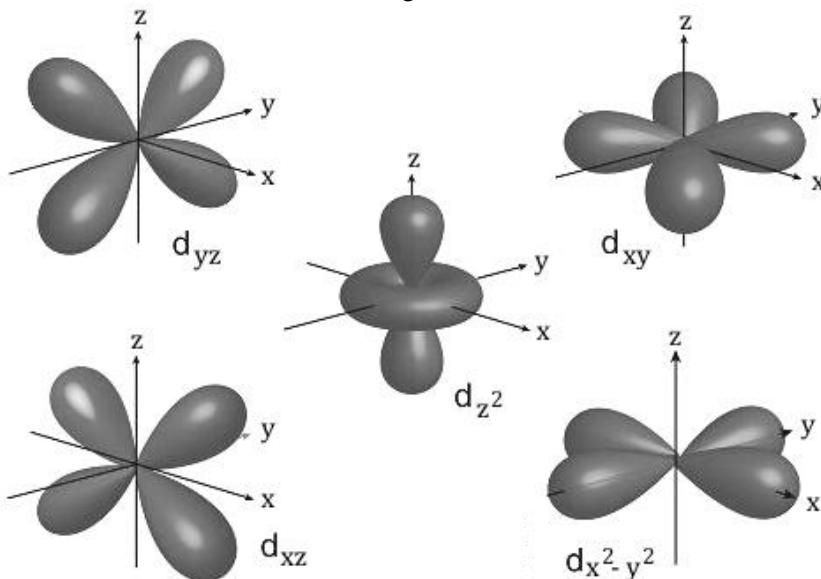
At any one energy level, we have three absolutely equivalent p orbitals pointing mutually at right angles to each other. These are arbitrarily given the symbols px, py and pz. This is simply for convenience, because what you might think of as the x, y or z direction changes constantly as the atom tumbles in space.

The p orbitals at the second energy level are called 2px, 2py and 2pz. There are similar orbitals at subsequent levels: 3px, 3py, 3pz, 4px, 4py, 4pz and so on. All levels except the first have p orbitals.



d-ORBITALS

In addition to s and p orbitals, there are two other sets of orbitals which become available for electrons to inhabit at higher energy levels. At the third level, there is a set of five d orbitals (with complicated shapes and names) as well as the 3s and 3p orbitals (3px, 3py, 3pz). At the third level there are a total of nine orbitals altogether.

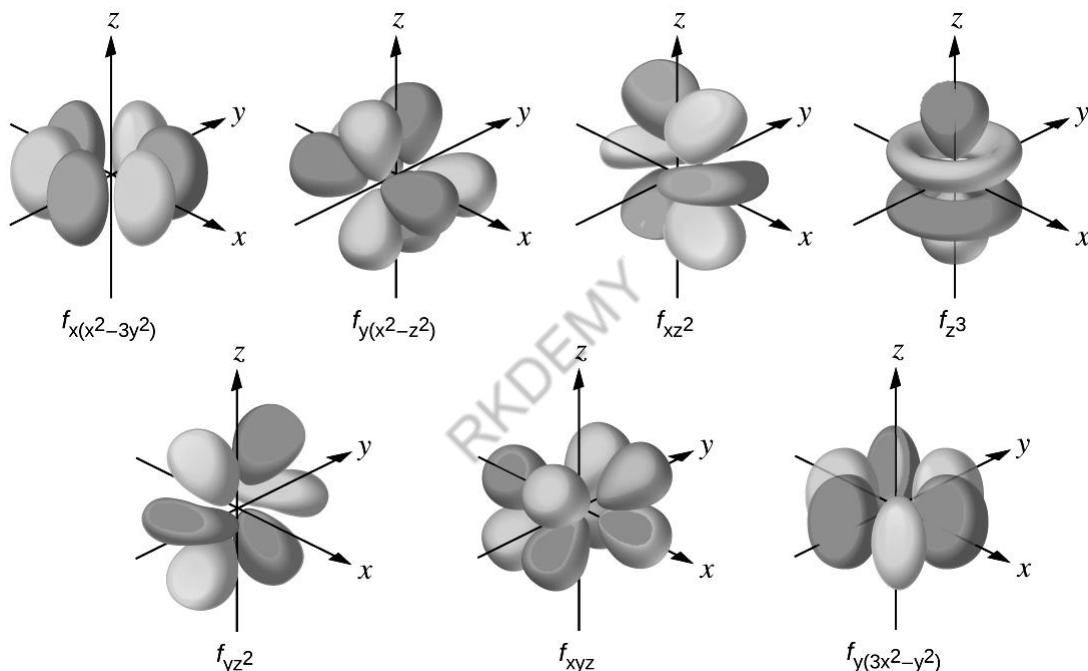


The five 3d orbitals are called: $3dx_{\text{xy}}$, $3dx_{\text{xz}}$, $3dy_{\text{yz}}$, $3dx^2-y^2$ and $3dz^2$

To make sense of the names, we need to look at them in two groups. The first group contains the $3dx_{\text{xy}}$, $3dx_{\text{xz}}$ and $3dy_{\text{yz}}$ orbitals. The names tell you that these orbitals lie in the x-y plane, the x-z plane, and the y-z plane, respectively. Each orbital has four lobes, and each of the lobes is pointing between two of the axes, not along them. The second group contains the $3dx^2 - y^2$ and $3dz^2$ orbitals. Their lobes point along the various axes. The $3dx^2 - y^2$ orbital looks exactly like the first group, except that that the lobes are pointing along the x and y axes, not between them. The $3dz^2$ looks like a p orbital wearing a doughnut around its waist.

f-ORBITALS

At the fourth and higher levels, there are seven f orbitals in addition to the 4s, 4p, and 4d orbitals.



Counting the 4s, 4p, and 4d orbitals, this makes a total of 16 orbitals in the fourth level. They have even more complicated shapes. s, p, d, and f orbitals are available at all higher energy levels as well. Fortunately, you will probably not have to memorize the shapes of the f orbitals. Just remember that there are seven f orbitals in each level from level 4 and onwards.

1.2 ELECTRONIC CONFIGURATION OF ATOMS

The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and subshells. Commonly, the electron configuration is used to describe the orbitals of an atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion by compensating with the loss of or gain of electrons in their subsequent orbitals. Many of the physical and chemical properties of elements can be correlated to their unique electron configurations. The valence electrons, electrons in the outermost shell, are the determining factor for the unique chemistry of the element.

Before assigning the electrons of an atom into orbitals, one must become familiar with the basic concepts of electron configurations. Every element on the Periodic Table consists of atoms, which are composed of protons, neutrons, and electrons. Electrons exhibit a negative charge and are found around the nucleus of the atom in electron orbitals, defined as the volume of space in which the electron can be found within 95% probability.

The four different types of orbitals (s, p, d and f) have different shapes, and one orbital can hold a maximum of two electrons. The p, d, and f orbitals have different sublevels, thus can hold more electrons.

As stated, the electron configuration of each element is unique to its position on the periodic table. The energy level is determined by the period and the number of electrons is given by the atomic number of the element. Orbitals on different energy levels are similar to each other, but they occupy different areas in space.

The 1s orbital and 2s orbital both have the characteristics of an s orbital (radial nodes, spherical volume probabilities, can only hold two electrons, etc.) but, as they are found in different energy levels, they occupy different spaces around the nucleus. Each orbital can be represented by specific blocks on the periodic table.

The s-block is the region of the alkali metals including helium (Groups 1 & 2), the d-block are the transition metals (Groups 3 to 12), the p-block are the main group elements from Groups 13 to 18, and the f-block are the lanthanides and actinides series.

Electron Configurations in the Periodic Table

1 H 1s	2 He 1s
3 Li 2s →	4 Be
11 Na 3s →	12 Mg
19 K 4s →	20 Ca
21 Sc ←	22 Ti
23 V	24 Cr
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 5s →	38 Sr
39 Y ←	40 Zr
41 Nb	42 Mo
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 6s →	56 Ba
57 La ←	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 7s →	88 Ra
89 Ac ←	104 Rf
105 Db	106 Sg
107 Bh	108 Hs
109 Mt	110 111 112
113 114	
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	71 Lu
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	103 Lr

Using the periodic table to determine the electron configurations of atoms is key, but also keep in mind that there are certain rules to follow when assigning electrons to different orbitals. The periodic table is an incredibly helpful tool in writing electron configurations.

1.3 RULES FOR ASSIGNING ELECTRON ORBITALS

1.3.1 THE AUFBAU PROCESS

Aufbau comes from the German word "aufbauen" meaning "to build." When writing electron configurations, orbitals are built up from atom to atom. When writing the electron configuration for an atom, orbitals are filled in order of increasing atomic number. However, there are some exceptions to this rule.

Example 1.2: 3rd row elements

Following the pattern across a period from B (Z=5) to Ne (Z=10), the number of electrons increases and the subshells are filled. This example focuses on the p subshell, which fills from boron to neon.

- B (Z=5) configuration: $1s^2 2s^2 2p^1$
- C (Z=6) configuration: $1s^2 2s^2 2p^2$
- N (Z=7) configuration: $1s^2 2s^2 2p^3$
- O (Z=8) configuration: $1s^2 2s^2 2p^4$
- F (Z=9) configuration: $1s^2 2s^2 2p^5$
- Ne (Z=10) configuration: $1s^2 2s^2 2p^6$

Exceptions

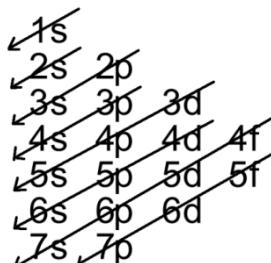
Although the Aufbau rule accurately predicts the electron configuration of most elements, there are notable exceptions among the transition metals and heavier elements. The reason these exceptions occur is that some elements are more stable with fewer electrons in some subshells and more electrons in others.

OCCUPATION OF ORBITALS

Electrons fill orbitals in a way to minimize the energy of the atom. Therefore, the electrons in an atom fill the principal energy levels in order of increasing energy (the electrons are getting farther from the nucleus). The order of levels filled looks like this:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, and 7p

One way to remember this pattern, probably the easiest, is to refer to the periodic table and remember where each orbital block falls to logically deduce this pattern. Another way is to make a table like the one below and use vertical lines to determine which subshells correspond with each other.

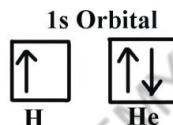


1.3.2 PAULI EXCLUSION PRINCIPLE

The Pauli's exclusion principle states that no two electrons in one atom can have the same four quantum numbers. The first three (n , l , and m_l) may be the same, but the fourth quantum number must be different. A single orbital can hold a maximum of two electrons, which **must** have opposing spins; otherwise they would have the same four quantum numbers, which is forbidden. One electron is spin up ($m_s = +1/2$) and the other would spin down ($m_s = -1/2$). This tells us that each subshell has double the electrons per orbital. The s subshell has 1 orbital that can hold up to 2 electrons, the p subshell has 3 orbitals that can hold up to 6 electrons, the d subshell has 5 orbitals that hold up to 10 electrons, and the f subshell has 7 orbitals with 14 electrons.

Example 1.3: Hydrogen and Helium

The first three quantum numbers of an electron are $n=1$, $l=0$, $m_l=0$. Only two electrons can correspond to these, which would be either $m_s = -1/2$ or $m_s = +1/2$. As we already know from our studies of quantum numbers and electron orbitals, we can conclude that these four quantum numbers refer to the 1s subshell. If only one of the m_s values are given then we would have $1s^1$ (denoting hydrogen) if both are given we would have $1s^2$ (denoting helium). Visually, this is represented as:



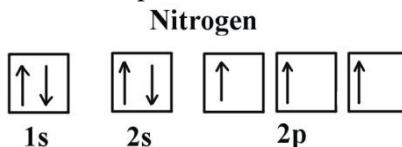
As shown, the 1s subshell can hold only two electrons and, when filled, the electrons have opposite spins.

1.3.3 HUND'S RULE

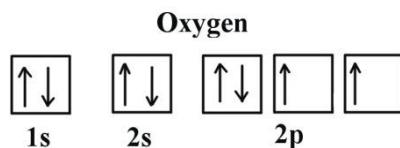
When assigning electrons in orbitals, each electron will first fill all the orbitals with similar energy (also referred to as degenerate) before pairing with another electron in a half-filled orbital. Atoms at ground states tend to have as many unpaired electrons as possible. When visualizing this processes,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

Example 1.4: Oxygen and Nitrogen

If we look at the correct electron configuration of the Nitrogen ($Z=7$) atom, a very important element in the biology of plants: $1s^2 2s^2 2p^3$



We can clearly see that p orbitals are half-filled as there are three electrons and three p orbitals. This is because Hund's Rule states that the three electrons in the 2p subshell will fill all the empty orbitals first before filling orbitals with electrons in them. If we look at the element after Nitrogen in the same period, Oxygen ($Z = 8$) its electron configuration is: $1s^2 2s^2 2p^4$ (for an atom).



Oxygen has one more electron than Nitrogen and as the orbitals are all half filled the electron must pair up.

1.4 WRITING ELECTRON CONFIGURATIONS

When writing an electron configuration, first write the **energy level** (the period), then the **subshell** to be filled and the **superscript**, which is the number of electrons in that subshell. The total number of electrons is the atomic number, Z. The rules above allow one to write the electron configurations for all the elements in the periodic table. Three methods are used to write electron configurations:

1. orbital diagrams
2. spdf notation
3. noble gas notation

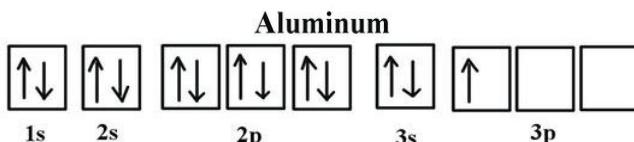
Each method has its own purpose and each has its own drawbacks.

1.4.1 ORBITAL DIAGRAMS

An orbital diagram, like those shown above, is a visual way to reconstruct the electron configuration by showing each of the separate orbitals and the spins on the electrons. This is done by first determining the subshell (s,p,d, or f) then drawing in each electron according to the stated rules above.

Example 1.5: Write the electron configuration for aluminum.

Solution: Aluminum is in the 3rd period and it has an atomic number of Z=13. If we look at the periodic table we can see that it is in the p-block as it is in group 13. Now we shall look at the orbitals it will fill: 1s, 2s, 2p, 3s, 3p. We know that aluminum completely fills the 1s, 2s, 2p, and 3s orbitals because mathematically this would be $2+2+6+2=12$. The last electron is in the 3p orbital. Also another way of thinking about it is that as you move from each orbital block, the subshells become filled as you complete each section of the orbital in the period. The block that the atom is in (in the case for aluminum: 3p) is where we will count to get the number of electrons in the last subshell (for aluminum this would be one electron because it is the first element in the period 3 p-block). This gives the following:



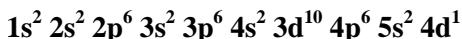
Note that in the orbital diagram, the two opposing spins of the electron can be visualized. This is why it is sometimes useful to think about electron configuration in terms of the diagram. However, because it is the most time consuming method, it is more common to write or see electron configurations in spdf notation and noble gas notation.

1.4.2 spdf NOTATION

The most common way to describe electron configurations is to write distributions in the spdf notation. Although the distributions of electrons in each orbital are not as apparent as in the diagram, the total number of electrons in each energy level is described by a superscript that follows the relating energy level. To write the electron configuration of an atom, identify the energy level of interest and write the number of electrons in the energy level as its superscript as follows: $1s^2$. This is the electron configuration of helium; it denotes a full s-orbital. The periodic table is used as a reference to accurately write the electron configurations of all atoms.

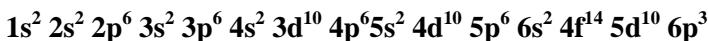
Example 1.6: Write the electronic configuration of Yttrium.

Solution: Start with the straightforward problem of finding the electron configuration of the element yttrium. As always, refer to the periodic table. The element yttrium (symbolized Y) is a transition metal, found in the fifth period and in Group 3. In total it has thirty-nine electrons. Its electron configuration is as follows:



This is a much simpler and more efficient way to portray electron configuration of an atom. A logical way of thinking about it is that all that is required is to fill orbitals across a period and through orbital blocks. The number of elements in each block is the same as in the energy level it corresponds. For example, there are 2 elements in the s-block, and 10 elements in the d-block. Moving across, simply count how many elements fall in each block. Yttrium is the first element in the fourth period d-block; thus there is one electron in that energy level. To check the answer, verify that the subscripts add up to the atomic number. In this case, $2+2+6+2+6+2+10+6+2+1 = 39$ and $Z=39$, so the answer is correct.

A slightly more complicated example is the electron configuration of bismuth (symbolized Bi, with $Z = 83$). The periodic table gives the following electron configuration:



The reason why this electron configuration seems more complex is that the f-block, the Lanthanide series, is involved. Most students who first learn electron configurations often have trouble with configurations that must pass through the f-block because they often overlook this break in the table and skip that energy level. It is important to remember that when passing the 5d and 6d energy levels that one must pass through the f-block lanthanoid and actinoid series. Keeping this in mind, this "complex" problem is greatly simplified.

1.4.3 NOBLE GAS NOTATION

This brings up an interesting point about elements and electron configurations. As the p subshell is filled in the above example about the Aufbau principle (the trend from boron to neon), it reaches the group commonly known as the noble gases. The noble gases have the most stable electron configurations, and are known for being relatively inert. All noble gases have their subshells filled and can be used them as a shorthand way of writing electron configurations for subsequent atoms. This method of writing configurations is called the noble gas notation, in which the noble gas in the period above the element that is being

analyzed is used to denote the subshells that element has filled and after which the valence electrons (electrons filling orbitals in the outer most shells) are written. This looks slightly different from spdf notation, as the reference noble gas must be indicated.

Example 1.7: What is the electronic configuration of vanadium (V, Z=23)?

Solution: Vanadium is the transition metal in the fourth period and the fifth group. The noble gas preceding it is argon (Ar, Z=18), and knowing that vanadium has filled those orbitals before it, argon is used as the reference noble gas. The noble gas in the configuration is denoted E, in brackets: [E]. To find the valence electrons that follow, subtract the atomic numbers: $23 - 18 = 5$. Instead of 23 electrons to distribute in orbitals, there are 5. Now there is enough information to write the electron configuration:



This method streamlines the process of distributing electrons by showing the valence electrons, which determine the chemical properties of atoms. In addition, when determining the number of unpaired electrons in an atom, this method allows quick visualization of the configurations of the valance electrons. In the example above, there are a full s orbital and three half filled d orbitals.

1.5 INTRODUCTION TO MOLECULAR ORBITAL THEORY

Valence Bond Theory fails to answer certain questions like Why He_2 molecule does not exist and why O_2 is paramagnetic? Therefore in 1932 F. Hood and RS. Mulliken came up with theory known as **Molecular Orbital Theory** to explain questions like above. According to Molecular Orbital Theory individual atoms combine to form molecular orbitals, as the electrons of an atom are present in various atomic orbitals and are associated with several nuclei.

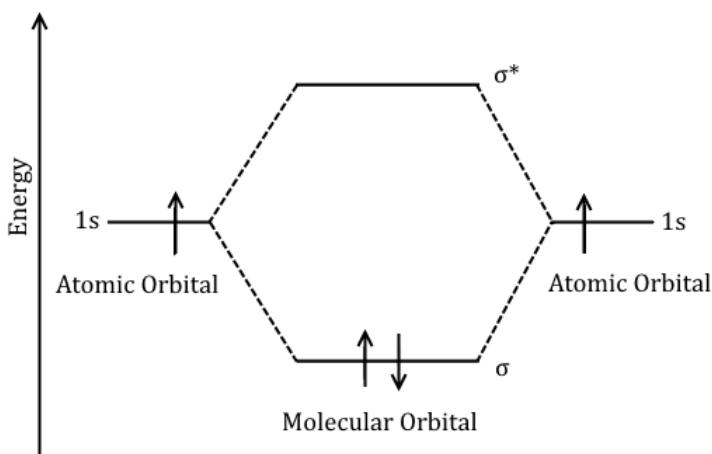


Fig. 1.1 Molecular Orbital Theory

Electrons may be considered either of particle or of wave nature. Therefore, an electron in an atom may be described as occupying an atomic orbital, or by a wave function Ψ , which are solution to the **Schrodinger wave equation**. Electrons in a molecule are said to occupy molecular orbitals. The wave function of a molecular orbital may be obtained by one of two method: 1. Linear Combination of Atomic Orbitals (LCAO). 2. United Atom Method.

1.5.1 LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

As per this method the formation of orbitals is because of Linear Combination (addition or subtraction) of atomic orbitals which combine to form molecule. Consider two atoms A and B which have atomic orbitals described by the wave functions Ψ_A and Ψ_B . If electron cloud of these two atoms overlap, then the wave function for the molecule can be obtained by a linear combination of the atomic orbitals Ψ_A and Ψ_B i.e. by subtraction or addition of wave functions of atomic orbitals.

$$\Psi_{MO} = \Psi_A \pm \Psi_B$$

The above equation forms two molecular orbitals

1.5.2 BONDING MOLECULAR ORBITALS

When addition of wave function takes place, the type of molecular orbitals formed are called Bonding Molecular orbitals and is represented by

$$\Psi_{MO} = \Psi_A + \Psi_B$$

They have lower energy than atomic orbitals involved. It is similar to constructive interference occurring in phase because of which electron probability density increases resulting in formation of bonding orbital. Molecular orbital formed by addition of overlapping of two s orbitals shown in fig. 1.2. It is represented by σ_s . Energy of Bonding Molecular Orbitals is less than that of Anti Bonding Molecular Orbitals because the attraction of both the nuclei for both the electron (of the combining atom) is increased.

1.5.3 ANTI-BONDING MOLECULAR ORBITALS

When molecular orbital is formed by subtraction of wave function, the type of molecular orbitals formed are called Antibonding Molecular Orbitals and is represented by

$$\Psi_{MO} = \Psi_A - \Psi_B$$

They have higher energy than atomic orbitals involved. It is similar to destructive interference occurring out of phase resulting in formation of antibonding orbitals.

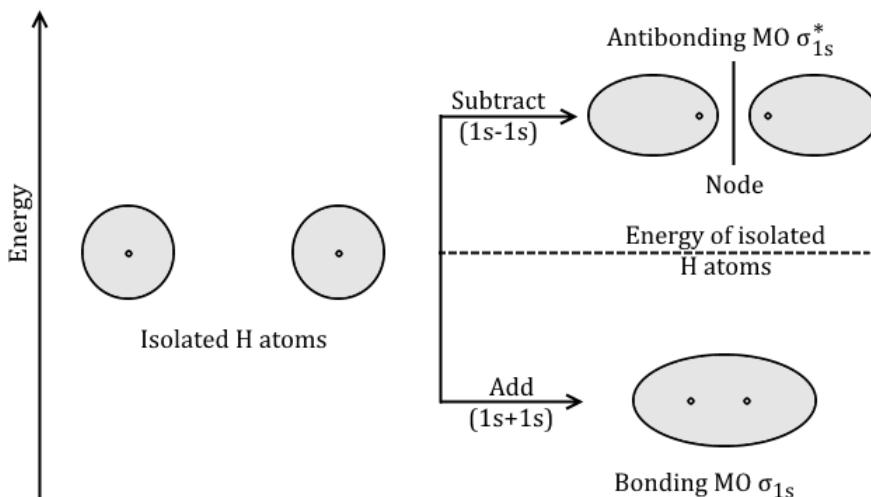


Fig. 1.2 Formation of Bonding and Anti-Bonding Orbital

Molecular Orbital formed by subtraction of overlapping of two s orbitals are shown in fig. 1.2. It is represented by σ_s^* , (*is used to represent antibonding molecular orbital) called Sigma Antibonding. Energy of Anti Bonding Molecular Orbitals is higher than Bonding Molecular Orbitals because the electrons try to move away from the nuclei and are in repulsive state.

Therefore, Combination of two atomic orbitals results in formation of two molecular orbitals, bonding molecular orbital (BMO), whereas other is anti-bonding molecular orbital (ABMO). BMO has lower energy and hence greater stability than ABMO. First BMO are filled then ABMO starts filling because BMO has lower energy than that of ABMO. Formation of molecular orbitals occurs by the combination of atomic orbitals of proportional symmetry and comparable energy. Therefore, a molecular orbital is polycentric and atomic orbital is monocentric. Number of molecular orbitals formed is equal to the number of atomic orbitals.

1.5.4 ENERGY LEVEL DIAGRAM FOR MOLECULAR ORBITALS

The factors upon which relative energies of molecular orbitals depend are:

- Energies of the Atomic orbitals combining to form Molecular Orbitals.
- The extent of overlapping between the atomic orbitals. The greater the overlap, the more the bonding orbital is lowered and the anti-bonding orbital is raised in energy relative to AOs. The greater the overlap, the more the bonding orbital is lowered and the anti-bonding orbital is raised in energy relative to atomic orbitals. For e.g., the extent of overlapping in case of σ -orbital is more than that in π -orbital.

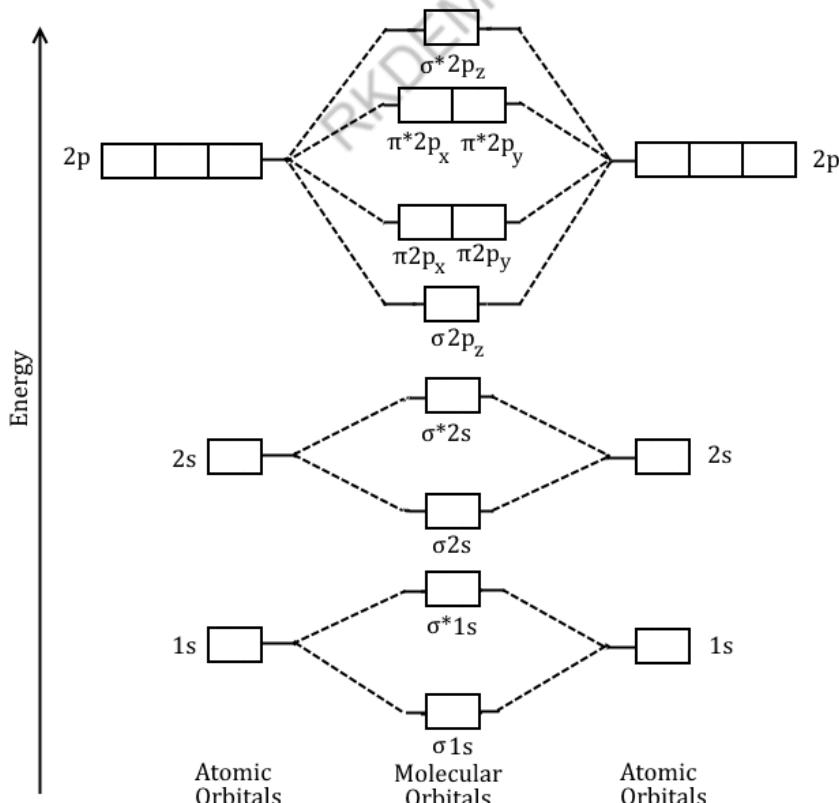


Fig. 1.3 Energy Level Diagram for Molecular Orbitals

Consequently, the energy of a $\sigma 2p_z$ is lower than the energy of bonding $\pi 2p_x$ or $\pi 2p_y$ MOs. Now, 1s atomic orbitals of two atoms form two molecular orbitals designated as $\sigma 1s$ and $\sigma^* 1s$. The 2s and 2p orbitals (eight atomic orbitals on two atoms) form four bonding molecular orbitals and four anti-bonding molecular orbitals as:

Bonding MOs: $\sigma 2s$, $\sigma 2p_z$, $\pi 2p_x$, $\pi 2p_y$

Anti-bonding MOs: $\sigma^* 2s$, $\sigma^* 2p_z$, $\pi^* 2p_x$, $\pi^* 2p_y$

The energy levels of these molecular orbitals have been determined experimentally by various methods. The order of increasing energy of molecular orbitals obtained by the combination of 1s, 2s and 2p orbitals of two atoms is:

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^*$$

1.5.5 BOND ORDER

It may be defined as the half of difference between the number of electrons present in the bonding orbitals and the antibonding orbitals that is,

$$\text{Bond order (B.O.)} = (\text{No. of electrons in BMO} - \text{No. of electrons in ABMO}) / 2$$

$$\text{B. O.} = \frac{N_B - N_A}{2}$$

1.5.6 ELECTRONIC CONFIGURATION OF THE MOLECULE AND ITS PROPERTIES

- Stability of molecules in terms of bonding and antibonding electrons:** Number of electrons present in the bonding orbitals is represented by N_B and the number of electrons present in antibonding orbitals by N_A .
 - If $N_B > N_A$, the molecule is stable because greater number of bonding orbitals are occupied than antibonding orbital, resulting in a net force of attraction.
 - If $N_B < N_A$, the molecule is unstable because the antibonding influence is greater than the bonding influence, resulting in net force of repulsion.
 - If $N_B = N_A$, the molecule is again unstable because influence of electrons in the antibonding molecular orbital is greater than the bond influence of electron in the bonding molecular orbitals.
- Stability of molecules in terms of bond order:** The molecule is stable if $N_B > N_A$ i.e. bond order is positive. The molecule is unstable if $N_B < N_A$ i.e. the bond order is negative or zero.
- Relative stability of molecule in terms of bond order:** For diatomic molecules, the stability is directly proportional to the bond order. A molecule with the bond order of 3 is more stable than a molecule with bond order of 2 and so on.
- Nature of bond in terms of bond order:** Bond order 1, 2 and 3 mean single, double and triple bond.
- Bond length in terms of bond order:** Bond length is found to be inversely proportional to the bond order. Greater the bond order, shorter is the bond length. **For Example** the bond length in nitrogen molecule is shorter than in oxygen molecule.

6. Diamagnetic and paramagnetic nature of the molecules: If all the electrons in the molecule are paired ($\uparrow\downarrow$), it is diamagnetic in nature. If the molecules has some unpaired electrons (\uparrow), it is paramagnetic in nature. Greater the number of unpaired electrons present in the molecular or ion, greater is its paramagnetic nature.

1.5.7 DIFFERENCES BETWEEN MOLECULAR ORBITAL AND ATOMIC ORBITAL

Molecular Orbital	Atomic Orbital
1. An electron Molecular orbital is under the influence of two or more nuclei depending upon the number of atoms present in the molecule.	1. An electron in atomic orbital is under the influence of only one positive nucleus of the atom.
2. Molecular orbitals are formed by combination of atomic orbitals	2. Atomic orbitals are inherent property of an atom.
3. They have complex shapes.	3. They have simple shapes.

1.6 MOLECULAR ORBITAL DIAGRAM FOR HOMONUCLEAR DIATOMICS MOLECULES

Molecules consisting of two identical atoms are said to be homonuclear diatomic, such as: H_2 , N_2 , O_2 , and F_2 .

1.6.1 MOLECULAR ORBITAL DIAGRAM FOR Be_2 MOLECULE

The electronic configuration of Be ($Z = 4$) is: $1s^2 2s^2$

Be_2 molecule is formed by the overlap of atomic orbitals of both beryllium atoms.

Number of valence electrons in Be atom = 2, thus in the formation of Be molecule, two outer electrons of each Be atom i.e. 4 in all, have to be accommodated in various molecular orbitals in the increasing order of their energies.

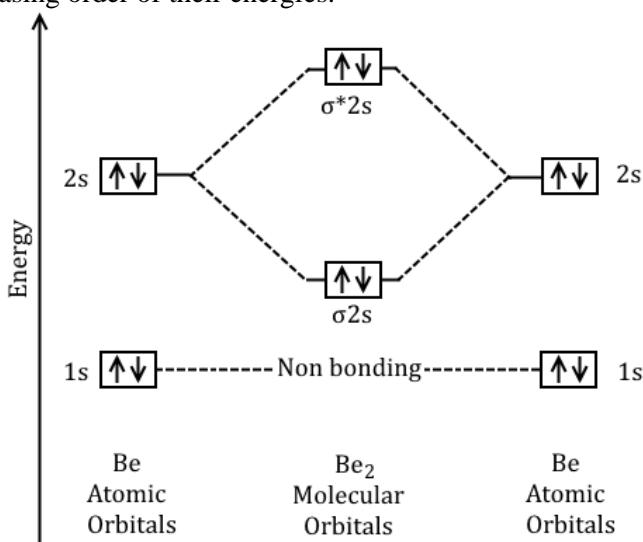


Fig. 1.4 MO diagram for Be_2 Molecule

The electronic configuration of $\text{Be}_2 = \text{KK} \sigma_{2s}^2 \sigma_{2s}^* {}^2$

Here KK represents two non bonding 1s orbitals of two Be atoms

$$\text{The B.O. of } \text{Be}_2 = \frac{N_B - N_A}{2} = \frac{2 - 2}{2} = 0$$

Since bond order is zero, Be molecule does not exist.

Magnetic property: It is diamagnetic due to the absence of any unpaired electron.

1.6.2 MOLECULAR ORBITAL DIAGRAM FOR O_2 (DIOXYGEN) MOLECULE

The electron configuration of oxygen ($Z=8$) is $1s^2 2s^2 2p^4$. In O_2 molecule there are total sixteen electrons. As 1s orbitals are considered to be non bonding, therefore, four electron of 1s orbitals of both oxygen atom can be ignored and we need to accommodate twelve valence electrons (six from each oxygen atom) in molecular orbitals.

As you can see from the diagram, this places two electrons in antibonding orbitals. Each of these electrons occupies a separate π^* orbital because this leads to less electron-electron repulsion (Hund's Rule). The bond energy of molecular oxygen is 498 kJ/mole. This is smaller than the 945 kJ bond energy of N_2^- not surprising, considering that oxygen has two electrons in an antibonding orbital, compared to nitrogen's one.

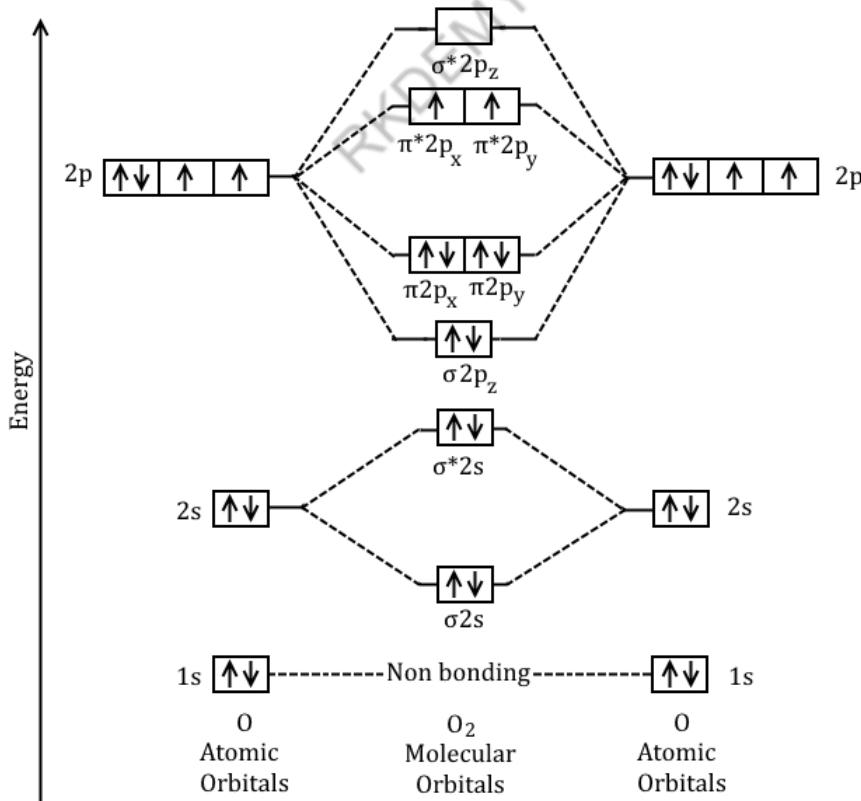
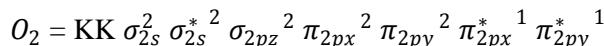


Fig. 1.5 MO diagram for O_2 Molecule

The electronic configuration of O₂ molecules can be given as



Here KK represents two non bonding 1s orbitals of two O atoms.

$$\text{The Bond Order (B.O.) of } O_2 = \frac{N_B - N_A}{2} = \frac{8 - 4}{2} = 2$$

The two unpaired electrons of the dioxygen molecule give this substance an unusual and distinctive property: **O₂ is paramagnetic**.

The paramagnetism of oxygen can readily be demonstrated by pouring liquid O₂ between the poles of a strong permanent magnet; the liquid stream is trapped by the field and fills up the space between the poles.

Since molecular oxygen contains two electrons in an antibonding orbital, it might be possible to make the molecule more stable by removing one of these electrons, thus increasing the ratio of bonding to antibonding electrons in the molecule. Just as we would expect, and in accord with our model, O₂⁺ has a bond energy higher than that of neutral dioxygen; removing the one electron actually gives us a more stable molecule. This constitutes a very good test of our model of bonding and antibonding orbitals.

In the same way, adding an electron to O₂ results in a weakening of the bond as evidenced by the lower bond energy of O₂⁻. The bond energy in this ion is not known, but the length of the bond is greater, and this is indicative of a lower bond energy. These two dioxygen ions, by the way, are highly reactive and can be observed only in the gas phase.

1.7 MOLECULAR ORBITAL DIAGRAM FOR HETERONUCLEAR DIATOMICS

Molecules consisting of two non-identical atoms are said to be heteronuclear diatomic, such as: CO, NO, HF, and LiF.

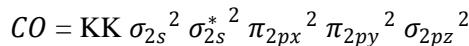
1.7.1 MOLECULAR ORBITAL DIAGRAM FOR CO MOLECULE

The electronic configuration of carbon and oxygen atom is 1s²2s²2p² and 1s²2s²2p⁴ respectively. As 1s orbitals are considered to be non bonding, therefore, two electron of 1s orbitals of both oxygen and carbon atom can be ignored. Therefore, there are 4 electrons in the outer shell of carbon and 6 electrons in the outer shell of oxygen. Thus, the total of 10 outer electrons is to be accommodated in the molecular orbitals of CO molecule. Because of higher electron negativity of oxygen, its atomic orbitals would be of lower energy than the corresponding atomic orbitals of carbon.

Due to this energy difference, the bonding and antibonding molecular orbitals will receive different contributions from atomic orbitals of carbon and oxygen. The bonding molecular orbitals will receive more contribution from atomic orbitals of lower energy i.e. the atomic orbitals of Oxygen and would be closer to it in energy than the antibonding molecular orbitals which would be closer to carbon in energy.

The bonding molecular orbitals would have more characteristics of atomic orbitals of Oxygen and antibonding Molecular orbitals would have more characteristics of carbon.

The electronic configuration of CO molecule is



Here KK represents two non bonding 1s orbitals of C and O atoms.

Bond order (B.O.) = (No. of electrons in BMO - No. of electrons in ABMO)/2

$$\text{The Bond Order (B. O.) of } CO = \frac{N_B - N_A}{2} = \frac{8 - 2}{2} = 3$$

Thus, CO contains a triple bond. Its bond dissociation energy is 1067 KJ/mol and bond length is equal to 1.14 Å. Molecular orbital diagram for CO molecule is given as.

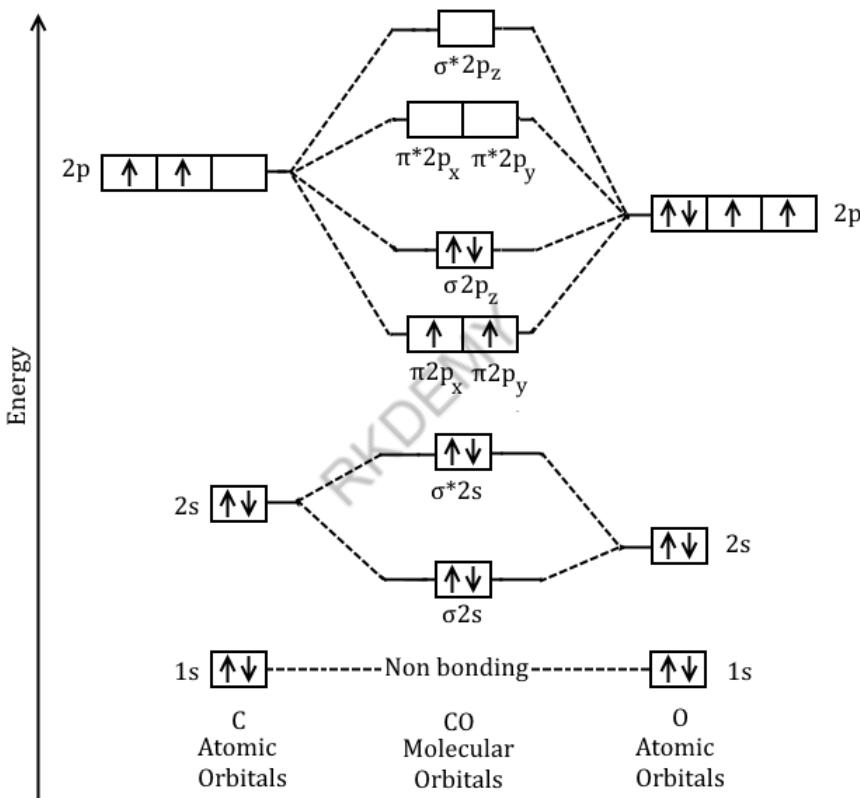


Fig. 1.6 Molecular Orbital Diagram for CO

Magnetic Behavior: If all the molecular orbitals in species are spin paired, the substance is diamagnetic i.e CO Molecule, it is **diamagnetic** as all the electron in CO are paired.

1.7.2 MOLECULAR ORBITAL DIAGRAM FOR NO MOLECULE

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O₂ with N₂ at high temperatures in internal combustion engines forms nitric oxide. The electronic configuration of nitrogen (7) and oxygen (8) atom is 1s² 2s² 2p³ and 1s² 2s² 2p⁴ respectively and total 15 electron. As 1s orbitals are considered to be non bonding, therefore, two electron of 1s orbitals of each oxygen and nitrogen atom can be ignored. Therefore, NO

has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory.

The molecular orbital energy-level diagram for NO shows that the general pattern is similar to that for the O₂ molecule. Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2p atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals.

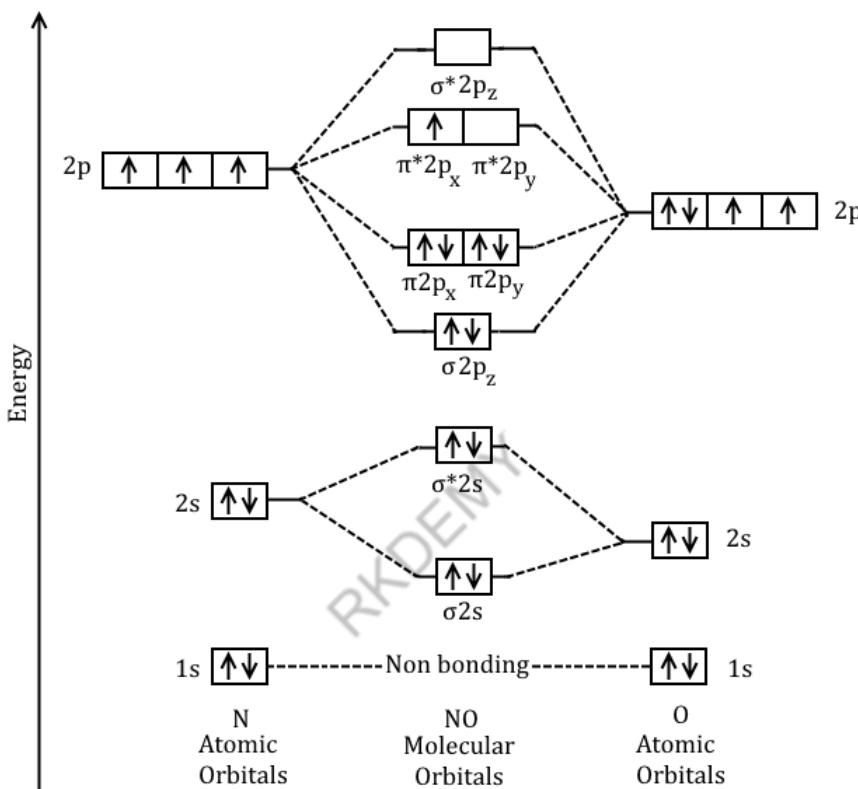


Fig. 1.7: Molecular Orbital Energy-Level Diagram for NO.

The electronic configuration of NO molecule is

$$NO = KK \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \pi_{2py}^2 \sigma_{2pz}^2 \pi_{2px}^{*2} \text{ or } \pi_{2py}^{*2}$$

Here KK represents two non bonding 1s orbitals of N and O atoms.

$$\text{Bond order (B.O.)} = (\text{No. of electrons in BMO} - \text{No. of electrons in ABMO})/2$$

$$\text{The Bond Order (B.O.) of } NO = \frac{N_B - N_A}{2} = \frac{8 - 3}{2} = 2.5$$

These values lie between those of the N₂ and O₂ molecules, which have triple and double bonds, respectively.

Magnetic Behavior: Since NO has 11 valence electrons, it is **paramagnetic**, with a single electron occupying the (π_{2px}^{*2} or π_{2py}^{*2}) pair of orbitals.

QUESTIONS

1. Define the term atomic orbitals
2. Explain with diagram, the shapes of 2s and 2p orbitals
3. Write electronic configuration of Hund's rule.
4. Show the pattern of electrons with configuration of element B to F.
5. Write note on MOT.
6. Define bonding and antibonding orbitals
7. Draw molecular orbital diagram of Be_2 and show why it does not exist
8. On the basis of MOT, explain bond order and magnetic behavior of O_2
9. Explain in detail the molecular orbital diagram of CO.
10. Draw molecular orbital diagram of NO and explain its bond order and show why it is less stable than N_2 .

RKDEMY

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Aromatic systems & their molecular structure

Define Aromaticity, Huckel's rule, Structure and bonding of benzene and pyrrole.

2.1 AROMATICITY

Aromaticity is a property of conjugated cycloalkenes in which the stabilization of the molecule is enhanced due to the ability of the electrons in the π orbitals to delocalize. This act as a framework to create a planar molecule.

Why do we care if a compound is aromatic or not? Because we encounter aromatics every single day of our lives. Without aromatic compounds, we would not only be lacking many material necessities, our bodies would also not be able to function. Aromatic compounds are essential in industry; about 35 million tons of aromatic compounds are produced in the world every year to produce important chemicals and polymers, such as polyester and nylon.

Aromatic compounds are also vital to the biochemistry of all living things. Three of the twenty amino acids used to form proteins ("the building blocks of life") are aromatic compounds and all five of the nucleotides that make up DNA and RNA sequences are all aromatic compounds. Needless to say, aromatic compounds are vital to us in many aspects.

The three general requirements for a compound to be aromatic are:

1. The compound must be cyclic
2. Each element within the ring must have a p-orbital that is *perpendicular* to the ring, hence the molecule is planar.
3. The compound must follow Hückel's Rule (the ring has to contain $4n+2 \pi$ electrons), where $n = 0, 1, 2, 3, \dots$.

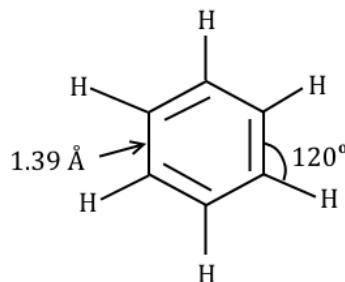
Among the many distinctive features of benzene, its aromaticity is the major contributor to for its reactivity. This section will try to clarify the theory of aromaticity and why aromaticity gives unique qualities that make these conjugated alkenes inert to compounds such as Br_2 and even hydrochloric acid. It will also go into detail about the unusually large resonance energy due to the six conjugated carbons of benzene.



The delocalization of the p-orbital electrons on the sp² hybridized carbons is what gives the aromatic qualities of benzene.

2.1.1 AROMACITY IN BENZENE

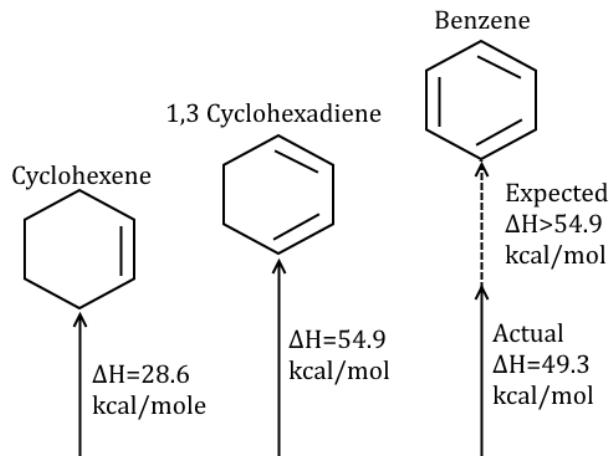
Because of the aromaticity of benzene, the resulting molecule is planar in shape with all C-C bond being 1.39 Å in length and each bond angle being 120°.



You may wonder how it's possible to have all of the bonds to be the same length if the ring is conjugated with both single (1.54 Å) and double (1.34 Å), but it is important to note that there are no distinct single or double bonds within the benzene. Rather, the delocalization of the ring makes each count as one and a half bonds between the carbons which makes sense because experimentally we find that the actual bond length is somewhere in between a single and double bond. Finally, there are a total of six p-orbital electrons that form the stabilizing electron clouds above and below the aromatic ring.

2.1.2 EVIDENCE OF AROMATICITY: HEATS OF HYDROGENATION

One of the ways to test the relative amounts of resonance energy in a molecule is to compare the heats of hydrogenation between similar compounds. For instance, if we compare cyclohexene, 1,3-cyclohexadiene, and benzene, we would expect that their heats of hydrogenation will increase since the number of double bonds increases respectively.



However, experimental evidence suggests that the actual heat of hydrogenation for benzene is actually 49.3 kcal/mole, making it even more stable than the 1,3-cyclohexadiene even though it has two double bonds, compared to benzene's three double bonds. This characteristic can be attributed to the aromaticity of benzene which delocalizes the electrons of the six pi orbitals.

Example 2.1: What is the hybridization of each carbon and the overall shape of benzene?

Answers: All six carbons are sp^2 hybridized and the aromaticity of the benzene creates a planar molecule.

Example 2.2: Place the following compounds in order of heats of hydrogenation from smallest to greatest: Benzene, 1, 3-Cyclohexadiene, and Cyclohexene.

Answers: Cyclohexene < Benzene < 1, 3-Cyclohexadiene.

2.2 AROMATIC SYSTEMS

Many unsaturated cyclic compounds have exceptional properties that we now consider characteristic of "aromatic" systems. The following cases are illustrative:

Compound	Structural Formula	Reaction with Br_2	Thermodynamic Stabilization
1,3-Cyclopentadiene		Addition (0 °C)	Slight
1,3,5-Cycloheptatriene		Addition (0 °C)	Slight
1,3,5,7-Cyclooctatetraene		Addition (0 °C)	Slight
Benzene		Substitution	Large
Pyridine		Substitution	Large
Furan		Substitution (0 °C)	Moderate
Pyrrole		Substitution	Moderate

The first three compounds (cyclic polyenes) have properties associated with alkenes in general. Each reacts readily with bromine to give addition products, as do most alkenes. The thermodynamic change on introducing double bonds into the carbon atom ring is also typical of alkenes (a destabilization of ca. 26 kcal/mol for each double bond). Conjugation offsets this increase in energy by a small amount (4-6 kcal/mol).

The remaining four compounds exhibit very different properties, and are considered aromatic. Benzene and pyridine are relatively unreactive with bromine, requiring heat and/or catalysts to force reaction, the result of which is substitution rather than addition.

Furan and pyrrole react more rapidly with bromine, but they also give substitution products. This tendency to favor substitution rather than addition suggests that the parent unsaturated ring system has exceptional stability. Thermodynamic measurements support this conclusion. The enhanced stability, often referred to as **aromatic stabilization**, ranges (in the above cases) from a low of 16 kcal/mol for furan to 36 kcal/mol for benzene.

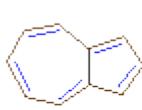
2.3 FACTORS REQUIRED FOR AROMATICITY

- ✓ A planar (or near planar) cycle of sp^2 hybridized atoms, the p-orbitals of which are oriented parallel to each other. These overlapping p-orbitals generate an array of π -molecular orbitals.
- ✓ These π -orbitals are occupied by $4n+2$ electrons (where n is an integer or zero). This requirement is known as **The Hückel Rule**. All the aromatic compounds discussed above have 6 π -electrons (n=1).

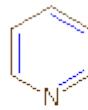
1,3-Cyclopentadiene and 1,3,5-cycloheptatriene both fail to meet the first requirement, since one carbon atom of each ring is sp^3 hybridized and has no p-orbital. Cyclooctatetraene fails both requirements, although it has a ring of sp^2 hybridized atoms. This molecule is not planar (a geometry that would have 135° bond angles). Angle strain is relieved by adopting a tub-shaped conformation; consequently, the p-orbitals can only overlap as isolated pairs, not over the entire ring. Furthermore, cyclooctatetraene has 8 π -electrons, a number not consistent with the Hückel Rule.

Benzene is the archetypical aromatic compound. It is planar, bond angles= 120° , all carbon atoms in the ring are sp^2 hybridized, and the pi-orbitals are occupied by 6 electrons. The aromatic heterocycle pyridine is similar to benzene, and is often used as a weak base for scavenging protons. Furan and pyrrole have heterocyclic five-membered rings, in which the heteroatom has at least one pair of non-bonding valence shell electrons.

By hybridizing this heteroatom to a sp^2 state, a p-orbital occupied by a pair of electrons and oriented parallel to the carbon p-orbitals is created. The resulting planar ring meets the first requirement for aromaticity and the π -system is occupied by 6 electrons, 4 from the two double bonds and 2 from the heteroatom, thus satisfying the Hückel Rule.



azulene



pyridine



thiophene



imidazole

Four illustrative examples of aromatic compounds are shown above. The first example is azulene, a 10 π -electron aromatic hydrocarbon isomeric with naphthalene. The second and third compounds are heterocycles having aromatic properties. Pyridine has a benzene-like six-membered ring incorporating one nitrogen atom. The non-bonding electron pair on the nitrogen is not part of the aromatic π -electron sextet, and may bond to a proton or other electrophile without disrupting the aromatic system.

In the case of thiophene, a sulfur analog of furan, one of the sulfur electron pairs participates in the aromatic ring π -electron conjugation. The last compound is imidazole, a heterocycle having two nitrogen atoms. Note that only one of the nitrogen non-bonding electron pairs is used for the aromatic π -electron sextet. The other electron pair behaves similarly to the electron pair in pyridine.

2.4 HÜCKEL'S RULE

In 1931, German chemist and physicist Erich Hückel proposed a rule to determine if a planar ring molecule would have aromatic properties. This rule states that if a cyclic, planar molecule has $4n+2\pi$ electrons, it is aromatic. This rule would come to be known as Hückel's Rule.

2.4.1 FOUR CRITERIA FOR AROMATICITY

When deciding if a compound is aromatic, go through the following checklist. If the compound does not meet all the following criteria, it is likely not aromatic.

1. The molecule is cyclic (a ring of atoms)
2. The molecule is planar (all atoms in the molecule lie in the same plane)
3. The molecule is fully conjugated (p orbitals at every atom in the ring)
4. The molecule has $4n+2\pi$ electrons ($n=0$ or any positive integer)

2.4.2 WHY $4n+2\pi$ ELECTRONS?

According to Hückel's Molecular Orbital Theory, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons. This is true of aromatic compounds, meaning they are quite stable. With aromatic compounds, 2 electrons fill the lowest energy molecular orbital, and 4 electrons fill each subsequent energy level (the number of subsequent energy levels is denoted by n), leaving all bonding orbitals filled and no anti-bonding orbitals occupied. This gives a total of $4n+2\pi$ electrons. You can see how this works with the molecular orbital diagram for the aromatic compound, benzene, below.

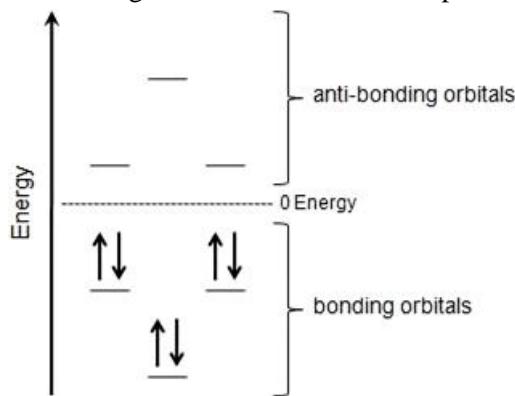


Fig. 2.1: Molecular Orbitals levels of Benzene

Benzene has 6π electrons. Its first 2π electrons fill the lowest energy orbital, and it has 4π electrons remaining. These 4 fill in the orbitals of the succeeding energy level. Notice how all of its bonding orbitals are filled, but none of the anti-bonding orbitals have any electrons.

Example 2.3: Confirm that benzene is aromatic.

Answer: To apply the $4n+2$ rule, first count the number of π electrons in the molecule. Then, set this number equal to $4n+2$ and solve for n . If n is 0 or any positive integer (1, 2, 3,...), the rule has been met. For example, benzene has six π electrons:

$$4n + 2 = 6$$

$$4n = 4$$

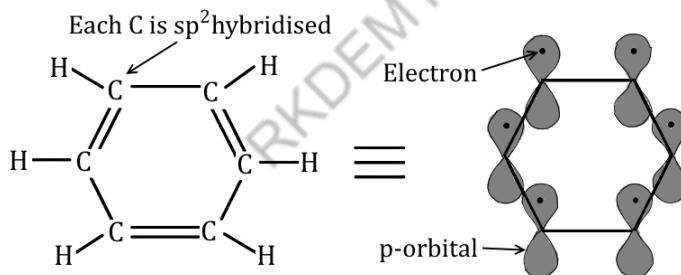
$$n = 1$$

For benzene, we find that $n=1$, which is a positive integer, so the rule is met.

2.4.3 HOW CAN YOU TELL WHICH ELECTRONS ARE π ELECTRONS?

Perhaps the toughest part of Hückel's Rule is figuring out which electrons in the compound are actually π electrons. Once this is figured out, the rule is quite straightforward. π electrons lie in p orbitals. sp^2 hybridized atoms have 1 p orbital each. So if every molecule in the cyclic compound is sp^2 hybridized, this means the molecule is fully conjugated (has 1 p orbital at each atom), and the electrons in these p orbitals are the π electrons.

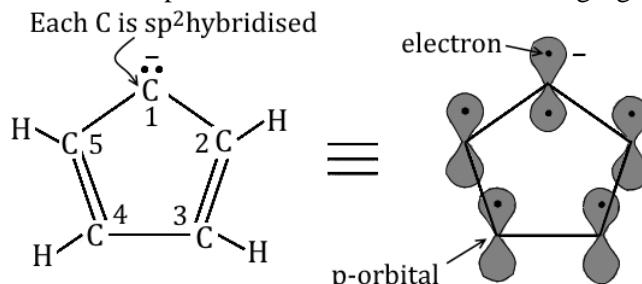
A simple way to know if an atom is sp^2 hybridized is to see if it has 3 attached atoms and no lone pairs of electrons. In a cyclic hydrocarbon compound with alternating single and double bonds, each carbon is attached to 1 hydrogen and 2 other carbons. Therefore, each carbon is sp^2 -hybridized and has a p-orbital. Let's look at example of benzene:



Each double bond (π bond) always contributes 2 π electrons. Benzene has 3 double bonds, so it has 6 π electrons.

2.4.4 AROMATIC IONS

Hückel's Rule also applies to ions. As long as a compound has $4n+2 \pi$ electrons, it does not matter if the molecule is neutral or has a charge. For example, cyclopentadienyl anion is an aromatic ion. How do we know that it is fully conjugated? That is, how do we know that each atom in this molecule has 1 p orbital? Let's look at the following figure.

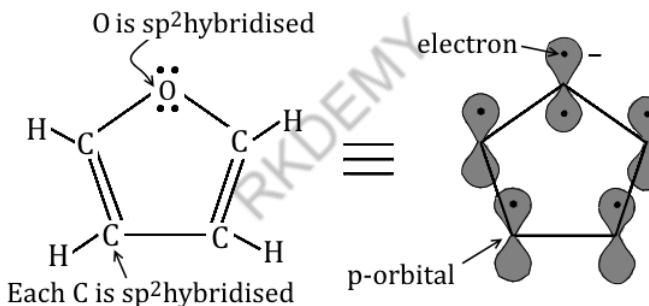


Carbons 2-5 are sp^2 hybridized because they have 3 attached atoms and have no lone electron pairs. What about carbon 1? Another simple rule to determine if an atom is sp^2 hybridized is if an atom has 1 or more lone pairs and is attached to an sp^2 hybridized atom, then that atom is sp^2 hybridized also. Therefore, carbon 1 has a p-orbital. Cyclopentadienyl anion has 6π electrons and fulfills the $4n+2$ rule.

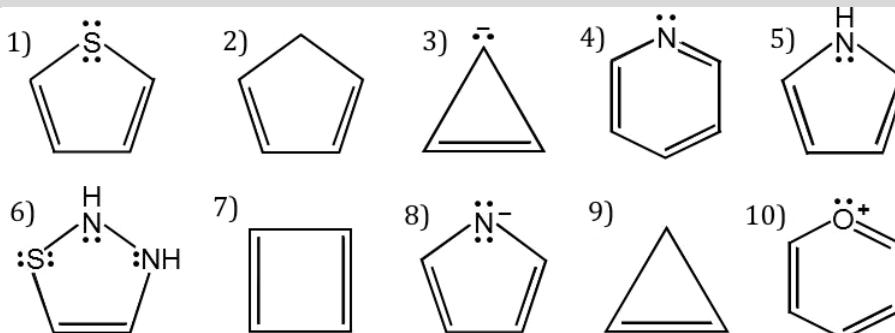
2.4.5 HETEROCYCLIC AROMATIC COMPOUNDS

So far, you have encountered many carbon homocyclic rings, but compounds with elements other than carbon in the ring can also be aromatic, as long as they fulfill the criteria for aromaticity. These molecules are called heterocyclic compounds because they contain 1 or more different atoms other than carbon in the ring. A common example is furan, which contains an oxygen atom. We know that all carbons in furan are sp^2 hybridized. But is the oxygen atom sp^2 hybridized? The oxygen has at least 1 lone electron pair and is attached to an sp^2 hybridized atom, so it is sp^2 hybridized as well.

Notice how oxygen has 2 lone pairs of electrons. How many of those electrons are π electrons? An sp^2 hybridized atom only has 1 p orbital, which can only hold 2 electrons, so we know that 1 electron pair is in the p orbital, while the other pair is in an sp^2 orbital. So, only 1 of oxygen's 2 lone electron pairs are π electrons. Furan has 6π electrons and fulfills the $4n+2$ rule.



Example 2.4: Using the criteria for aromaticity, determine if the following molecules are aromatic:



Answers

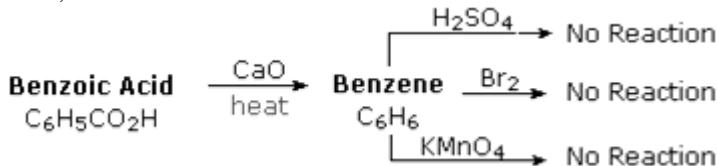
1. Aromatic - only 1 of S's lone pairs counts as π electrons, so there are 6π electrons, $n=1$
2. Not aromatic - not fully conjugated, top C is sp^3 hybridized
3. Not aromatic - top C is sp^2 hybridized, but there are 4π electrons, $n=1/2$

4. Aromatic - N is using its 1 p orbital for the electrons in the double bond, so its lone pair of electrons are not π electrons, there are 6 π electrons, n=1
5. Aromatic - there are 6 π electrons, n=1
6. Not aromatic - all atoms are sp^2 hybridized, but only 1 of S's lone pairs counts as π electrons, so there 8 π electrons, n=1.5
7. Not aromatic - there are 4 π electrons, n=1/2
8. Aromatic - only 1 of N's lone pairs counts as π electrons, so there are 6 π electrons, n=1
9. Not aromatic - not fully conjugated, top C is sp^3 hybridized
10. Aromatic - O is using its 1 p orbital for the electrons in the double bond, so its lone pair of electrons are not π electrons, there are 6 π electrons, n=1

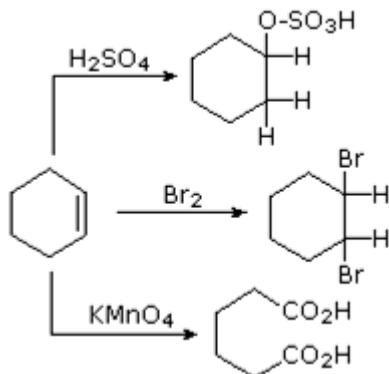
2.5 STRUCTURE AND BONDING IN BENZENE

Benzene is the archetypical aromatic compound. It is planar, bond angles=120°, all carbon atoms in the ring are sp^2 hybridized, and the pi-orbitals are occupied by 6 electrons. Because of the low hydrogen to carbon ratio in aromatic compounds (note that the H:C ratio in an alkane is >2), it is expected their structural formulas would contain a large number of double or triple bonds. Since double bonds are easily cleaved by oxidative reagents such as $KMnO_4$ or ozone, and rapidly add bromine and chlorine, these reactions were applied to these aromatic compounds. Surprisingly, products that appeared to retain many of the double bonds were obtained, and these compounds exhibited a high degree of chemical stability compared with known **alkenes** and cycloalkenes (aliphatic compounds).

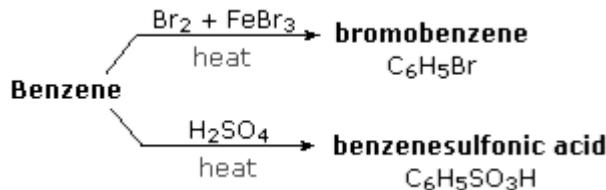
On treatment with hot permanganate solution, cinnamaldehyde gave a stable, crystalline $C_7H_6O_2$ compound, now called benzoic acid. The H:C ratio in benzoic acid is <1, again suggesting the presence of several double bonds. Benzoic acid was eventually converted to the stable hydrocarbon benzene, C_6H_6 , which also proved unreactive to common double bond transformations, as shown below.



For comparison, reactions of cyclohexene, a typical **alkene**, with these reagents are also shown



Benzene was found to undergo substitution reactions. It reacted with bromine in the presence of catalyst FeBr_3 to give mono-bromo benzene or with hot H_2SO_4 to give benzene sulphonic acid.



Only one monobromo product is obtain with Br_2 in presence of catalyst, suggest that all hydrogen atom in benzene were identical.

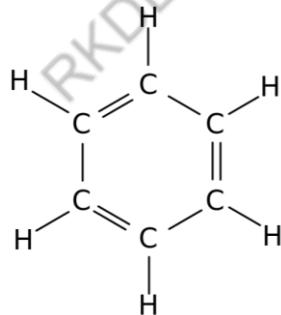
Benzene add 3 hydrogen molecule in presence of Ni catalyst and pressure to give cyclohexane.

Above both reactions confirms that benzene has cyclic structure and six carbon attached with each hydrogen and three carbon-carbon double bond.

As experimental evidence for a wide assortment of compounds was acquired, those incorporating this exceptionally stable six-carbon core came to be called “aromatic”.

2.5.1 THE KEKULÉ STRUCTURE FOR BENZENE (C_6H_6)

Kekulé was the first to suggest a sensible structure for benzene. The carbons are arranged in a hexagon, and he suggested alternating double and single bonds between them. Each carbon atom has a hydrogen attached to it.



This diagram is often simplified by leaving out all the carbon and hydrogen atoms!

In diagrams of this sort, there is a carbon atom at each corner. You have to count the bonds leaving each carbon to work out how many hydrogens there are attached to it. In this case, each carbon has three bonds leaving it. Because carbon atoms form four bonds, that means you are a bond missing - and that must be attached to a hydrogen atom.

2.5.2 PROBLEMS WITH THE KEKULÉ STRUCTURE

Although the Kekulé structure was a good in its time, there are serious problems with it.

- (a) **Problems with the chemistry:** Because of the three double bonds, you might expect benzene to have reactions like ethene - only more so! Ethene undergoes addition reactions in which one of the two bonds joining the carbon atoms breaks, and the electrons are used to bond with additional atoms.



Benzene rarely does this. Instead, it usually undergoes substitution reactions in which one of the hydrogen atoms is replaced by something new. i.e. Benzene reacts with chlorine or bromine in an electrophilic substitution reaction, but only in the presence of a catalyst.



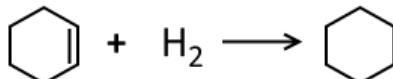
- (b) Problems with the shape:** Benzene is a planar molecule (all the atoms lie in one plane), and that would also be true of the Kekulé structure. The problem is that C-C single and double bonds are different lengths.

C-C	0.154 nm
C=C	0.134 nm

That would mean that the hexagon would be irregular if it had the Kekulé structure, with alternating shorter and longer sides. In real benzene all the bonds are exactly the same - intermediate in length between C-C and C=C at 0.139 nm. Real benzene is a perfectly regular hexagon.

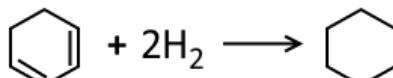
- (c) Problems with the stability of benzene:** Real benzene is a lot more stable than the Kekulé structure would give it credit for. Every time you do a thermochemistry calculation based on the Kekulé structure, you get an answer which is wrong by about 150 kJ mol⁻¹. This is most easily shown using enthalpy changes of hydrogenation. In order to do a fair comparison with benzene (a ring structure) we're going to compare it with cyclohexene. Cyclohexene, C₆H₁₀, is a ring of six carbon atoms containing just one C=C.

The hydrogenation equation could be written:



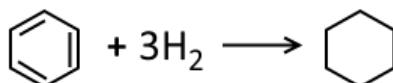
The enthalpy change during this reaction is -120 kJ mol⁻¹. In other words, when 1 mole of cyclohexene reacts, 120 kJ of heat energy is evolved.

If the ring had *two* double bonds in it initially (*cyclohexa-1,3-diene*), exactly twice as many bonds would have to be broken and exactly twice as many made. In other words, you would expect the enthalpy change of hydrogenation of cyclohexa-1,3-diene to be exactly twice that of cyclohexene - that is, -240 kJ mol⁻¹.

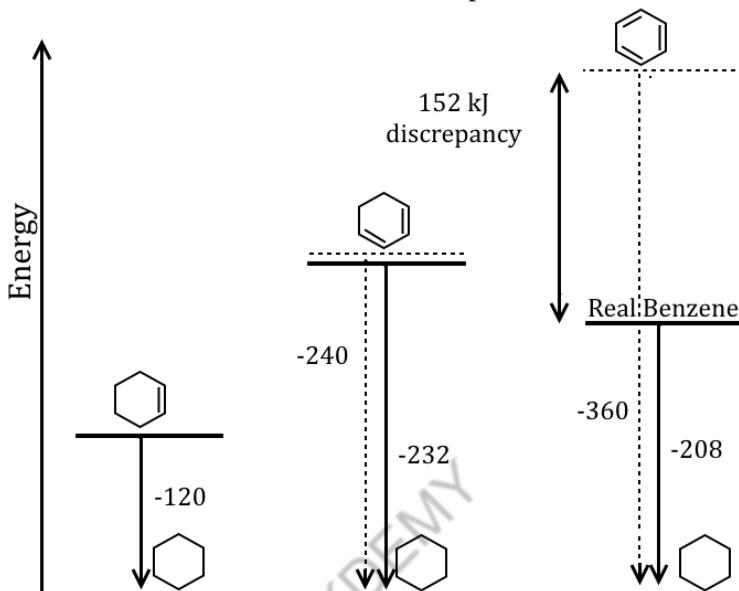


In fact, the enthalpy change is **-232 kJ mol⁻¹** - which isn't far off what we are predicting.

Applying the same argument to the Kekulé structure for benzene (what might be called *cyclohexa-1,3,5-triene*), you would expect an enthalpy change of -360 kJ mol⁻¹, because there are exactly three times as many bonds being broken and made as in the cyclohexene case.



In fact what you get is -208 kJ mol^{-1} - not even within distance of the predicted value! This is very much easier to see on an enthalpy diagram. Notice that in each case heat energy is released, and in each case the product is the same (cyclohexane). That means that all the reactions "fall down" to the same end point.

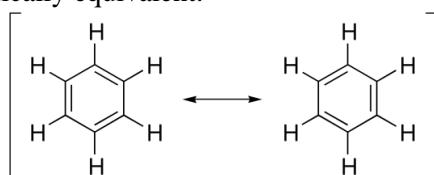


The most important point to notice is that real benzene is much lower down the diagram than the Kekulé form predicts. The lower down a substance is, the more energetically stable it is. This means that real benzene is about 150 kJ mol^{-1} more stable than the Kekulé structure gives it credit for. This increase in stability of benzene is known as the **delocalisation energy** or **resonance energy** of benzene.

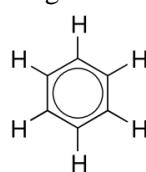
2.6 RESONANCE STRUCTURES OF BENZENE

Benzene, a double-bond conjugated six member hydrocarbon ring, can be represented by two structures that are equivalent in energy. A simple model representing oscillation between the two primary structures is, however, insufficient as it does not explain one of the principle chemical properties of the molecule - its inability to saturate. The application of the theory of resonance permitted the determination of a more accurate model.

In the resonance model, the molecular configuration of benzene is such that all possible structures contribute to the true structure – a combination of all structures at once, with each carbon-carbon bond energetically equivalent.



Based on this theory, the benzene molecule is now often depicted as a hexagon with a circle in the middle representing the true resonating nature of the molecule.



This structure has since been verified by multiple experimental techniques such as electron diffraction, x-ray diffraction, and molecular spectroscopy.

2.7 MOLECULAR ORBITAL STRUCTURE OF BENZENE

A molecular orbital description of benzene provides a more satisfying and more general treatment of "aromaticity". We know that benzene has a planar hexagonal structure in which all the carbon atoms are sp^2 hybridized, and all the carbon-carbon bonds are equal in length. As shown below, the remaining cyclic array of six p-orbitals (one on each carbon) overlap to generate six molecular orbitals, three bonding and three antibonding.

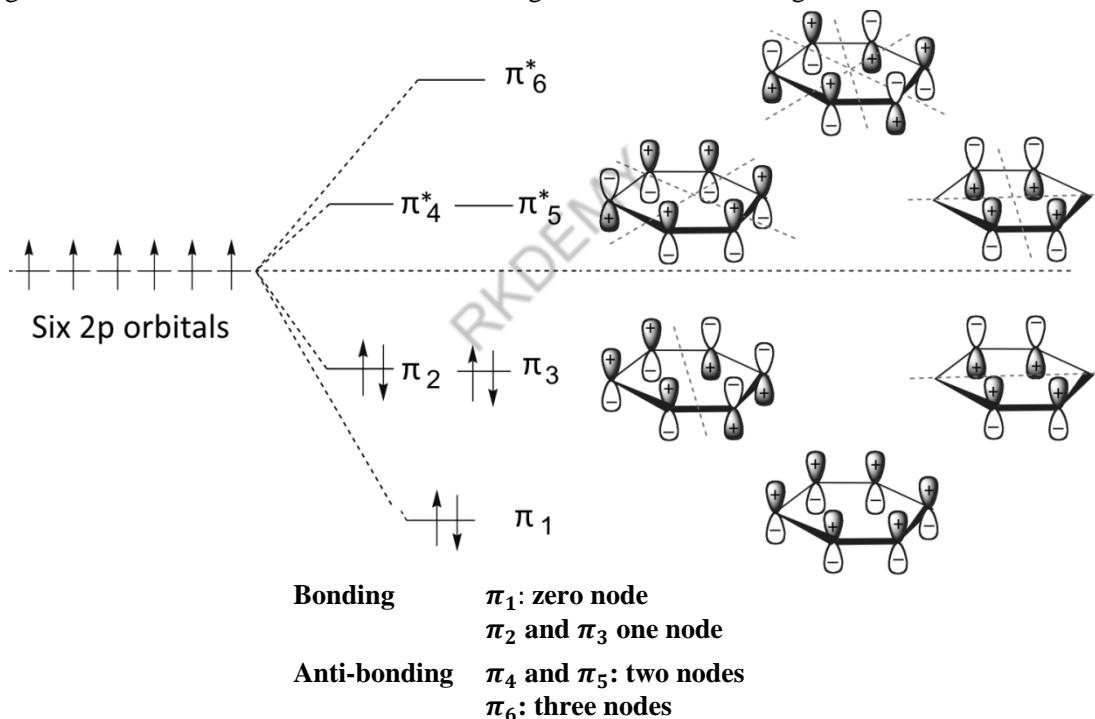


Fig. 2.2 Molecular orbital structure of Benzene

The plus and minus signs shown in the diagram do not represent electrostatic charge, but refer to phase signs in the equations that describe these orbitals. When the phases correspond, the orbitals overlap to generate a common region of like phase, with those orbitals having the greatest overlap (e.g. π_1) being lowest in energy. The remaining carbon valence electrons then occupy these molecular orbitals in pairs, resulting in a fully occupied (6 electrons) set of bonding molecular orbitals. It is this completely filled set of bonding orbitals, or **closed shell** that gives the benzene ring its thermodynamic and chemical stability, just as a filled valence shell octet confers stability on the inert gases.

2.7 STRUCTURE AND BONDING IN PYRROLE

Structure of pyrrole is explained by two theories

- (a) **Resonance structure of Pyrrole:** According to resonance theory pyrrole is resonance hybrid of following resonance structure

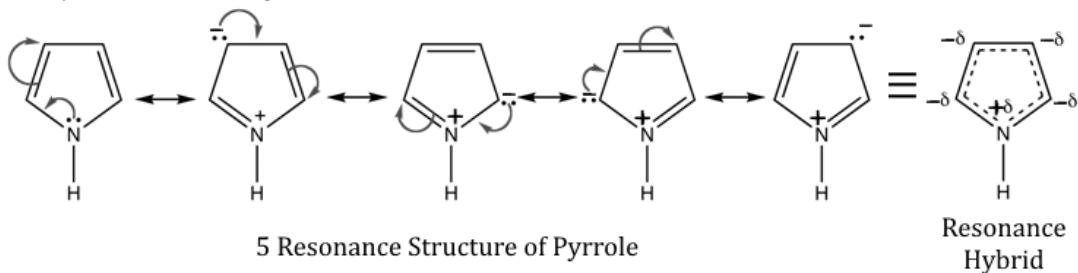


Fig. 2.3 Resonance structure of Pyrrole

In this resonance structure, single bonded N atom donates lone pair of electrons to adjacent C atom with the shifting of double bond, so adjacent C atom gets +ve charge. In next resonance structure, the lone pair and -ve charge is delocalized at adjacent position. The bond length measurement by X-ray analysis confirms hybrid character of Pyrrole.

C-N bond length in Pyrrole is 1.4\AA . It is less than normal C-N single bond length (i.e. 1.5\AA). This shows that C-N bond in pyrrole has double bond character. Similarly, the carbon-carbon bond length is intermediate of C-C single and C=C double bond. The resonance stabilization energy of Pyrrole is 21.0 kcal/mol

- (b) **Molecular orbital structure of Pyrrole by M.O. Theory:** According to M.O. theory sigma bond M.O. diagram and cyclic delocalized pi bond M.O. diagram of pyrrole are represented as below.

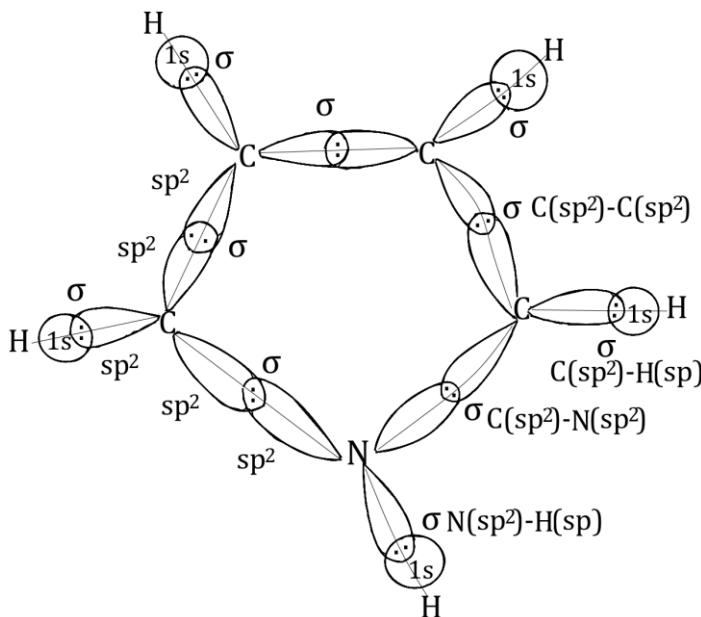


Fig. 2.4 Sigma bond Molecular Orbital structure of pyrrole

According to M.O. theory pyrrole molecule is planer i.e. all carbon, hydrogen and nitrogen atoms lay in same plane. All ring atoms (C, H and N) are in sp^2 hybridized state i.e. they contain three sp^2 hybrid orbitals & one unhybridized p-orbital. Each sp^2 hybrid orbital of C and N is half filled. The p-orbital of C atom is half filled. P-orbital of N atom contains lone pair of electron. These p-orbital are perpendicular to the plane of sp^2 hybrid orbitals.

FORMATION OF SIGMA BOND MO DIAGRAM

The two sp^2 hybrid orbitals of each ring atom overlap axially to form sigma bonds. (C-C and C-N). The remaining sp^2 hybrid orbitals of each ring atom overlaps axially with half filled 1s orbital of H atom to form C-H and N-H sigma bonds.

FORMATION OF CYCLIC DELOCALIZED π BOND MO DIAGRAM

The unhybridized p-orbitals of all ring atoms overlap laterally (sidewise) and equally in both direction to form cyclic delocalized π bond M.O.s containing six π electrons. It is called as aromatic sextet. Fig. 2.5

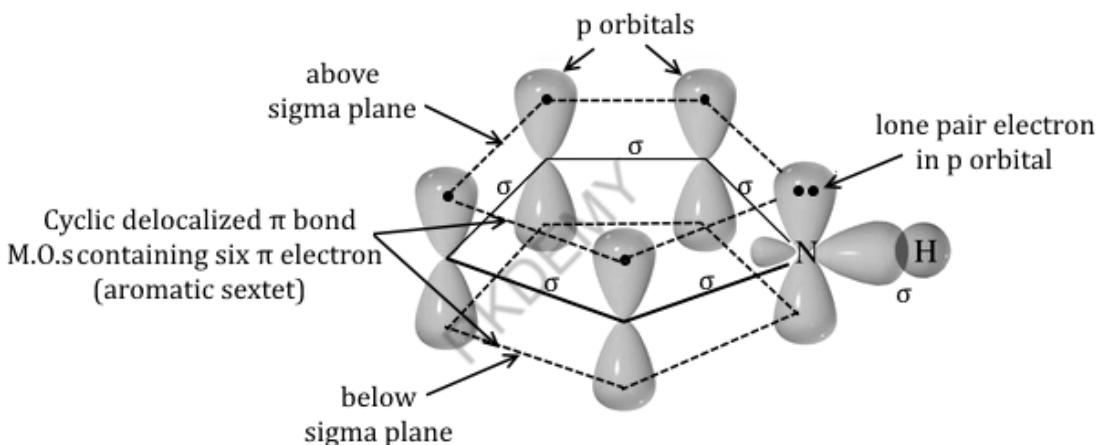
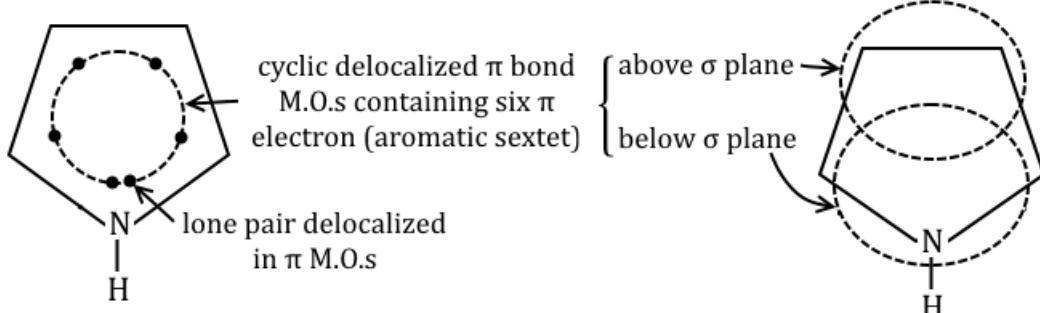


Fig. 2.5

The delocalized π bonds M.O.s lie above & below the plane of sigma ring. The delocalized π bond M.O.s containing six π electron (aromatic sextet) is represented by putting a circle inside the sigma ring of pyrrole i.e. fig.



Thus pyrrole shows aromatic character due to presence of aromatic sextet. This aromatic sextet opposes additional reaction and favours E.S.

QUESTIONS

1. Define aromaticity
2. State Huckel rule with suitable example.
3. How you will confirm that benzene is aromatic.
4. Draw molecular orbital diagram for Benzene.
5. Explain structure and bonding of pyrrole.
6. Explain resonance in pyrrole
7. Explain kekule's structure and resonance in benzene
8. Explain formation of sigma and pi bond in pyrrole
9. Explain structure and bonding of Benzene in detail.

RKDEMY

RKDEMY

Intermolecular Forces & Critical Phenomena

Ionic, dipolar and Vander Waal's interactions, Equations of state of real gases and critical phenomena

3.1 INTERMOLECULAR FORCES

The properties of liquids are intermediate between those of gases and solids but are more similar to solids. In contrast to *intramolecular* forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *intermolecular* forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C.

Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

The properties of liquids are intermediate between those of gases and solids but are more similar to solids. Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures.

The intermolecular forces between neutral molecules are **dipole–dipole interactions**, **London dispersion forces**, and **hydrogen bonds**. There are two additional types of electrostatic interaction: the ion–ion interactions that are responsible for ionic bonding and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water.

3.2 VAN DER WAALS FORCE

The intermolecular forces known as **dipole–dipole interactions** and **London dispersion forces** are collectively known as van der Waals forces, named after Dutch scientist Johannes Diderik van der Waals, is a distance-dependent interaction between atoms or molecules. They are comparatively weak and therefore more susceptible to disturbance. The van der Waals force quickly vanishes at longer distances between interacting molecules.

3.2.1 DIPOLE–DIPOLE INTERACTIONS

The polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a **dipole**). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in part (a) in Fig. 3.1.

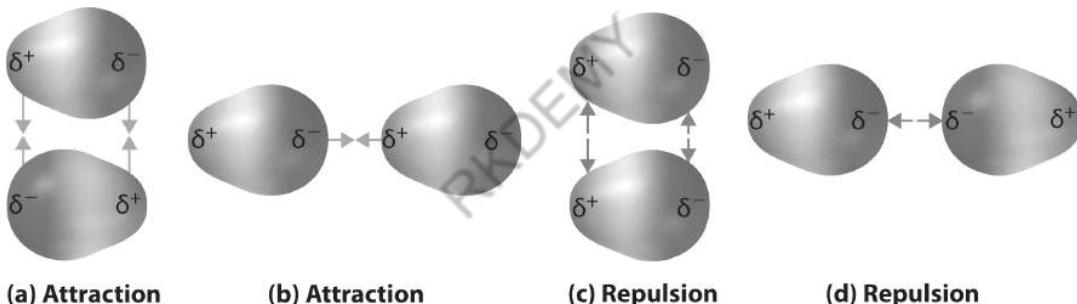


Fig. 3.1 Attractive and Repulsive Dipole–Dipole Interactions (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (part (c) in Fig. 3.1). Hence dipole–dipole interactions is a kind of intermolecular interaction (force) that results between molecules with net dipole moments., such as those in part (b) in Fig. 3.1, are **attractive intermolecular interactions**, whereas those in part (d) in Fig. 3.1 are **repulsive intermolecular interactions**. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Fig. 3.2. On average, however, the attractive interactions dominate.

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ± 1 , or between a dipole and an ion, in which one of the species has at least a full positive or negative charge.

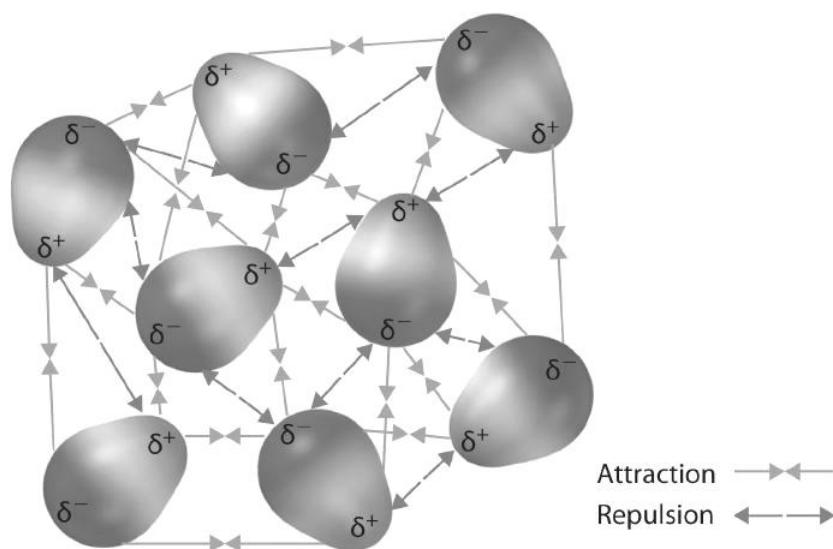


Fig. 3.2 Both Attractive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. The attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half.

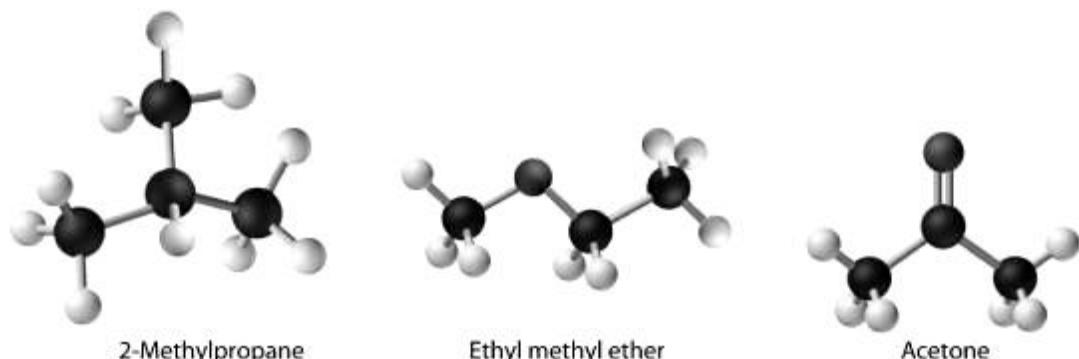
In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^6 , or 64-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid.

Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 3.1.

Table 3.1 Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C ₃ H ₆ (cyclopropane)	42	0	240
CH ₃ OCH ₃ (dimethyl ether)	46	1.30	248
CH ₃ CN (acetonitrile)	41	3.9	355

Example 3.1: Arrange ethyl methyl ether (CH₃OCH₂CH₃), 2-methylpropane [isobutane, (CH₃)₂CHCH₃], and acetone (CH₃COCH₃) in order of increasing boiling points. Their structures are as follows:



Answer: The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to H_2O ; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point.

Thus we predict the following order of boiling points:



This result is in good agreement with the actual data: 2-methylpropane, boiling point = -11.7°C , and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

3.2.2 LONDON DISPERSION FORCES

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both.

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments. The short-lived dipole moment in atoms and nonpolar molecules caused by the constant motion of their electrons, which results in an asymmetrical distribution of charge at any given instant, which produce attractive forces called **London dispersion forces**. A kind of intermolecular interaction (force) that results from temporary fluctuations in the electron distribution within atoms and nonpolar molecules, between otherwise nonpolar substances.

Table 3.2 Melting and Boiling Points of Some Elements and Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	-189.4	-185.9
Xe	131	-111.8	-108.1
N ₂	28	-210	-195.8
O ₂	32	-218.8	-183.0
F ₂	38	-219.7	-188.1
I ₂	254	113.7	184.4
CH ₄	16	-182.5	-161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Fig. 3.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an **induced dipole**.

A short-lived dipole moment that is created in atoms and nonpolar molecules adjacent to atoms or molecules with an instantaneous dipole moment, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance.

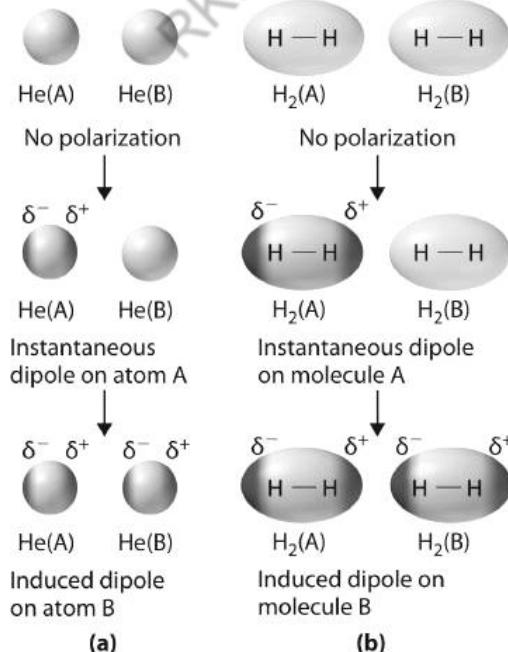


Fig. 3.3 Instantaneous Dipole Moments: The formation of an instantaneous dipole moment on one He atom (a) or an H₂ molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole-induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H₂ molecules in part (b) in Fig. 3.3 tends to become more pronounced as atomic and molecular masses increase.

For example, Xe boils at -108.1°C , whereas He boils at -269°C . The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1s electrons are held close to the nucleus in a very small volume, and electron-electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. The ease of deformation of the electron distribution in an atom or molecule. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones. For similar substances, London dispersion forces get stronger with increasing molecular size.

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes.

The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C₅H₁₂. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is lower than the boiling point of *n*-pentane (36.1°C).

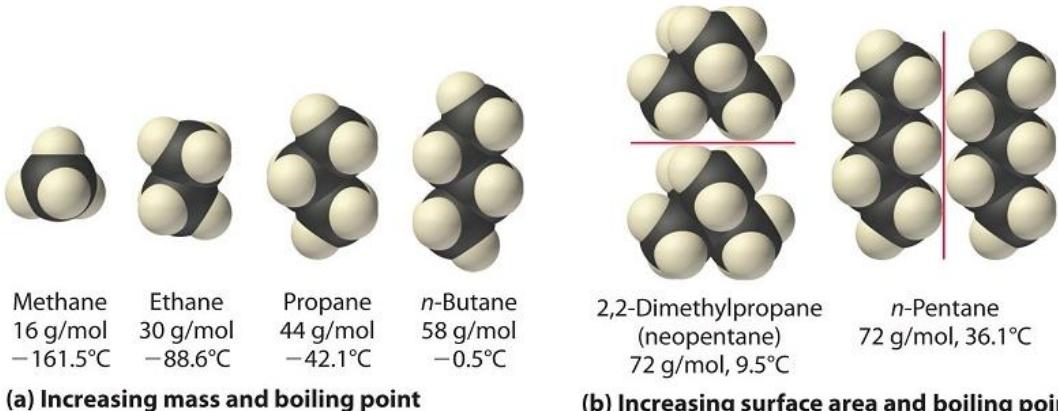


Fig. 3.4 Mass and Surface Area Affect the Strength of London Dispersion Forces (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

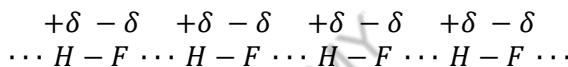
All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

3.3 HYDROGEN BONDS

Molecules with hydrogen atoms bonded to electronegative atoms such as as fluorine, oxygen and nitrogen, the electron pair shared between the two atoms lies far away from the hydrogen atom as a result of which the hydrogen atom becomes highly electropositive with respect to the other atom which becomes electronegative. This phenomenon of charge separation in the case of hydrogen fluoride is represented as $H^{+\delta} - F^{-\delta}$.

Such a molecule is said to be polar. The molecule behaves as a one end carries a positive charge and the other end a negative charge. The electrostatic force of attraction between such molecules should be very strong. This is because the positive end of one molecule attracts and is attracted by the negative end of the other molecule. Thus, two or more molecules may associate together to form large clusters of molecules.

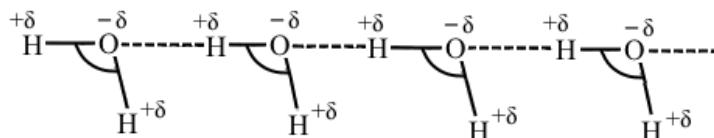
This is shown below for the association of several molecules of hydrogen fluoride:



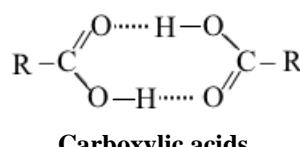
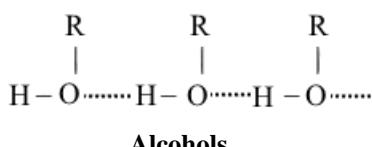
In above case, while the length of the covalent bond between F and H atoms is found to 1.00 Å, the length of the hydrogen bond between F and H atoms of neighbouring molecules has been found to be 1.55 Å.

The attractive force which binds hydrogen atom of one molecule with electronegative atom (such as fluorine) of another molecule, generally of the same substance, is known as **hydrogen bond**.

Water molecule, because of its bent structure, is also a dipole, the oxygen end carrying a negative charge and the hydrogen end carrying a positive charge. Hydrogen bonding takes place in this case as well, as shown as below.



Alcohols and carboxylic acids also form associated molecules for the same reason i.e. hydrogen bond as shown below



3.3.1 SOME UNIQUE PROPERTIES OF WATER BASED ON HYDROGEN BOND

Water has some unique properties. Two of these are discussed below.

1. Density in the solid state (ice) is less than that in the liquid state. This is somewhat unusual because in most substances density in the solid state is more than that in the liquid state.
2. Water contracts when heated between 0°C and 4°C. This is again unusual because most substances expand when heated in all temperature ranges.

Both these peculiar features can be explained as due to hydrogen bonding, as discussed below.

Case 1: The hydrogen bonding between H₂O molecules is more extensive in ice than in liquid water. A substance in solid state has a definite structure and the molecules are more rigidly fixed relative to one another than in liquid state. In ice, the H₂O molecules are tetrahedrally oriented with respect to one another. At the same time, each oxygen atom is surrounded tetrahedrally by four hydrogen atoms, two of these are bonded covalently and the other two by hydrogen bonds.

The hydrogen bonds are weaker and therefore, longer than the covalent bonds. This arrangement gives rise to an open cage like structure with a number of holes' or open spaces. These 'holes' are formed because the hydrogen bonds

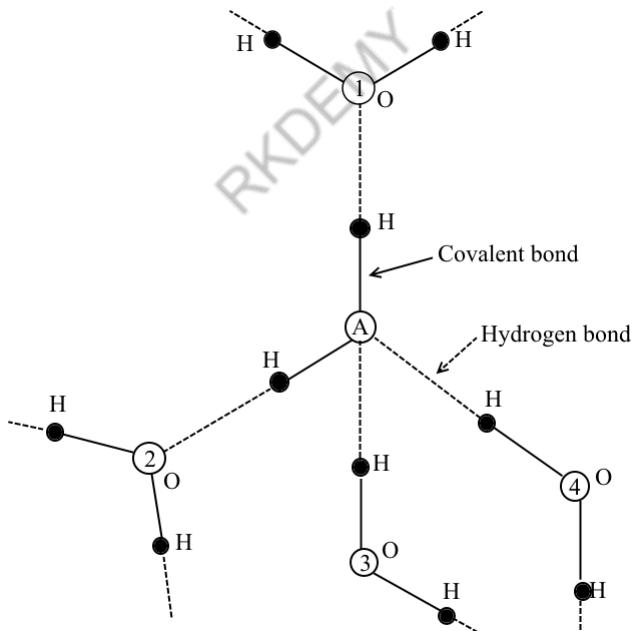


Fig. 3.5 The tetrahedral open cagelike crystal structure of ice

The central oxygen atom A is surrounded tetrahedrally by the oxygen atoms marked 1, 2, 3 and 4 holding the H₂O molecules in ice are directed at certain definite angles. In liquid water such hydrogen bonds are fewer in number. Therefore, as ice melts, a large number of hydrogen bonds are broken. The molecules, therefore, move into the 'holes' or open spaces and come closer to one another than they were in the solid state. This results in a sharp increase in the density. The density of liquid water is, therefore, higher than that of ice.

Case 2: As liquid water is heated from 0° to 4°C, hydrogen bonds continue to be broken and the molecules come closer and closer together. This leads to contraction. However, there is also some expansion of water due to rise in temperature as in other liquids. It appears that upto 4°C, the former effect predominates and hence there is net contraction in volume.

Above 4°C, however, the normal expansion effect, due to rise in temperature, predominates and hence the volume increases as the temperature rises.

3.3.2 IMPORTANCE OF HYDROGEN BONDING IN SUSTAINING LIFE

It can be easily realized that without hydrogen bonding, water would have existed as a gas like hydrogen sulphide. In that case, no life would have been possible on this globe.

Hydrogen bonding also exists in all living organisms whether of animal or of vegetable kingdom. Thus, it exists in various tissues, organs, blood, skin and bones in animal life. It plays an important role in determining structure of proteins which are so essential for life.

Hydrogen bonding plays important role in making wood fibres rigid and thus makes it an article of great utility to meet requirements of housing, furniture, etc. The cotton, silk or synthetic fibres owe their rigidity and tensile strength to hydrogen bonding. Thus, hydrogen bonding is of vital importance for our clothing as well. Most of our food materials also consist of hydrogen bonded molecules.

Sugars and carbohydrates, for example, have many -OH groups. The oxygen of one such group in one molecule is bonded with -OH group of another molecule through hydrogen bonding. The stickiness of glue (a protein) or honey (which consists mainly of water and sugar) is also due to hydrogen bonding between the -OH or other such groups of different molecules with one another.

Hydrogen bonding is thus a phenomenon of great importance in everyday life.

3.4 REAL AND IDEAL GASES

The behavior of a molecule depends a lot on its structure. We can have two compounds with the same number of atoms and yet they act very differently. Ethanol (C_2H_5OH). Is a clear liquid that has a boiling point of about 79 °C. Dimethylether (CH_3OCH_3) has the same number of carbons, hydrogens, and oxygens, but boils at a much lower temperature (-25°C). The difference lies in the amount of intermolecular interaction (strong H-bonds for ethanol, weak van der Waals force for the ether).

An **ideal gas** is one that follows the gas laws at all conditions of temperature and pressure. To do so, the gas would need to completely abide by the kinetic-molecular theory. The gas particles would need to occupy zero volume and they would need to exhibit no attractive forces whatsoever toward each other. Since neither of those conditions can be true, there is no such thing as an ideal gas.

A **real gas** is a gas that does not behave according to the assumptions of the kinetic-molecular theory. Fortunately, at the conditions of temperature and pressure that are normally encountered in a laboratory, real gases tend to behave very much like ideal gases.

Under what conditions gases behave least ideally?

When a gas is put under high pressure, its molecules are forced closer together as the empty space between the particles is diminished. A decrease in the empty space means that the assumption that the volume of the particles themselves is negligible is less valid. When a gas is cooled, the decrease in kinetic energy of the particles causes them to slow down. If the particles are moving at slower speeds, the attractive forces between them are more prominent. Another way to view it is that continued cooling of the gas will eventually turn it into a liquid and a liquid is certainly not an ideal gas anymore. In summary, a real gas deviates most from an ideal gas at low temperatures and high pressures. Gases are most ideal at high temperature and low pressure.

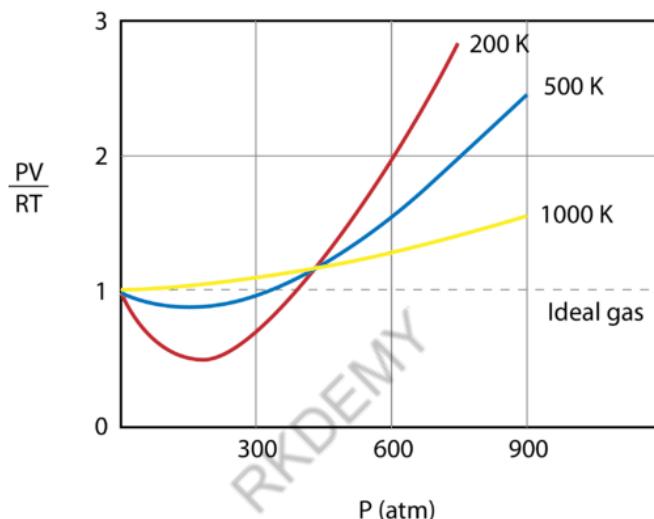


Fig. 3.6: Real gases deviate from ideal gases at high pressures and low temperatures.

The graph shows a graph of PV/RT plotted against pressure for 1mol of a gas at three different temperatures - 200K, 500K, and 1000K. An ideal gas would have a value of 1 for that ratio at all temperatures and pressures and the graph would simply be a horizontal line. As can be seen, deviations from an ideal gas occur. As the pressure begins to rise, the attractive forces cause the volume of the gas to be less than expected and the value of PV/RT drops under 1. Continued pressure increase results in the volume of the particles to become significant and the value of PV/RT rises to greater than 1. Notice, that the magnitude of the deviations from ideality is greatest for the gas at 200K and least for the gas at 1000K.

3.4.1 DEVIATIONS OF REAL GASES FROM IDEAL BEHAVIOUR

The equation of state, $PV = nRT$, derived from the postulates of the kinetic theory, is valid for an ideal gas only. Real gases obey this equation only approximately and that too under conditions of low pressure and high temperature. The higher pressure and the lower temperature lead to the greater deviations from the ideal behavior.

In general, the most easily liquefiable and highly soluble gases show larger deviations. Thus, gases like CO_2 , SO_2 and NH_4 show much larger deviations than H_2 , O_2 and N_2 etc.

The deviations from ideal behaviour are best represented in terms of the **compressibility factor (Z)**, which is also called **compression factor** is defined as

$$Z = \frac{PV}{(PV)_{ideal}} = \frac{PV}{nRT} = \frac{PV_m}{RT} \dots \dots \dots (3.1)$$

For an ideal gas, $Z = 1$ under all conditions of temperature and pressure. The deviation of Z from unity is a measure of the imperfection of the gas under consideration.

The graphs plotted for the compressibility factors determined for a number of gases over a range of pressures at a constant temperature (0°C) are shown in Fig. 3.7. At extremely low pressures, all the gases have Z close to unity which means that the gases behave almost ideally. At very high pressures, all the gases have Z more than unity indicating that the gases are less compressible than an ideal gas. This is due to the fact that at high pressures, the molecular repulsive forces are dominant

As can be seen from Fig. 3.7, at moderately low pressures, carbon monoxide, methane and ammonia are more compressible than an ideal gas, i.e., PV is less than PV_{ideal} so that $Z < 1$. This is due to the fact that at low pressures, the long range attractive forces are dominant and favour compression. The compressibility factor Z goes on decreasing with increase in pressure, passes through a minimum at a certain stage and then begins to increase with increase in pressure. The gases now become less compressible than an ideal gas, i.e., PV is more than PV_{ideal} so that $Z > 1$.

It is evident from the figure that while carbon monoxide and methane exhibit marked deviations from ideal behaviour only at high pressures, ammonia shows large deviation even at low pressures. Hydrogen and helium at 0°C , however, are seen to be less compressible than the ideal gas at all pressures, i.e., $Z > 1$.

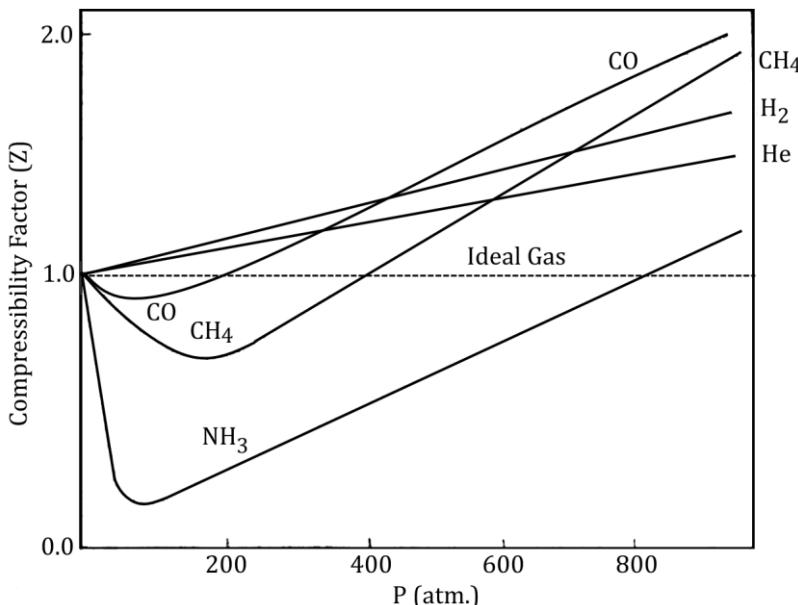


Fig. 3.7 Derivations of real gases from ideal behaviour

However, if the temperature is sufficiently low (e.g., below -165°C for hydrogen and below -240°C for helium) these gases also give the same type of $Z - P$ plots as are shown by ammonia, carbon monoxide and methane at 0°C . On the other hand, if the temperature is sufficiently high, the $Z - P$ plots of ammonia, carbon monoxide and methane will be similar to those of hydrogen and helium at 0°C , i.e., the value of Z will increase continuously with increase in pressure.

3.4.2 EFFECT OF TEMPERATURE ON DEVIATIONS FROM IDEAL BEHAVIOUR

The $Z - P$ plots of nitrogen at different temperatures varying between -70° and 50°C , are shown in Fig. 3.8.

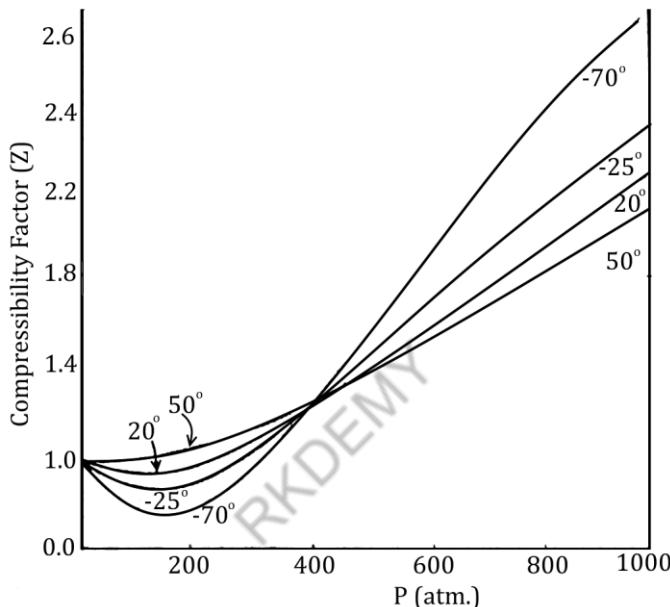


Fig. 3.8 Effect of temperature on deviation of nitrogen from ideal behaviour

It is seen that as the temperature is raised, the dip in the curve becomes smaller and smaller. At 50°C , the curve seems to remain almost horizontal for an appreciable range of pressure varying between 0 and about 100 atmospheres, showing that the compressibility factor Z becomes almost equal to unity under these conditions. In other words, the product PV remains constant and hence Boyle's law is obeyed within this range of pressure at 50°C . This temperature is called the **Boyle point** or **Boyle temperature**.

Below this temperature, the value of Z at first decreases, approaches a minimum and then increases as the pressure is increased continuously. Above 50°C , the value of Z shows a continuous rise with increase in pressure.

The Boyle temperature is different for different gases. For example, the Boyle temperature for hydrogen is -165°C and for helium it is -240°C . Thus, at -165°C , hydrogen gas obeys Boyle's law for an appreciable range of pressure. However, at any temperature below -165°C , the plot of Z vs P first shows a fall and then a rise as pressure is increased continuously. At a temperature above -165°C , however, Z shows a continuous rise with increase in pressure.

3.4.3 EXPLANATION FOR THE DEVIATIONS

In order to explain deviations from ideal behaviour, it is necessary to modify the kinetic theory of gases. The following two postulates of the kinetic theory do not appear to hold good under all conditions. Let us examine them more critically.

Postulate No. 1: ‘The volume occupied by the molecules themselves is negligibly small as compared to the total volume occupied by the gas.’

This postulate can be justified only under ordinary conditions of temperature and pressure. It can be shown by calculations that in some of the common gases, the volume occupied by the molecules themselves, under ordinary conditions, is only 0.014 per cent of the total volume of the gas. This is a negligible fraction indeed. But, if the pressure becomes too high (say, 100 atmosphere or more), the total volume of the gas will decrease appreciably whereas the volume of the molecules will remain almost the same because the molecules are incompressible. Hence, under the conditions of high pressure, the volume occupied by the gas molecules will no longer be negligible in comparison with the total volume of the gas.

The same thing happens when the temperature is lowered to a large extent. The total volume of the gas decreases considerably, no doubt, but the volume occupied by the molecules themselves remains practically the same. In this case, too, the volume occupied by the molecules will no longer be negligible. Therefore, the postulate No. 1 is not valid at high pressures and low temperatures.

Postulate No. 2: ‘The forces of attraction between gas molecules are negligible’.

This assumption is valid at low pressures or at high temperatures because under these conditions the molecules lie far apart from one another, but at high pressures or at low temperatures, the volume is small and molecules lie closer to one another. The intermolecular forces of attraction, therefore, are appreciable and cannot be ignored. Hence, the postulate No. 2 also does not hold under conditions of high pressure and low temperature. It is necessary, to apply suitable corrections to the ideal gas equation so as to make it applicable to real gases.

3.5 EQUATIONS OF STATE FOR REAL GASES

A number of equations of state have been suggested to describe the P-V-T relationship in real gases. The earliest and the best known equation is that of van der Waals.

3.5.1 THE VAN DER WAALS EQUATION OF STATE

In 1873, J.D. van der Waals proposed his famous equation of state for a non-ideal (i.e., imperfect gas). He modified ideal gas equation by suggesting that the gas molecules were not mass points but behave like rigid spheres having a certain diameter and that there exist intermolecular forces of attraction between them.

The two correction terms introduced by van der Waals are as follows

- 1. Correction due to volume of gas molecules:** The ideal gas equation $PV = nRT$ is derived on the assumption that the gas molecules are mass points, i.e., they do not have finite volume. Van der Waals abandoned this assumption and suggested that a correction term nb should be subtracted from the total volume V , in order to get the ideal volume which is compressible.

In order to understand the meaning of the correction term nb , let us consider two gas molecules as impenetrable and incompressible spheres, each of which has a diameter d as shown in Fig. 3.9.

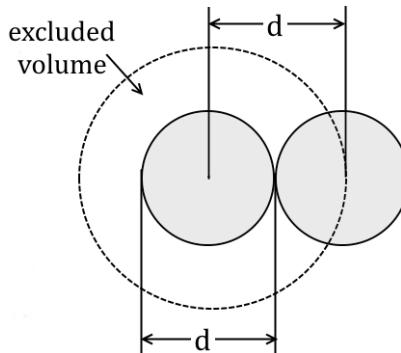


Fig. 3.9 Illustration of excluded volume

It is evident that the centres of the two spheres cannot approach each other more closely than the distance d . For this pair of molecules, therefore, a sphere of radius d and hence of volume $\frac{4}{3}\pi d^3$, constitutes what is known as the **excluded volume**.

The excluded volume per molecule is thus half the above volume, i.e., equal to $\frac{4}{3}\pi d^3$.

The actual volume of one gas molecule of radius r is $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi \left(\frac{d}{2}\right)^3 = \frac{1}{6}\pi d^3$.

∴ Excluded volume per molecule $\frac{2}{3}\pi d^3 = 4 \times \frac{1}{6}\pi d^3 = 4$ times the actual volume of the gas molecule.

The excluded volume per mole of the gas would be

$$N_A \times 4 \times \frac{4}{3}\pi d^3 = b$$

where N_A is the Avogadro number.

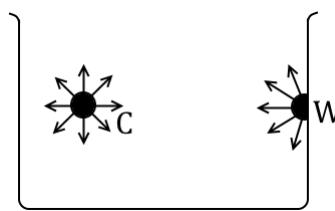
The compressible volume per mole of the gas would thus be $V - b$.

If volume V of the gas contains n moles, then the excluded volume would be nb . Hence the ideal volume which is compressible would be $V - nb$.

The volume b per mole is also known as **co-volume**.

- 2. Correction due to intermolecular forces of attraction:** In the derivation of the ideal gas equation, it was assumed that there are no intermolecular forces of attraction but in actual it is not so. In order to take into account the effect of intermolecular forces of attraction, let us consider a molecule lying somewhere in the midst of the vessel, as shown at the point C as shown in Fig. 3.10.

As it can be seen, it is being attracted uniformly on all sides by the neighboring molecules. These forces neutralize one another and there is no resultant attractive force on the molecule.

**Fig. 3.10 Molecular attraction**

However, as the molecule approaches the wall of the vessel, as shown at *W*, it experiences attractive forces from the bulk of the molecules behind it. Hence, it will strike the wall with a lower velocity and will exert a lower pressure than it would have done if there was no force of attraction. It is, therefore, necessary to add a certain quantity to the pressure of the gas in order to get the ideal pressure. The correct pressure, therefore, should be $P + p$.

CALCULATION OF THE CORRECTION FACTOR (P)

The force of attraction exerted on a single molecule which is about to strike the wall evidently depends upon the number of molecules per unit volume in the bulk of the gas, i.e., it depends directly upon the density of the gas. Further, the number of molecules striking the wall at any given instant also depends directly upon the density of the gas.

Thus, the total inward attractive pull on the molecules which gives a measure of the correction factor, *p*, is proportional to the square of the density (*p*) of the gas, i.e.,

$$p \propto \rho^2 \dots \dots \dots \dots \dots \quad (3.2)$$

But, density is inversely proportional to the volume and if *V* is the volume occupied by one mole of a gas, the value of *p* for one mole of a gas will be inversely proportional to the square of volume.

$$\therefore p \propto \frac{1}{V^2} = \frac{a}{V^2} \dots \dots \dots \dots \dots \quad (3.3)$$

where *a* is a constant depending upon the nature of the gas.

The kinetic gas equation for one mole of a real gas, therefore, takes the form

$$\left(P + \frac{a}{V_m^2} \right) (V_m - b) = RT \dots \dots \dots \dots \dots \quad (3.4)$$

where V_m stands for the molar volume of the gas.

The equation (3.4) is known as the van der Waals equation. The constants *a* and *b* are known as the van der Waals constants. These are characteristic of each gas.

The equation (3.4) is valid for one mole of a gas only. If there are *n* moles of a gas occupying volume *V*, then, as explained above, the excluded volume will be given by *nb* and the compressible volume, will $V - nb$. The pressure correction factor *p* for *n* moles, in the light of equation 3.2, will be proportional to $n^2 \rho^2$, i.e.

$$p \propto n^2 \rho^2 \propto n^2 \times \frac{1}{V^2}$$

$$p = \frac{an^2}{V^2} \dots \dots \dots \quad (3.5)$$

∴ The van der Waals equation for n moles of a gas becomes

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \dots \dots \dots \dots \dots \dots \quad (3.6)$$

Equation 3.6 is more accurate than the ideal gas equation $PV = nRT$ for expressing the P - V - T behaviour of real gases. Thus, if we take one mole of carbon dioxide at 47°C and compress it to different pressures, the volume, as observed by experiment, is found to be closer to that calculated from the van der Waals equation than to that calculated from the ideal gas equation. The departure from ideal gas equation becomes more and more wide as the pressure increases.

Table 3.3 Volume of Carbon Dioxide at 47°C under Different Pressures

Pressure (atm)	Volume (dm ³) of the gas		
	Observed experimentally	Calculated from the van der Waals equation	Calculated from the ideal gas equation
1	27.20	26.20	26.30
10	2.52	2.53	2.63
40	0.54	0.54	0.66
100	0.098	0.10	0.20

3.5.2 THE UNITS FOR THE VAN DER WAALS CONSTANTS

The units for the van der Waals constants a and b depend upon the units in which P and V are expressed. It is evident from equation 3.5 that the constant a is expressed by the factor pV^2/n^2 , i.e., pressure \times (volume) $^2/mol^2$.

If pressure is expressed in atm. and volume in dm^3 , the value of a will be in $\text{dm}^6 \text{ atm mol}^{-2}$. As regards b , is incompressible volume per mole of a gas. Hence, it must have the same units as volume per mole, e.g., $\text{dm}^3 \text{ mol}^{-1}$.

The van der Waals constants for some common gases are given in Table 3.4.

Table 3.4: The van der Waals Constants for Some Common Gases

Gas	$a (dm^6 atm mol^{-2})$	$b (dm^3 mol^{-1})$
Ammonia	4.17	0.0371
Argon	1.35	0.0322
Carbon dioxide	3.59	0.0427
Carbon monoxide	1.49	0.0399
Chlorine	6.49	0.0562

Ethane	5.49	0.0638
Ethylene	4.47	0.0571
Helium	0.034	0.0237
Hydrogen	0.024	0.0266
Hydrogen chloride	3.67	0.0408
Hydrogen bromide	4.45	0.0443
Methane	2.25	0.0428
Neon	0.21	0.0171
Nitric oxide	1.34	0.0279
Nitrogen	1.39	0.0319
Oxygen	1.36	0.0318
Sulphur dioxide	6.71	0.0564

The constant a is a measure of the van der Waals forces of cohesion existing between the molecules of a given gas. The greater the value of a , the greater is the strength of the van der Waals forces. The values of a for hydrogen and helium are very small, being 0.024 and 0.034, respectively, indicating that the cohesive forces (van der Waals forces) in these gases are very weak. The values of a for ammonia, carbon dioxide, chlorine and sulphur dioxide are very high being 4.17, 3.59, 6.49 and 6.71, respectively. This shows that the van der Waals forces in these gases are very strong. The greater the value of a , the greater is the ease with which a gas can be liquefied.

3.6 CRITICAL CONSTANTS OF A GAS

The most characteristic property of gases is that their molecules lie far apart from one another and are in continuous rapid motion. Each molecule, therefore, leads almost an independent existence. This is particularly at low pressure. However, if the temperature of a gas is lowered, the kinetic energy of the molecules decreases. Therefore, volume occupied by the gas also decreases. At a sufficiently low temperature, some of the slow moving molecules cannot resist the force of attraction and they come closer and ultimately the gas changes into the liquid state. Thus, liquefaction of gases results from decrease of

Increase of pressure has also the effect of bringing the gaseous molecules closer and closer to one another because of decrease in volume. This is also helpful in converting a gas into liquid. Thus, increase of pressure and decrease of temperature both tend to cause liquefaction of gases. For instance, sulphur dioxide can be liquefied at -8°C if the pressure is 1 atm. But it can be liquefied even at a higher temperature of 20°C if the pressure is increased to 3.24 atm.

The effect of temperature is more important than the pressure, because for each gas there is a certain temperature above which it cannot be liquefied, no matter how high a pressure may be applied. This temperature is known as the **critical temperature**. Thus, the **critical temperature** of a gas may be defined as that temperature above which it cannot be liquefied

howsoever high the pressure may be. For example, the critical temperature of carbon dioxide is 31.1°C. This means that it is not possible to liquefy carbon dioxide above 31.1°C by any means. At the critical temperature, a certain pressure is needed to liquefy the gas. This pressure is called the critical pressure. For instance, at 31.1°C carbon dioxide can be liquefied under a pressure of 72.9 atm. Thus, the critical pressure of the gas is 72.9 atm.

The critical temperature of oxygen is -118°C and that of hydrogen is -240°C. These gases, therefore, cannot be liquefied at ordinary temperatures; their critical pressures are 49.7 and 12.8 atm. respectively.

The volume occupied by one mole of a gas at its critical temperature and critical pressure is known as the **critical volume**. For example, critical volumes of carbon dioxide, oxygen and hydrogen are 940.0, 78.2 and 61.5 ml per mole, respectively.

3.7 DETERMINATION OF CRITICAL TEMPERATURE AND CRITICAL PRESSURE

These constants can be determined together by a simple method and it is generally used when the substance is in liquid state at ordinary temperatures. The method is based on the principle that at the critical temperature, the surface of separation (i.e., the meniscus) between the liquid and vapour phases disappears.

The liquid under examination is taken in vessel V enclosed in a glass jacket J as shown in Fig.3.11, the temperature of which can be varied gradually by circulating a suitable liquid from a thermostat. The vessel V is attached to a mercury manometer M containing air.

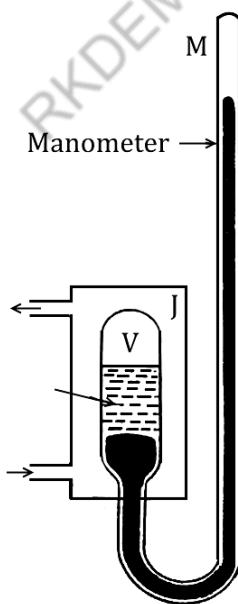


Fig. 3.11 Determination of critical temperature and critical pressure

The temperature is first lowered so that the vessel is cooled and the surface of separation between the liquid and its vapour becomes sharp. The temperature of the jacket is then raised gradually, this is continued until the meniscus between the liquid and its vapour just disappears and this temperature is noted.

The jacket is then cooled gradually until cloudiness due to the condensation of vapour appears again and this temperature is also noted. The mean of the two temperatures gives the critical temperature. The mean of the pressures read from the manometer M, corresponding to the two temperatures gives the critical pressure.

3.8 DETERMINATION OF CRITICAL VOLUME

In the determination of critical volume, advantage is taken of the observation made by Cailletet and Mathias that when the mean densities of liquid and saturated vapour of a substance are plotted against the corresponding temperatures, a straight line is obtained.

In Fig. 3.12, densities of saturated vapours are plotted along VC and those of liquid along LC , against the corresponding temperatures.

The point C where the two curves meet gives the critical temperature. This point is not sharp as the curve in this range is rather flat, as shown. The mean densities are then plotted against the various temperatures when a straight line MC is obtained. The point C where this line cuts the curve VCL , gives the critical temperature as the density of liquid now becomes identical with that of vapour. The point C also gives critical density. The critical volume is then obtained by dividing the molar mass of the substance by the critical density.

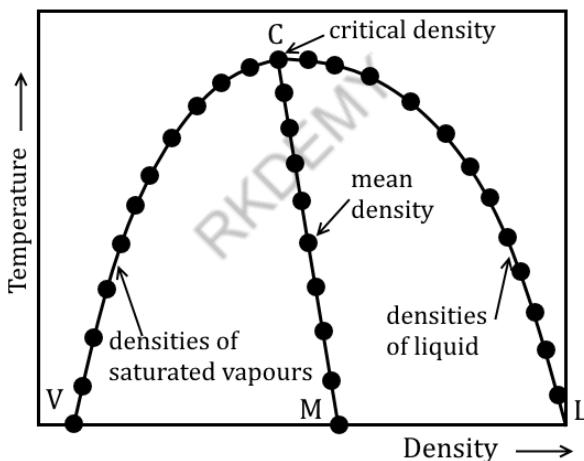


Fig. 3.12 Determination of the critical volume

3.9 CONDENSATION AND THE CRITICAL POINT

The most striking feature of real gases is that they cease to remain gases as the temperature is lowered and the pressure is increased. Figure illustrates this behavior; as the volume is decreased, the lower-temperature isotherms suddenly change into straight lines. Under these conditions, the pressure remains constant as the volume is reduced. This can only mean that the gas is "disappearing" as we squeeze the system down to a smaller volume. In its place, we obtain a new state of matter, the liquid. In the shaded region (condensation), two phases, liquid, and gas, are simultaneously present.

Finally, at very small volume all the gas has disappeared and only the liquid phase remains. At this point the isotherms bend strongly upward, reflecting our common experience that a liquid is practically incompressible.

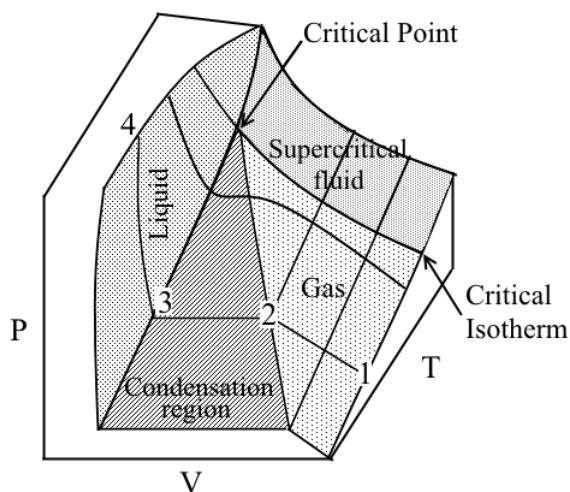


Fig. 3.13

To better understand this plot, look at the isotherm labeled (1). As the gas is compressed from (1) to (2), the pressure rises in much the same way as Boyle's law predicts. Compression beyond (2), however, does not cause any rise in the pressure. What happens instead is that some of the gas condenses to a liquid. At (3), the substance is entirely in its liquid state. The very steep rise to (4) corresponds to our ordinary experience that liquids have very low compressibilities. The range of volumes possible for the liquid diminishes as the critical temperature is approached.

3.10 THE CRITICAL POINT

Liquid and gas can coexist only within the regions indicated by the shaded area (condensation region) in the diagram above. As the temperature and pressure rise, this region becomes more narrow, finally reaching zero width at the *critical point*. The values of P , T , and V at this juncture are known as the *critical constants* P_c , T_c , and V_c .

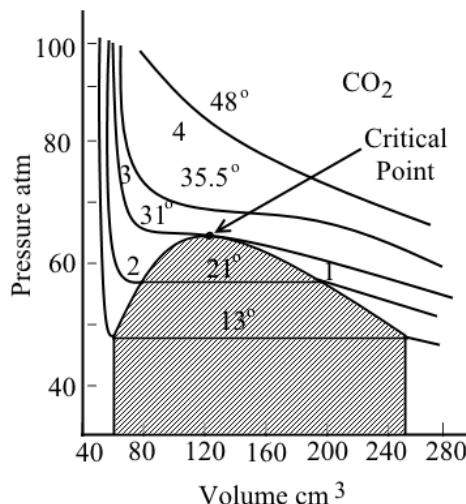
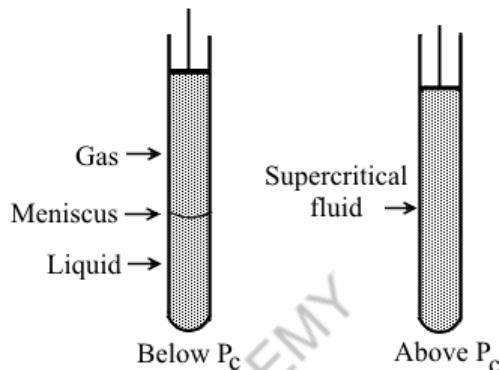


Fig. 3.14

The isotherm that passes through the critical point is called the *critical isotherm*. Beyond this isotherm, the gas and liquids become indistinguishable; there is only a single fluid phase, sometimes referred to as a *supercritical liquid*.

At temperatures below 31°C (the *critical temperature*), CO₂ acts somewhat like an ideal gas even at a rather high pressure (4). Below 31°C, an attempt to compress the gas to a smaller volume eventually causes condensation to begin. Thus at 21°C, at a pressure of about 62 atm (1), the volume can be reduced from 200 cm³ to about 55 cm³ without any further rise in the pressure. Instead of the gas being compressed, it is replaced with the far more compact liquid as the gas is essentially being "squeezed" into its liquid phase. After all of the gas has disappeared (2), the pressure rises very rapidly because now all that remains is an almost incompressible liquid. Above this isotherm (3), CO₂ exists only as a *supercritical fluid*.



What happens if you have some liquid carbon dioxide in a transparent cylinder at just under its P_c of 62 atm, and you then compress it slightly? Nothing very dramatic until you notice that the meniscus has disappeared. By successively reducing and increasing the pressure, you can "turn the meniscus on and off".

3.11 SUPERCRITICAL FLUIDS

The *supercritical* state of matter, as the fluid above the critical point is often called, possesses the flow properties of a gas and the solvent properties of a liquid. The density of a supercritical fluid can be changed over a wide range by adjusting the pressure; this, in turn, changes its solubility, which can thus be optimized for a particular application. The picture at the right shows a commercial laboratory device used for carrying out chemical reactions under supercritical conditions.

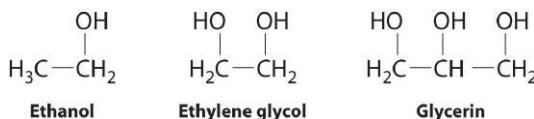
Supercritical carbon dioxide is widely used to dissolve the caffeine out of coffee beans and as a dry-cleaning solvent. Supercritical water has recently attracted interest as a medium for chemically decomposing dangerous environmental pollutants such as PCBs.

Supercritical fluids are being increasingly employed as substitutes for organic solvents (so-called "green chemistry") in a range of industrial and laboratory processes. Applications that involve supercritical fluids include extractions, nano particle and nano structured film formation, supercritical drying, carbon capture and storage, as well as enhanced oil recovery studies.

QUESTIONS

1. What is the main difference between intramolecular interactions and intermolecular interactions? Which is typically stronger? How are changes of state affected by these different kinds of interactions?
2. Describe the three major kinds of intermolecular interactions discussed in this chapter and their major features. The hydrogen bond is actually an example of one of the other two types of interaction. Identify the kind of interaction that includes hydrogen bonds and explain why hydrogen bonds fall into this category.
3. Which are stronger—dipole–dipole interactions or London dispersion forces? Why?
4. Explain why hydrogen bonds are unusually strong compared to other dipole–dipole interactions. How does the strength of hydrogen bonds compare with the strength of covalent bonds?
5. Liquid water is essential for life as we know it, but based on its molecular mass, water should be a gas under standard conditions. Why is water a liquid rather than a gas under standard conditions?
6. Describe the effect of polarity, molecular mass, and hydrogen bonding on the melting point and boiling point of a substance.
7. In group 17, elemental fluorine and chlorine are gases, whereas bromine is a liquid and iodine is a solid. Why?
8. The boiling points of the anhydrous hydrogen halides are as follows: HF, 19°C; HCl, –85°C; HBr, –67°C; and HI, –34°C. Explain any trends in the data, as well as any deviations from that trend.
9. Identify the most important intermolecular interaction in each of the following.
 1. SO₂
 2. HF
 3. CO₂
 4. CCl₄
 5. CH₂Cl₂
10. Identify the most important intermolecular interaction in each of the following.
 1. LiF
 2. I₂
 3. ICl
 4. NH₃
 5. NH₂Cl

11. Would you expect London dispersion forces to be more important for Xe or Ne? Why? (The atomic radius of Ne is 38 pm, whereas that of Xe is 108 pm.)
12. Both water and methanol have anomalously high boiling points due to hydrogen bonding, but the boiling point of water is greater than that of methanol despite its lower molecular mass. Why? Draw the structures of these two compounds, including any lone pairs, and indicate potential hydrogen bonds.
13. The structures of ethanol, ethylene glycol, and glycerin are as follows:



- Arrange these compounds in order of increasing boiling point. Explain your rationale.
14. Do you expect the boiling point of H₂S to be higher or lower than that of H₂O? Justify your answer.
15. Ammonia (NH₃), methylamine (CH₃NH₂), and ethylamine (CH₃CH₂NH₂) are gases at room temperature, while propylamine (CH₃CH₂CH₂NH₂) is a liquid at room temperature. Explain these observations.
16. Why is it not advisable to freeze a sealed glass bottle that is completely filled with water?
17. Which compound in the following pairs will have the higher boiling point? Explain your reasoning.
1. NH₃ or PH₃
 2. ethylene glycol (HOCH₂CH₂OH) or ethanol
 3. 2,2-dimethylpropanol [CH₃C(CH₃)₂CH₂OH] or n-butanol
(CH₃CH₂CH₂CH₂OH)
18. How does the O–H distance in a hydrogen bond in liquid water compare with the O–H distance in the covalent O–H bond in the H₂O molecule? What effect does this have on the structure and density of ice?
19. Explain why the hydrogen bonds in liquid HF are stronger than the corresponding intermolecular interactions in liquid HI.
20. For which substance will hydrogen bonding have the greater effect on the boiling point: HF or H₂O?

RKDEMY

Phase Rule

Statement of Gibbs' Phase Rule, Terms involved with examples, One Component System (Water), Reduced Phase Rule, Two Component System (Pb-Ag), Advantages and Limitations of Phase Rule. Numerical problems on Phase Rule.

4.1 GIBB'S PHASE RULE

The 'phase rule' was given by J.W. Gibbs in 1874 and further studied by H.W.B. Roozeboom in 1884. The phase rule is able to predict the conditions necessary to be specified for a heterogeneous system to exhibit equilibrium. The equilibrium conditions of a heterogeneous system involving number of components, and is influenced by temperature, pressure and concentrations of reactants. Under such conditions, there exists a relationship between the phases present, components taking part in equilibrium and degrees of freedom available. This relationship was first proposed by Willard Gibb's and is known as Gibb's Phase Rule.

It is represented as follows.

$$F + P = C + 2 \text{ or } F = C - P + 2$$

where P = phase, C = component, F = degree of freedom.

It is assumed that the equilibrium is not affected by gravitational, electrical, magnetic forces, or by surface tension. With the help of phase rule by using diagram, one can predict quantitatively the effect of changing temperature, pressure and concentration on heterogeneous system.

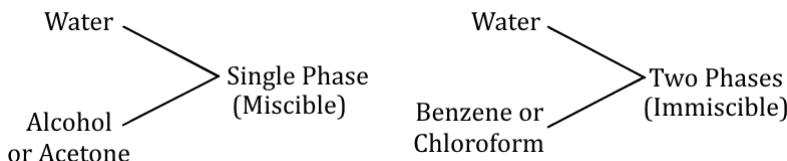
4.2 DEFINITION OF VARIOUS TERMS

4.2.1 PHASE

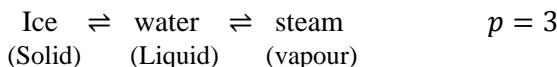
It is defined as "any homogeneous and physically distinct part of system which is separated from such other parts of system by well-defined boundary surfaces".

- Air is a mixture of various gases such as oxygen, nitrogen, carbon dioxide; argon, etc. constitute a single phase. This is because, air is homogeneous, the different gases are uniformly distributed and there is no definite boundary surfaces separating them. Hence, air, a mixture of gases, constitutes a single phase.
- Two liquids like alcohol and water which are miscible in all proportions constitute a single phase, since there is no separating boundary surface between alcohol and water. Other examples are acetone and water, ethanol and water, etc.

- (c) When two liquids are immiscible, they constitute two phases, e.g., benzene or chloroform and water.



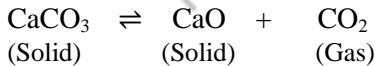
- (d) A solution of salt constitutes a single phase even though salt may be complex salt. For instant Mohrs salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ containing FeSO_4 and $(\text{NH}_4)_2\text{SO}_4$ constitute a single phase solution.
- (e) Each solid constitutes separate phase. For instance, different forms of sulphur when present in equilibrium, each form constitutes separate phase.
- (f) Homogeneous solid solution constitutes a single phase.
- (g) Water can exist in solid form as ice, in liquid form as water and in vapour form as steam. Each is a phase and can be represented as:



4.2.2 COMPONENT

The number of components of a system at equilibrium is the smallest number of independently variable constituents by means of which, the composition of each phase, can be directly expressed or represented by chemical equation.

Consider the decomposition of CaCO_3 into CaO and CO_2 .



Since each solid constitutes a single phase, this system has three phases, 2 solids and one gaseous, namely, CO_2 . Since the reaction is represented by chemical equation, by knowing any two the third one can be calculated. The composition of each phase can be represented as follows.

Phase 1 due to CaCO_3 is represented as



Phase 2 due to CaO is represented as



Phase 3 due to CO_2 is represented as

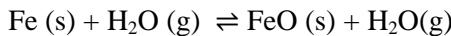


Thus, composition of each can be represented by knowing CaCO_3 , CaO or CaCO_3 , CO_2 or by CaO and CO_2 . This means only two constituents are sufficient to represent each phase in the system and hence it is a two-component system.

Considering water system, though water is present as solid, liquid and gaseous phases, it is the same substance chemically. Hence, it is a single component system.

In a similar way all the different forms of sulphur can only represent sulphur. It is once again a single component system.

The decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ into $\text{CuSO}_4 \cdot 3\text{H}_2\text{O} + 2\text{H}_2\text{O}$ is a two-component system. The decomposition of steam by iron can be shown as three-component system.



4.2.3 DEGREE OF FREEDOM OR VARIANCE

The number of degrees of freedom of a system is the number of variable factors like temperature, pressure and concentration which must be specified so that the system can be defined completely.

In order to understand this aspect, consider a single-component system like water system. If we consider any one phase individually only, then by applying the phase rule,

$$F = C - P + 2$$

We have

$$C = 1, P = 1$$

Substituting,

$$F = 1 - 1 + 2 = 2$$

The degree of freedom is two. The system is bivariant. This means to define the system consisting of a single phase, two variables, namely, temperature and pressure should be known.

When two phases are in equilibrium, say liquid water and water vapour, and then the number of phases is two.

By applying the phase rule,

$$F = C - P + 2,$$

We have

$$C = 1, P = 2$$

$$\therefore F = 1 - 2 + 2 = 1$$

That means, the degree of freedom is one. The system is univariant. Consider water boiling at 100°C . It is a case of liquid water being in equilibrium with water vapour. Two phases are in equilibrium at 100°C and 1 atmospheric pressure. In other words, two phases, liquid water and water vapour can be in equilibrium at 100°C , only at 1 atmospheric pressure or at 1 atmospheric pressure, the two phases can coexist at 100°C . That is either pressure or temperature alone can define the system.

When we consider all the three phases to be present in equilibrium, the number of phases is three and by applying the phase rule,

$$F = C - P + 2,$$

We have

$$C = 1, P = 3$$

$$\therefore F = 1 - 3 + 2 = 0$$

The degree of freedom is zero, the system is invariant. That means, all three phases can coexist only at an unique temperature and pressure. When one of them is altered, the number of phases will not remain three, one of the phases will disappear.

4.3 ONE-COMPONENT SYSTEM (WATER)

It is a single-component system and water can exist in different phases - solid phase as ice, liquid phase as water and gaseous phase as steam or water vapour. Hence water is only one chemical involved, therefore one component system. i.e. $C = 1$.

\therefore From Gibb's Phase rule,

$$F = C - P + 2$$

$$F = 1 - P + 2$$

$$\therefore F = 3 - P$$

i.e. the degree of freedom depends on the number of phases present at equilibrium.

Three different cases are possible

- (a) $P = 1$, $\therefore F = 3 - 1 = 2$ \therefore bivariant system
- (b) $P = 2$, $\therefore F = 3 - 2 = 1$ \therefore univariant system
- (c) $P = 3$, $\therefore F = 3 - 3 = 0$ \therefore invariant system

Thus, for any one-component system maximum number of degree of freedom is two. The most convenient variables are temperature and pressure.

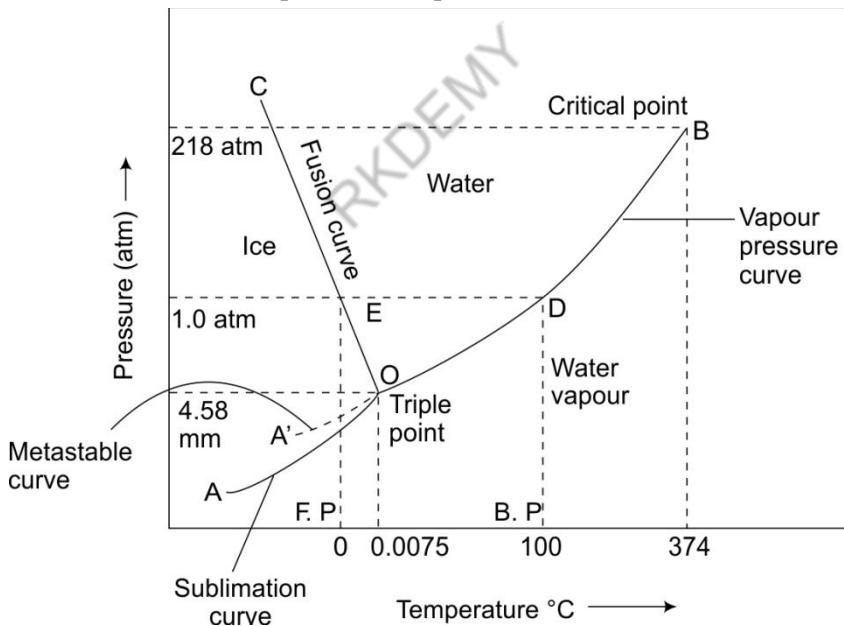


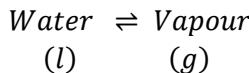
Fig 4.1 Phase equilibrium in water

The water system is shown in fig. consist of

CURVES

The **Curve OB** represents the equilibrium between liquid water and water vapours. Water boils at 100°C to get converted into vapour at atmospheric pressure, i.e. if the pressure is reduced, water will vaporise at lower temperature and if pressure is increased water will vaporise at higher temperature.

That means water can remain in liquid form even at high temperatures provided, the pressure is high. The upper limit is 374°C at 218 atmospheric pressure, above this temperature water cannot exist in liquid state.



Again along the curve for every temperature there is a corresponding pressure when both liquid water and water vapour can coexist. By applying the phase rule,

$$F = C - P + 2$$

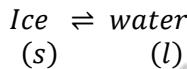
We have

$$C = 1, P = 2$$

$$\therefore F = 1 - 2 + 2 = 1$$

The system is univariant, the degree of freedom is one. That means by knowing the pressure or temperature, the system can be completely defined.

Similarly, the **Curve OC** represents the equilibrium between solid ice and liquid water. Here again for every pressure, there is a corresponding temperature when solid ice is in equilibrium with liquid water. This curve is also known as freezing point curve and degree of freedom along this line is one. The system is univariant.



Since by applying the phase rule,

$$F = C - P + 2$$

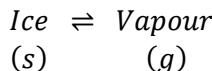
We have

$$C = 1, P = 2$$

$$F = 1 - 2 + 2 = 1$$

As the curve slopes towards the pressure axis, it can be inferred that freezing point of water is lowered as the pressure increases.

Curve OA represents the equilibrium between solid and vapour phases of water. This curve is also known as vapour pressure curve or sublimation curve. Along this line OA, for every temperature, there is a corresponding pressure at which both solid ice and water vapour coexist in equilibrium.



Applying the phase rule,

$$F = C - P + 2,$$

We have

$$C = 1, P = 2$$

$$F = 1 - 2 + 2 = 1$$

The degree of freedom is 1, the system is univariant and by knowing either the temperature or the pressure, the system can be completely defined.

AREA

The three curves OA, OB, OC represent the equilibrium conditions between two phases solid with vapour, vapour with liquid and liquid with solid phase of water. These curves divide the diagram into three areas representing single phase system, i.e., AOB representing vapour, BOC representing liquid and COA representing solid phase. Within these regions of single phase, both temperature and pressure have to be stated to define the system completely.

$$P = 1, \quad C = 1$$

$$\therefore F = C - P + 2 = 1 - 1 + 2 = 2 \text{ System is bivariant.}$$

METASTABLE CURVE (OA')

An unstable equilibrium can exist when cooling is carried under careful conditions without the separation of solid phase. This is represented by curve OA'. Under these conditions equilibrium can exist even at lower temperatures. However, such equilibrium is very unstable and can easily be disturbed by providing small amounts of nucleating substances. This will immediately result in solidification of super cooled liquid to solid ice.

TRIPLE POINT

Now consider the existence of all the three phases in equilibrium. The point where the curves OA, OB, OC meet, the point O is called the triple point, signifies an unique situation. Such equilibrium is only possible at a particular temperature 0.0075°C and pressure 4.58 mm.



$$F = C - P + 2$$

$$\therefore F = 3 - P = 3 - 3 = 0$$

$$\therefore F = 0 \qquad \text{System is invariant}$$

This means the degree of freedom is zero. Any change in temperature or pressure will disturb the equilibrium between the three phases, resulting in the disappearance of one of the phases.

4.4 TWO-COMPONENT SYSTEM

For a two-component system, the phase equation becomes:

$$F = 2 - P + 2 = 4 - P$$

Since in any equilibrium, at least one phase must be present, i.e.

$$F = 4 - 1 = 3$$

The degrees of freedom for a two-component system becomes three. This means, all the three factors like temperature, pressure and concentrations have to be specified in order to define the system completely. It is only possible to represent such equilibria by three-dimensional diagram. To depict such diagram on paper, will be a difficult proposition.

If one of the variables can be kept constant, the other two variables can be used for representing the equilibrium. It is also possible that one of the phases may have little effect on the equilibrium condition and can thus be ignored.

Examples of two-component system can be made up of the following types:

1. liquid – solid equilibria
2. liquid – liquid equilibria
3. liquid – gas equilibria
4. solid – gas equilibria

Of these four, liquid-solid equilibria is of practical importance and will be studied. Further such systems do not have gas phase and effect of pressure under such conditions is negligible. These equilibria exist under atmospheric pressure so that the degree of freedom is reduced by one. The phase equation can be written as:

$$F = C - P + 1$$

This is known as **condensed (reduced) phase equation** and is used to represent equilibrium with only two variables, namely, temperature and concentrations. Let us study a two-component system with the two components completely miscible in liquid state.

4.4.1 LEAD - SILVER SYSTEM

An example of liquid-solid system is the extraction of silver from lead ores. The lead ores contain 0.1% of silver and it is difficult to extract such small quantities. The silver content can be increased by adopting the following procedure. The ore is melted and cooled. As the cooling takes place, lead begins to separate out and is removed from the molten liquid.

Further cooling separates out more lead, so that the resulting mixture is more of silver. The maximum concentration of silver that can be obtained by this method is 2.6% Ag with 97.4% lead to 303°C.

The temperature composition curve for such a system can be represented as follows

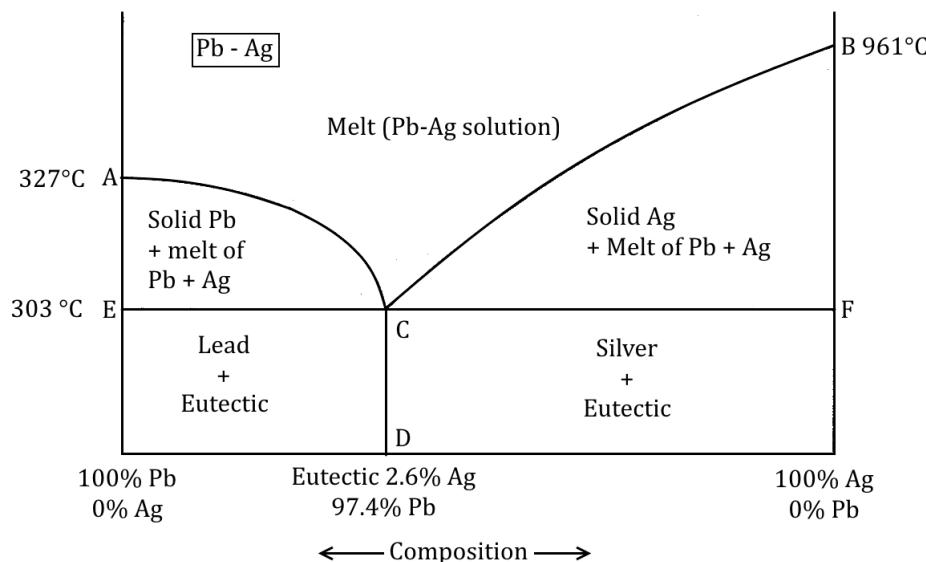


Fig. 4.2 Two Component (Ex. Pb-Ag) System

The two components of the system are represented by A and B, and they are miscible in molten state completely.

In the figure point A and point B represent the melting points of pure Pb and pure Ag. If Ag is added to Pb in molten state, the melting point decreases along the line AC. Similarly, point B represents the melting of pure Ag and any addition of Pb, lowers its melting point as represented by line BC.

The **Curve AC** is also called freezing point curve of Pb and represents the composition of the solutions saturated with component Pb in the range of temperatures from A to E.

Similarly, **Curve BC** is known as freezing point of component Ag and represents the composition of solution saturated with Ag and at temperature range from B to F

Since two phases are present, applying the reduced phase rule to the system, we have

$$F = C - P + 1,$$

We have

$$C = 2, P = 2$$

$$\therefore F = 2 - 2 + 1 = 1$$

The system is univariant along the lines AC and BC.

The two curves intersect at C, where both solids Pb and Ag are in equilibrium with the liquid phase. There are three phases in equilibrium at C and applying the reduced phase rule,

$$F = C - P + 1$$

We have

$$C = 2, P = 3$$

$$\therefore F = 2 - 3 + 1 = 0$$

The system is invariant and thus at C the temperature and composition remains constant as long as all the three phases coexist. If either the temperature or composition is changed the equilibrium will be changed where composition is 2.6% Ag and 97.4% Pb at 303°C are in equilibrium.

Further, C represents the lowest temperature at which any liquid state can exist since below this temperature, the liquid phase completely disappears. **Point C** is called as **Eutectic point**, temperature corresponding to this state is called as eutectic temperature and the composition of solids is called eutectic composition.

4.5 APPLICATIONS OF PHASE RULE

- It indicates the behaviour of a system under a particular set of conditions. Different systems with the same degree of freedom behave in a similar manner.
- It helps to find out, under a set of conditions whether all substances involved in an equilibrium can exist or whether a particular phase ceases to exist or whether any transformation has taken place.
- It does not require any knowledge of molecular or microstructure and it does not take into consideration nature and quantities of components present in equilibrium.
- Phase rule facilitates study of different equilibria and classify them accordingly.

5. Phase rule also has variety of applications in Electronic industries, Food Processing pharmaceutical science, etc. Some major applications of phase rule are as follows:
- (a) **Solders:** Solder is an alloy, which is homogenous mixture having melting point lower than that of the corresponding metal pieces, which have to be joined together. Most common solder is 'Soft solder' alloy of Pb and Sn.
 - (b) **Electrical Fuses:** Electric fuse is a device which acts as a circuit breaker and prevents electrical appliances from being damaged. It is generally composed of an alloy wire (typically tin and copper) which is thin and has a low melting point and an insulated outer casing of ceramic, fibre glass, plastic etc
 - (c) **Freezing mixture:** is a mixture of two or more substances (e.g. ice water and salt, or dry ice and alcohol) which can be used to produce temperatures below the freezing point of water.
 - (d) **Lyophilisation:** is also known as freeze drying, is a low temperature dehydration process that involves freezing the product, lowering pressure, and then removing the ice by sublimation. This is in contrast to dehydration by most conventional methods that evaporate water using heat.

4.6 LIMITATIONS OF PHASE RULE

1. Phase rule deals with systems in equilibrium and is not of much help in study for systems which attain equilibrium slowly.
2. Since no quantitative analysis is done, it is necessary to determine exactly the number of phases present under equilibrium conditions.
3. Though each solid is supposed to constitute a single phase, phase rule cannot be applied to solids in finely divided state.
4. It does not furnish enough information regarding the extent of changes that take place when the system shifts from one equilibrium to another.

SOLVED EXAMPLES

Example 1: Calculate number of Component and number of degree of freedom in

- (a) An aqueous solution of glucose.
- (b) A mixture of $\text{H}_2(\text{g})$, $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$
- (c) A mixture of $\text{CaCO}_3(\text{s})$, $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{g})$

Solution: (a) An aqueous solution of glucose.

In this Case $C = 2$, $P = 1$

$$\text{Hence } F = C - P + 2$$

$$F = 2 - 1 + 2$$

$$F = 3$$

The Choice of variables is T, P and concentration of the solution.

(b) A mixture of $H_2(g)$, $O_2(g)$ and $H_2O(g)$

In this Case $C = 3, P = 1$

$$\text{Hence } F = C - P + 2$$

$$F = 3 - 1 + 2$$

$$F = 4$$

This means that Temperature, Pressure and concentration of two of three components must be specified.

(c) A mixture of $CaCO_3(s)$, $CaO(s)$ and $CO_2(g)$

In this Case $C = 3, P = 3$

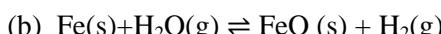
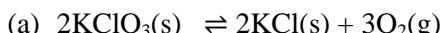
$$\text{Hence } F = C - P + 2$$

$$F = 3 - 3 + 2$$

$$F = 2$$

Need to specify two variables such as T and P.

Example 2: Find out number of Component and number of degree of freedom in



Solution: (a) Here $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$

In this Case $C = 2, P = 3$

$$\text{Hence } F = C - P + 2$$

$$F = 2 - 3 + 2$$

$$F = 1$$

Need to specify one variable such as T or P.

(b) $Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$

In this Case $C = 3, P = 3$

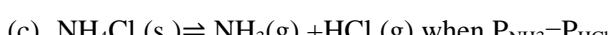
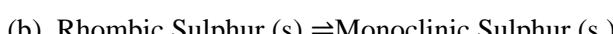
$$\text{Hence } F = C - P + 2$$

$$F = 3 - 3 + 2$$

$$F = 2$$

Need to specify two variables such as T and P.

Example 3: Determine the number of components, number of phases and the degree of freedom Phases in the following Systems



Solution: (a) $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(s)$

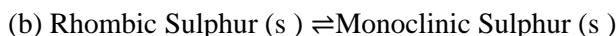
In this Case $C = 2, P = 3$

$$\text{Hence } F = C - P + 2$$

$$F = 2 - 3 + 2$$

$$F = 1$$

Need to specify one variable such as T or P.



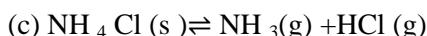
In this Case $C = 1, P = 2$

$$\text{Hence } F = C - P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

Need to specify one variable such as T or P.



In this Case $C = 2, P = 2$

$$\text{Hence } F = C - P + 2$$

$$F = 2 - 2 + 2$$

$$F = 2$$

Need to specify two variables such as T and P.

Example 4: Determine the number of components, number of phases and the degree of freedom Phases in the following Systems



Solution: (a) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$.

In this Case $C = 2, P = 1$

$$\text{Hence } F = C - P + 2$$

$$F = 2 - 1 + 2$$

$$F = 3$$

Need to specify three variables such as T, P and C.



In this Case $C = 2, P = 1$

$$\text{Hence } F = C - P + 2$$

$$F = 2 - 1 + 2$$

$$F = 3$$

Need to specify three variables such as T, P and C.

QUESTIONS

1. State Gibb's phase rule. Explain various terms involved in it.
2. Define phase with some examples.
3. What are the components of a system? Explain with examples.
4. Explain the terms (i) phase (ii) component (iii) degree of freedom.
5. Explain the applications of phase rule to one-component system.
6. Define degree of freedom of a system and explain with examples.
7. How many degrees of freedom are possible for a mixture of gases?
8. Explain the term condensed phase rule.
9. State and explain limitations of phase rule.
10. Discuss in brief lead – silver equilibrium with diagram.
11. What do you mean by reduced phase rule?
12. How many phases are present in a homogeneous system?
13. How many phases and components are present in each of the following systems:
 - (a) $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$
 - (b) An aqueous solution of salt (NaCl)
 - (c) Toluene in equilibrium with its vapour
14. Calculate the maximum possible number of phases and degrees of freedom for a one-component system.
15. Calculate the number of components and degree of freedom in the system of an aqueous solution of glucose.
16. Calculate the degree of freedom in a mixture of $\text{CaCO}_3(\text{s})$, $\text{CaO}(\text{l})$ and $\text{CO}_2(\text{g})$.
17. Is it possible to have a quadruple point (point having $P = 4$) in the phase diagram of a one-component system?
18. What is metastable equilibrium? Explain with reference to the water system.
19. What do you understand by a triple point? What is the variance of a one- component system at this point?
20. What is a condensed or reduced system? Explain with some example.
21. Can the phase rule equation in its original form be applied to a condensed system?
Write the reduced phase rule equation.
22. What do you understand by a eutectic point?
23. Draw the phase diagram for Pb-Ag system.
24. Define congruent melting point and name a system, which forms a compound with such a melting point.

Polymers

Introduction, Definition- Polymer, polymerization, Properties of Polymers, Molecular weight (Number average and Weight average), Numerical problems on molecular weight, effect of heat on polymers (glass transition temperature), Viscoelasticity, Conducting Polymers, Classification: Thermoplastic and Thermosetting polymers; Compounding of plastic, Fabrication of plastic by Compression, Injection, Transfer and Extrusion moulding, Preparation, properties and uses of PMMA and Kevlar.

Man used eight kinds of materials such as different metals, wood, ceramics, glasses, skins, horns and natural fibers until nineteenth century. In the nineteenth century, plastics and rubber were developed. The mass production of these materials was possible only after the Second World War with the growth of oil industry. Oil industry provided cheap raw materials for the production of synthetic polymers and synthetic rubbers. Since then these materials are contributing in raising the standard of living of mankind significantly.

Everyday features of the modern life such as motor cars, scooters, refrigerators, washing machines, telephones, etc. depend for their existence on these materials. The construction of printed circuit boards for electronic instruments and controls, computers, televisions, etc. is possible only with the use of polymers.

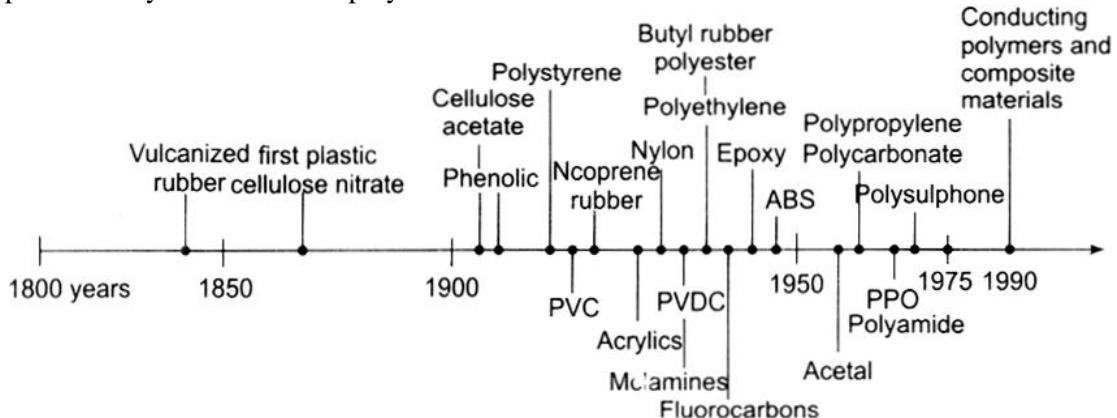


Fig. 5.1 Chronological development of important engineering polymers

Polymeric materials are extensively used as cheap substitute to older materials. Sometimes polymeric materials are used because the properties shown by these materials are unattainable by any other materials. The polymers are they are most versatile materials available in the wide range of strength, toughness, abrasion resistance and flexibility.

They are resistant to corrosion. Some of them have non-stick properties, electrical insulation capacity and transparency. They can be produced in a variety of colours and show colour fastness. They are available in wide range of chemical and solvent resistance. Being light in weight their transportation and labour cost is low. The strength to weight ratios is high. The ability of polymers to soften and flow at least once, one of their most valuable assets, as it allows them to be formed into complex shapes easily and inexpensively by processing them.

Petroleum oil is the major source of raw materials required for manufacturing of polymeric materials. The cost of polymeric materials is thus dependent on the cost of oil. Fabrication is shaping of already processed parts. Thus, it involves additional shaping operation, e.g., extruded sheets are vacuum formed into finished product, such as case of some instrument or PVC plastic film is laminated to cloth, etc. Finishing, assembly and integration, include operations as cutting, bonding, painting, etc.

5.1 DEFINITION OF POLYMERS AND ELASTOMERS

The word polymer derives from two Greek words “poly’ meaning many and “mer” meaning parts or units. Polymers are macromolecules built up by the repeated linking of a large number of small molecules called monomer ('mono' means single and 'mer' means part or unit). In order to facilitate polymerization, functionality of a monomer must be two or more than two. Such a monomer is known as polyfunctional monomer.

Functionality of a monomer refers to its ability to form new bonds. Thus, the functionality is the number of reactive sites or functional groups in the molecule (e.g., $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$, $-\text{SH}$, etc.). Thus, ethylene glycol ($\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$), adipic acid ($\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$) are bifunctional monomers.

The unsaturated compounds show polyfunctionality due to the presence of either double or triple bond in them. Thus, ethylene, ($\text{H}_2\text{C}=\text{CH}_2$) is a bifunctional monomer as double bond can open up and form two new sigma bonds.

5.2 DEGREE OF POLYMERIZATION (DP)

The degree of polymerization (DP) refers to the number of repeat units in the chain. The number of repeat units (DP) in chain specify the length of polymer chain. The molecular weight of a polymer can be calculated by multiplying DP by molecular weight of repeat unit. The molecular weight of polyethylene with DP equal to 1000 is 28,000 as the molecular weight of repeat unit involved $-(-\text{CH}_2-\text{CH}_2-)_n$ is $28n$ refers to DP.

By controlling DP (chain length and thus the molecular weight), it is possible to vary the physical properties of polymers. The polymers having low molecular weight are quite soft and gummy and those having higher molecular weight are tougher and heat resistant. This is because in linear and branched chain polymers the individual chains are held together by weak intermolecular forces of attraction.

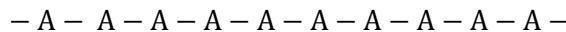
The strength of these forces increases with the chain length or molecular weight. For the polymers to be used for plastic films, etc., the molecular weight should be more than a certain critical value referred to as Mc-critical molecular weight. DP increases with time and temperature also depends upon concentration of monomer and the initiator. Strength of a polymer increases with increase in DP.

5.3 CLASSIFICATION OF POLYMERS

Polymers are classified as:

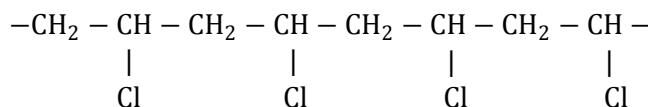
5.3.1 ON THE BASIS OF MONOMER

Whenever a polymer chain is made up of a single monomer, (represented as A), it is known as a **homopolymer**. It can be represented as



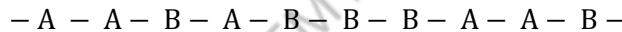
A homopolymer

Polyvinyl chloride is a homopolymer, the monomer $\left[\begin{array}{c} -\text{CH}_2 - \text{CH} - \\ | \\ \text{Cl} \end{array} \right]$ is repeated throughout the chain as shown in the structure.



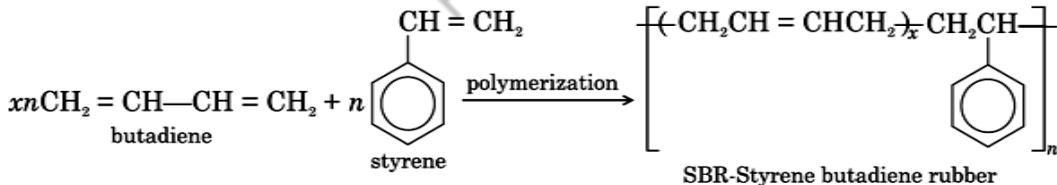
Polyvinyl Chloride [A homopolymer]

The polymer which has more than one monomer, repeated throughout the chain is known as a **copolymer**. If the two different repeat units are represented as A and B, the copolymer can be represented as



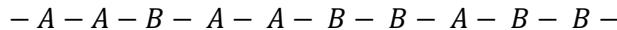
A copolymer

SBR (styrene butadiene rubber) is a copolymer obtained from styrene and butadiene.



5.3.2 ON THE BASIS OF STRUCTURAL ARRANGEMENT

When two different repeat units in a copolymer are distributed at random throughout the chain, the polymer is called a random copolymer. It can be represented as



A random copolymer

When two repeat units are distributed alternately throughout the chain, the polymer is known as alternating copolymer. It can be represented as



An alternating copolymer

When the sequence or block of one repeat unit is followed by a block of other repeat unit, which in turn is followed by a block of first repeat unit, and so on, then the polymer is known as block copolymer.

They are usually linear polymers and can be represented as



A block copolymer

The branched polymer in which, main chain is made up of entirely one repeat unit and the branch chain is made up of other repeat unit, is known as graft copolymer. It can be represented as

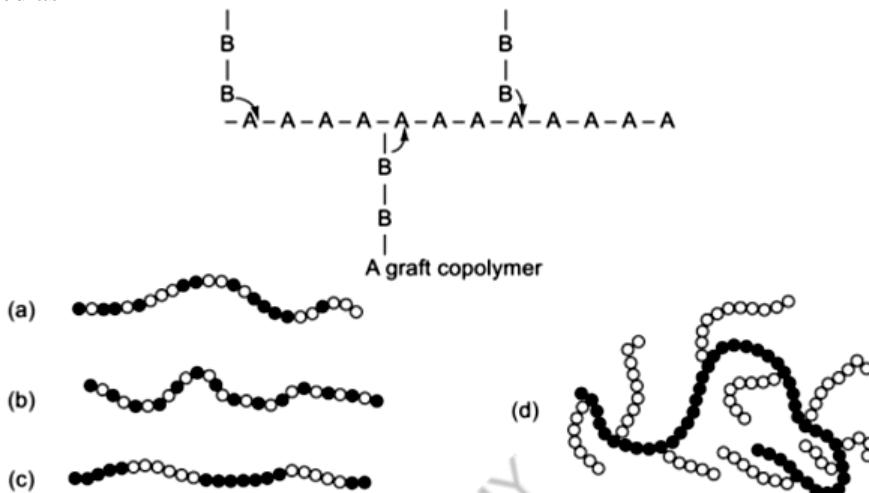
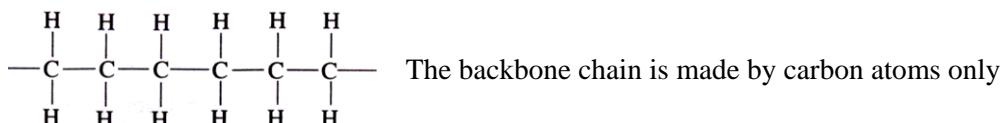
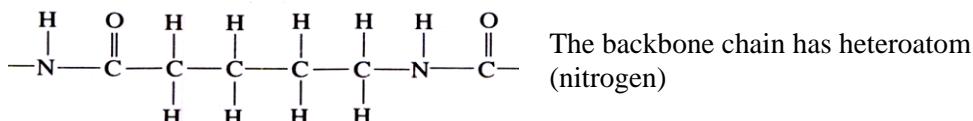


Fig. 5.2 Schematic copolymer arrangements, (a) A copolymer in which the different units are randomly distributed along the chain (b) A copolymer in which the units alternate regularly, (c) A block copolymer, (d) A graft copolymer.

When the same type of atoms are present in the polymer backbone chain, it is known as a homochain polymer, e.g. polyethylene (polythene).



When the polymer chain is made up of more than one type of atoms, it is known as heterochain polymer, e.g., polyamides (nylon), polyester, etc.



Linear Polymers: Repeating units have been linked together in a continuous length to form polymer molecules.

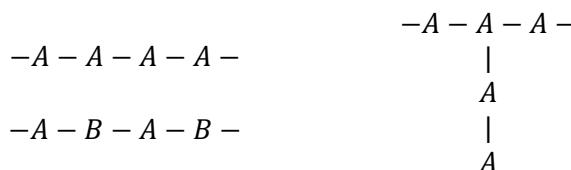


Fig 5.3 (a) Linear polymer

5.3 (b) Branched polymer

Branched Polymers: Attached to main chain there can be short branches. e.g. (1) Low density linear polyethylene (LDPE). Fig. 5.4 (a) or there can be long branches, e.g. (2) Fig. 5.4(b) or there can be branched branches Fig. 5.4(c).

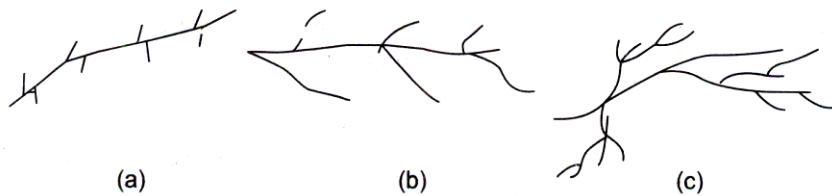


Fig. 5.4 A schematic representation of different types of branched polymers

Linear and branched polymers can be amorphous or semi crystalline depending on either secondary force between the polymer chains or close packing possible due to regularity in their structure. 100% crystalline structure is not possible in polymers because when solidification starts, the viscosity of material rises and long chains of polymer find it difficult to move around and arrange them in a symmetrical pattern needed for crystallisation.

Examples of amorphous polymers: Polystyrene, Polyvinyl chloride (PVC), Polymethyl methacrylate (PMMA), Some of the amorphous polymers are rubbery at ambient temperature (e.g., natural rubber, SBR), while some are rigid and transparent (e.g., PMMA, polystyrene, polycarbonates, PVC, etc.)

Examples of semicrystalline polymers: Polyethylene, polypropylene, poly-amide (nylons such as nylon 6, nylon 66), etc. Semicrystalline polymers may be transparent, translucent or opaque depending upon the size of crystallites present in amorphous matrix of the polymer (Crystallites are regions of crystallinity embedded in amorphous matrix).

Crystallites have dense packing of polymer chains and thus there are strong intermolecular forces in this region. Thus, presence of crystallinity enhances heat resistance, tensile strength, hardness while amorphous region may constitute to toughness and flexibility of the polymer.

Cross-linked Polymers: The cross-linked polymers have primary bonds between polymer chains and thus resultant structure is strong and rigid, three-dimensional structure. Most of the thermosetting polymers have such structure. Greater the cross-linking, greater is the rigidity (less is the mobility of polymer chains) of materials, less is its solubility and less it responds to remelting. Most thermosetting polymers have a cross-linked structure and some can withstand high temperature. Linear polymers with their less complicated structure can be rarely used at higher temperature. The cross-linking can be brought about after polymerization by various chemical reactions.

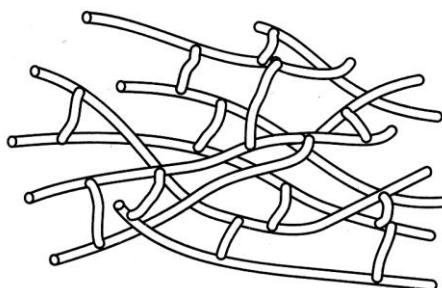


Fig. 5.5 Cross-linked polymer (A schematic representation)

The number of cross-links and their length can be controlled by using specific reaction conditions. Vulcanization of rubber provides light cross-links due to which rubber gets good elastic properties. High degree of cross-linking leads to impart high rigidity and dimensional stability, e.g., urea formaldehyde or phenol formaldehyde resins, ebonite. Monomers having two functional groups can produce long linear chain polymers. Monomers having three or more functional groups can give a cross-linked structure.

5.3.3 ON THE BASIS OF COMPOSITION

Organic and Inorganic Polymers: This classification is based on chemical composition of polymer chain. The backbone chain of organic polymers is essentially made up of carbon atoms. The hetero atoms such as O, N, and S usually satisfy the side valencies of carbon atoms, e.g., polyethylene, polymethyl methacrylate, PVC etc.

5.3.4 ON THE BASIS OF END USES

- (a) **Plastics** are the polymers which are shaped into hard and tough utility articles by application of heat and pressure, e.g., polyethylene, nylon, polystyrene, PVC, etc.
- (b) **Elastomers** or rubbers are the polymers which can be vulcanized into rubbery product exhibiting good strength and can undergo large reversible elongation at relatively low stress, e.g., natural rubber, synthetic rubbers such SBR (styrene butadiene rubber), BR (butyl rubber), etc.
- (c) **Synthetic fibers** are the polymers used for clothing. They can give rise to long filament-like materials having good strength and low elongation, e.g., nylon, terelene.
- (d) **Liquid resins** are potentially reactive chemicals which on curing give cross-linked polymers which can be used as adhesives, potting compounds, sealants etc. Examples are epoxy adhesives, melamine formaldehyde resin, poly-sulfide sealants, etc.

5.4 MOLECULAR WEIGHT OF POLYMERS

Molecular weight of a polymer influences various properties of it, such as solution viscosities, tensile and impact strength, softening temperature, and heat resistance. The low molecular weight polymers are generally soft and gum-like resins. The high molecular weight polymers are tougher and more heat resistant. Thus, control of molecular weight of a polymer is an important aspect of industrial polymerization. Hence, the determinations of molecular weight are of great importance in both the research and industry.

The molecular weight of a polymer depends upon the number of simple molecules joined together during polymerization reactions, i.e., upon the degree of polymerization. But the polymerization chains are broken at different stages; hence, the final product will contain the macromolecules of different weights. Most of the polymers are polydisperse, i.e., the molecules of the polymers sample do not have identical molecular weights (M). Hence it is necessary in their case to take average molecular weight. There are two types of average molecular weights.

5.4.1 THE NUMBER-AVERAGE MOLECULAR WEIGHT (M_n).

The Number-Average Molecular Weight (M_n) is obtained by dividing the total weight of the dispersed material with the number of molecules present, i.e.,

$$M_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots \dots}{n_1 + n_2 + n_3 + \dots \dots} \quad (5.1)$$

where $n_1, n_2, n_3, \dots \dots$ are the number of molecules having masses $M_1, M_2, M_3, \dots \dots$ respectively. The equation (5.1) can be written as

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} \quad (5.2)$$

where, n_i = number of monomer molecules

M_i = mass of simple monomer molecule

The number average molecular weight \bar{M}_n , assumes that each molecule makes an equal contribution to polymer properties irrespective of its size or weight of the polymer is obtained from measurement of colligative properties like osmotic pressure.

5.4.2 THE WEIGHT-AVERAGE MOLECULAR WEIGHT (M_w)

The weight average molecular weight gives representation to various molecular species in proportion to their weight in the given material. Light scattering and sedimentation equilibrium techniques, which not only depend upon the number of particles in a given mass or volume but also on the molecular size.

Hence, in the averaging process, molecular weight of each individual species is multiplied by the weight and not by the number, i.e.,

$$\bar{M}_w = \frac{m_1 M_1 + m_2 M_2 + m_3 M_3 + \dots \dots}{m_1 + m_2 + m_3} \quad (5.3)$$

If $n_1, n_2, n_3 \dots \dots$ denote the number of molecules having masses $M_1, M_2, M_3 \dots \dots$, then $m_1 = n_1 M_1$, $m_2 = n_2 M_2$, $m_3 = n_3 M_3 \dots \dots$, hence the equation (5.3) can be written as

$$\bar{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + \dots \dots}{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots \dots} = \frac{\sum n_i M_i^2}{\sum n_i M_i} \quad (5.4)$$

From equations (5.2) and (5.4), it is clear that M_w , is always greater than M_n , for polydisperse systems. For monodisperse system, $M_n = M_w$.

The ratio $\frac{M_w}{M_n}$, is known as distribution ratio or an index of polydispersity.

The molecular weight of a polymer can be determined by using following methods

- (a) Colligative property measurements such as Osmometry, Ebullioscopy and Cryoscopy
- (b) Light scattering measurements
- (c) Viscosity measurements.
- (d) Ultracentrifuge
- (e) Chemical analysis of end groups

Example 5.1: A protein sample consist of an equimolar mixture hemoglobin ($M_m = 15.5 \text{ kg mol}^{-1}$), ribonuclease ($M_m = 13.7 \text{ kg mol}^{-1}$) and myoglobin ($M_m = 17.2 \text{ kg mol}^{-1}$). Calculate the number average and weight average molar masses. Which is greater?

Solution: For number average

$$\begin{aligned}\overline{M}_n &= \frac{\sum n_i M_i}{\sum n_i} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3} \\ &= \frac{[(0.333 \times 15.5) + (0.333 \times 13.7) + (0.333 \times 17.2)] \text{ kg mol}^{-1}}{0.333 + 0.333 + 0.333} \\ &= 15.5 \text{ kg mol}^{-1}\end{aligned}$$

For weight average

$$\begin{aligned}\overline{M}_w &= \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2}{n_1 M_1 + n_2 M_2 + n_3 M_3} \\ &= \frac{[(0.333 \times 15.5^2) + (0.333 \times 13.7^2) + (0.333 \times 17.2^2)] \text{ kg mol}^{-1}}{(0.333 \times 15.5) + (0.333 \times 13.7) + (0.333 \times 17.2)} \\ &= 15.6 \text{ kg mol}^{-1}\end{aligned}$$

$$\therefore \overline{M}_w > \overline{M}_n$$

Example 5.2: Equal numbers of molecules with $M_1 = 10000$ and $M_2 = 100000$ are mixed. Calculate \overline{M}_n and \overline{M}_w . Which is greater ?

Hint: Assume $n_1 = n_2 = 10$

Solution: Let $n_1 = n_2 = 10$, then

For number average

$$\begin{aligned}\overline{M}_n &= \frac{\sum n_i M_i}{\sum n_i} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} \\ &= \frac{(10 \times 10000) + (10 \times 100000)}{10 + 10} \\ &= \frac{10^5(1 + 10)}{20} = 55000\end{aligned}$$

For weight average

$$\begin{aligned}\overline{M}_w &= \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{n_1 M_1^2 + n_2 M_2^2}{n_1 M_1 + n_2 M_2} \\ &= \frac{(10 \times 10000^2) + (10 \times 100000^2)}{(10 \times 10000) + (10 \times 100000)} \\ &= \frac{10^9(1 + 100)}{10^5(1 + 10)} = 91818\end{aligned}$$

$$\therefore \overline{M}_w > \overline{M}_n$$

Example 5.3: Equal masses of polymer molecules with $M_1 = 10,000$ and $M_2 = 100,000$ are mixed. Calculate \overline{M}_n and \overline{M}_w . Which is greater ? Hint: Assume $m_1 = m_2 = 200,000$

Solution: Let $m_1 = m_2 = 200,000$, then

$$n_1 = \frac{\text{mass } m_1}{\text{molar mass } M_1} = \frac{200000}{10000} = 20$$

$$n_2 = \frac{\text{mass } m_2}{\text{molar mass } M_2} = \frac{200000}{100000} = 2$$

For number average

$$\begin{aligned}\overline{M}_n &= \frac{\sum n_i M_i}{\sum n_i} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} \\ &= \frac{(20 \times 10000) + (2 \times 100000)}{20 + 2} \\ &= \frac{2 \times 10^5}{11} = 18182\end{aligned}$$

For weight average

$$\begin{aligned}\overline{M}_w &= \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{n_1 M_1^2 + n_2 M_2^2}{n_1 M_1 + n_2 M_2} \\ &= \frac{(20 \times 10000^2) + (2 \times 100000^2)}{(20 \times 10000) + (2 \times 100000)} \\ &= \frac{10^9(1 + 10)}{2 \times 10^5} = 55000\end{aligned}$$

$$\therefore \overline{M}_w > \overline{M}_n$$

Example 5.4: If a polymer sample has a population as:

5 molecules of molecular mass each = 25000

10 molecules of molecular mass each = 5000

20 molecules of molecular mass each = 7500

20 molecules of molecular mass each = 10000

25 molecules of molecular mass each = 15000

20 molecules of molecular mass each = 20000

Calculate its number average and weight average molecular mass of polymer.

Solution: For number average

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$= \frac{5 \times 25000 + 10 \times 5000 + 20 \times 7500 + 20 \times 10000 + 25 \times 15000 + 20 \times 20000}{5 + 10 + 20 + 20 + 25 + 20}$$

$$= \frac{125000 + 50000 + 150000 + 200000 + 375000 + 400000}{100} = \frac{1.3 \times 10^6}{100} = 13000$$

For weight average

$$\begin{aligned}\overline{M}_w &= \frac{\sum n_i M_i^2}{\sum n_i M_i} \\ &= \frac{5 \times 25000^2 + 10 \times 5000^2 + 20 \times 7500^2 + 20 \times 10000^2 + 25 \times 15000^2 + 20 \times 20000^2}{13,00,000} \\ &= \frac{3125 \times 10^6 + 250 \times 10^6 + 1125 \times 10^6 + 2000 \times 10^6 + 5625 \times 10^6 + 8000 \times 10^6}{1.3 \times 10^6} \\ &= 15480\end{aligned}$$

$$\therefore \overline{M}_w > \overline{M}_n$$

Example 5.5: In a sample, 20% of molecules have molecular weight of 20000; 30% have molecular weight of 30000 and remaining has molecular weight 60000. Calculate polydispersity index.

Solution: Let assume 100 molecules of

20% molecules means 20 molecules of molecular weight 20000

30% molecules means 30 molecules of molecular weight 30000

Remaining 50% molecules means 50 molecules of molecular weight 60000

For number average

$$\begin{aligned}\overline{M}_n &= \frac{\sum n_i M_i}{\sum n_i} \\ &= \frac{20 \times 20000 + 30 \times 30000 + 50 \times 60000}{100} \\ &= \frac{4 \times 10^5 + 9 \times 10^5 + 30 \times 10^5}{100} = \frac{43 \times 10^5}{100} = 43000\end{aligned}$$

For weight average

$$\begin{aligned}\overline{M}_w &= \frac{\sum n_i M_i^2}{\sum n_i M_i} \\ &= \frac{20 \times 20000^2 + 30 \times 30000^2 + 50 \times 60000^2}{20 \times 20000 + 30 \times 30000 + 50 \times 60000} \\ &= \frac{20(4 \times 10^8) + 30(9 \times 10^8) + 50(36 \times 10^8)}{4 \times 10^5 + 9 \times 10^5 + 30 \times 10^5} \\ &= \frac{80 \times 10^8 + 270 \times 10^8 + 1800 \times 10^8}{43 \times 10^5} \\ &= 50 \times 10^3 = 50000\end{aligned}$$

$$\therefore \frac{\overline{M}_w}{\overline{M}_n} = \frac{50000}{43000} = 1.163$$

Example 5.6: If 1000g of a polymer of molecular weight 1000g/mole and 1000g of a polymer of molecular weight 10^6 g/mole is mixed, what is the ratio $\frac{M_w}{M_n}$.

Solution: On converting data in tabular form

Fraction	M_i moles	n_i	$n_i M_i$	$n_i M_i^2$
1	1000 g/mole	1	1000	10^6
2	10^6 g/mole	10^{-3}	1000	10^9

For number average

$$\begin{aligned}\overline{M}_n &= \frac{\sum n_i M_i}{\sum n_i} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} \\ &= \frac{1000 + 1000}{1 + 10^{-3}} = \frac{2000}{1.001} = 2000\end{aligned}$$

For weight average

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

$$= \frac{10^6 + 10^9}{1000 + 1000} = \frac{10^6(1 + 10^3)}{2000} = 5 \times 10^5$$

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{5 \times 10^5}{2000} = 250.$$

5.5 TYPES OF POLYMERIZATION

There are three main types of polymerization

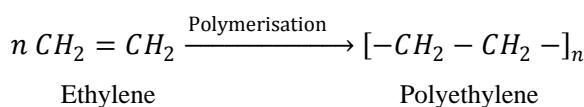
1. Addition polymerization
 2. Copolymerization
 3. Condensation polymerization

5.5.1 ADDITION OR CHAIN POLYMERIZATION

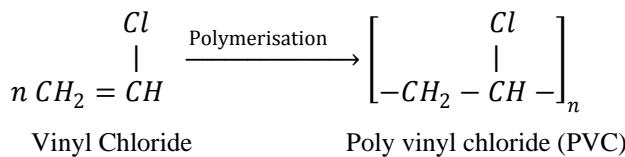
It is the union of two or more similar type of monomers which are unsaturated compounds through multiple bonds. The monomer usually contains one or more double bonds when by intermolecular rearrangement make the molecule bi-functional.

Examples

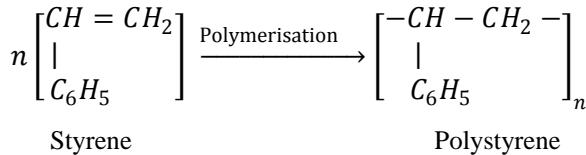
(a) Addition polymerisation of ethylene to give polyethylene.



(b) Polymerisation of vinyl chloride



(c) Polymerisation of styrene



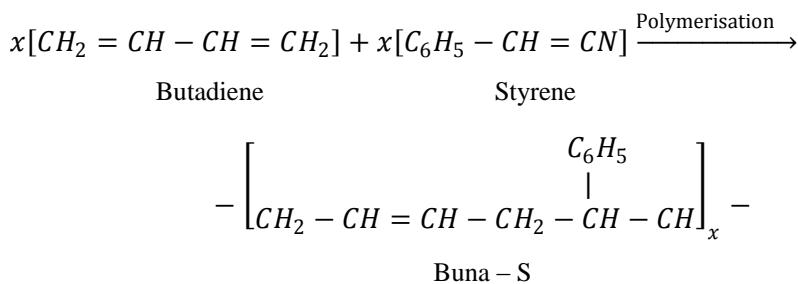
This type of polymerisation occurs in three stages. In the first stage, the monomer is activated in the presence of heat, light, catalyst or even an ionizing radiations like α, β, γ radiations which bring about the breakdown of the double bond. This kind of initiation is also brought about by certain substances called initiators. In the next stage, the monomer which is activated links to similar units forming long chains.

The propagation of the chain does not continue indefinitely though it is quite rapid. Finally, the chain undergoes termination due to either covalent bond formation or due to reaction with certain class of chemical substances known as polymerisation inhibitors.

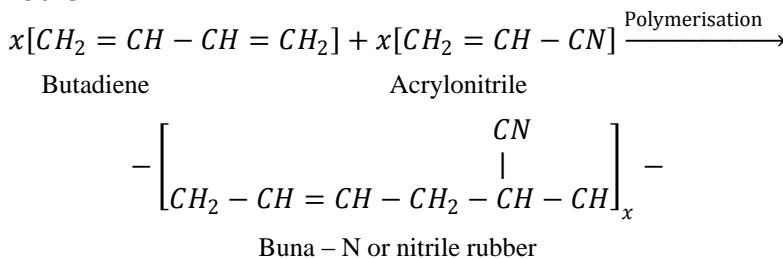
5.5.2 COPOLYMERISATION

Copolymerisation is the union of two or more different type of molecules without elimination of small unit like H_2O, NH_3 etc.

(a) **Buna-S-(GRS) or Butadiene styrene rubber** three parts of butadiene and one part of styrene are refluxed at $55^\circ C$ for 12-14 hours



(b) **Buna-N (Nitrile rubber):** obtained by polymerisation of Butadiene and acrylonitrile at $25 - 50^\circ C$



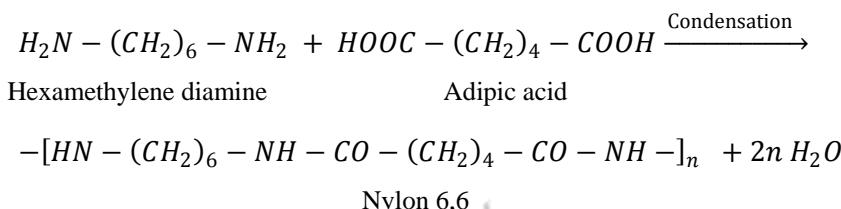
The chief advantage of copolymerisation is the production of wide range of materials differing very much in their properties. For example, poly acrylonitrile (PAN) and polyvinyl chloride (PVC) are not soluble in low boiling point solvents, whereas copolymer of acrylonitrile and vinyl chloride is easily soluble in acetone.

Similarly, PAN fibres are difficult to dye whereas copolymer acrylonitrile vinyl pyridine can be dyed. Further Buna-N synthetic rubber obtained by copolymerisation of acrylonitrile and butadiene is resistant to petrol and oil.

5.5.3 CONDENSATION POLYMERISATION

Condensation polymerisation is the union of two or more different type of molecules with elimination of small molecule like H_2O , NH_3 , etc., e.g. Nylon 6.6 phenol formaldehyde, urea formaldehyde.

Formation of polyhexa methylene adipamide (Nylon 6.6)



5.6 PLASTICS

A material consists of an essential ingredient, an organic material of high molecular weight which has the property of plasticity. Plastics are very important materials. Polymers are the materials made by polymerisation have repeated units in its structure. The plastic is the material in finished form. It is processed by either forming or moulding into a shape.

They are classified into thermoplastics and thermosetting on the basis of their structure and thermal stability.

S. N.	Thermoplastics	Thermosetting
1.	Linear structure	Cross-linked structure
2.	Softens on heating and becomes hard or rigid on cooling	Softens on first heating and becomes hard on further heating
3.	They can be reclaimed from waste	They cannot be reclaimed from waste
4.	Low molecular weights as compared to thermosetting	High molecular weights
5.	They are soft, weak and less brittle	Harder, stronger and more brittle than thermoplastics
6.	E.g. polyethylene, polyvinyl chloride, polystyrene, etc.	Silicones, phenol formaldehyde, urea formaldehyde, etc.

5.6.1 COMPOUNDING OF PLASTIC

In order to impart certain definite properties to finished products, plastic is compounded with other substances or ingredients. These ingredients either discharge a useful function during moulding or imparts some useful property to the finished product. This is called as compounding of plastic or mixing.

The various constituents which are added for compounding are:

- 1. Binders or Resins:** A plastic is usually classified depending on the type of binder used for its manufacture. It also determines the type of treatment needed to mould the articles from the plastic material. The function of binder is to hold the other constituents of the plastics together. A binder may compose of 30 to 100% of the plastic. Natural or synthetic resins are used as binder. In presence of catalyst they get converted into infusible cross link form. They also influence the properties of plastic. i.e. If the binder used in, has comparatively low molecular weight, the plastic gets moulded very easily and if binder have high molecular weight it will be hard.
- 2. Fillers or Extenders:** Fillers serve important functions as they reduce the cost of plastic per unit weight. They improve tensile strength, hardness of plastic material, finish of product and workability, opacity etc. They reduce shrinkage and brittleness. They impart certain specific properties to the finished products for instance. Addition of Quartz and mica-Improve hardness, whereas addition Barium salts make plastic impervious to X-rays. Also asbestos and mica-Improves heat and electrical resistance. In addition to these mentioned above, other materials in common use as fillers includes cotton, corn husks, graphite, carbon black, clay, paper pulp, wood flour, metallic oxide and metal powders (such as Fe, Cu, Pb and Al).
- 3. Lubricants:** Lubricants help in easy moulding of plastic. They prevent sticking of plastic to the mould. They impart flawless (flaw cracks in glass) glossy and elegant finish to the products. e.g. waxes, oils, oleates, stearates, soap etc.
- 4. Plasticizers:** The main function of plasticizer in plastic is to improve the plasticity and flexibility, so as to reduce the temperature and pressure required for moulding. Plasticizing properties are believed to be due to partial neutralization of intermolecular forces of attraction between macromolecules thereby increasing greater freedom of movement between the polymeric molecules but at the same time it reduces tensile strength and chemical strength. Plasticizers are often used with thermosetting plastics, particularly with cellulose derivatives. For instance, cellulose acetate has a tendency to decolour when moulded. Unless the moulding temperature is reduced by the addition of a suitable plasticizer. Varieties of organic materials are used as Plasticizers. They include non-drying vegetable oils, tributyl phosphate, triphenyl phosphate, camphor, esters of oleic stearic or phthalic acids etc.
- 5. Stabilizers:** Improves thermal stability during processing. For example Vinyl chloride and Vinylidene chloride polymers undergo decomposition and decolouration on moulding temperature so heat stabilizers are used. Commonly used stabilizers are:
 - (a) For **opaque moulding**: Salts of lead eg. White lead, Red lead, Lead chromate, Lead silicate, Lead naphthenate and litharge
 - (b) For **transparent moulding**: Stearates of lead, cadmium and barium.

6. **Catalyst or accelerator:** They are used in case of thermosetting plastic to accelerate the condensation polymerization to form the cross linked product. Catalyst used are H_2O_2 , Benzoyl peroxides, acetyl sulphuric acid, metals like Ag, Cu and Pb, metallic oxides-ZnO, ammonia and its salt.
7. **Dyes and pigments:** These are meant for providing decorative colours to plastic. Colour appeal is often important in high-polymer artifacts. The main colouring materials are organic dyestuffs and opaque inorganic pigments.

5.7 FABRICATION OF POLYMERS

Fabrication is the techniques of giving desired shape to plastic using mould. All plastic resins can be shaped into a variety of products by initially making them plastic and then subjecting them to the action of temperature and pressure in a mould. The different fabrication methods available are as follows.

5.7.1 COMPRESSION MOULDING

Thermoplastic and thermosetting resins can be moulded by this method. The die used for moulding purposes consists of two parts, upper and lower parts of male and female parts. In closed condition, the clearance between the two halves gives the desired shape to the product.

Generally, the lower part of mould is fixed, the upper part moves up and down, the movement being properly aligned because of guide pins present. The lower part of the die also has arrangement for heating and cooling by circulating fluids through pipe work.

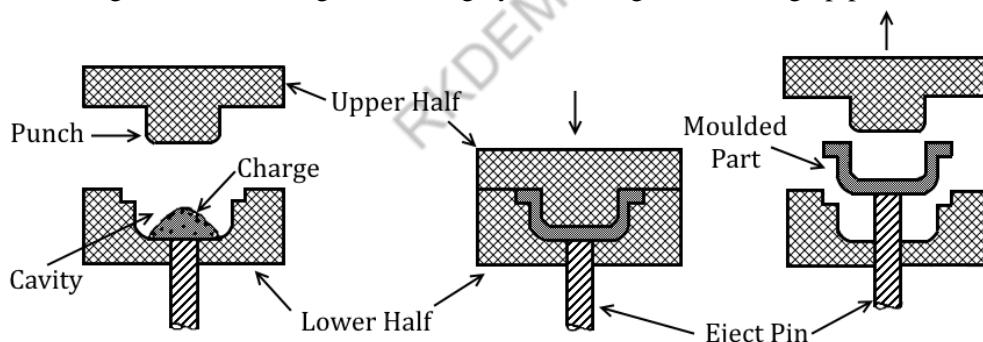


Fig 5.6 Fabrication by Compression molding for thermoplastics: (a) charge is loaded, (b) charge is compressed, cured, and (c) opening the mold halves and removing the part from the cavity.

Compression moulding involves transfer of required quantity of polymer mix consisting of other ingredients and polymer, into the cavity. A slight excess of material is taken to ensure that the cavity gets completely filled with material during the compression process. The charge in cavity is heated to make it easy to mould.

The upper part of mould is then lowered and the mould cavity closed by applying the necessary pressure and heat. This ensures the plastic mass get completely distributed uniformly in the mould, taking the shape of mould. Any excess runs off in the form of 'flash'.

For thermoplastic material, the die is allowed to cool so that the article becomes rigid enough to be expelled from the mould by the eject in mechanism. For thermosetting resins, the temperature is maintained at the curing temperature for the desired time to ensure the articles are properly cured.

Moulding temperatures and pressures for thermosetting polymers can be as high as 200°C and 70 kg/cm² respectively. The mould cycle starts with filling up of cavity with the material and end with the ejection of product formed from the mould cavity. This may vary from article to article depending upon its size and complexity. After the removal of article, the mould is made ready to receive the next charge by cleaning the mould with a blast of compressed air.

Few examples of article prepared by compression moulding are door handles, handles or electric iron, bottle cap. Screw cap, TV, radio cabinets toilet sheets.

5.7.2 TRANSFER MOULDING

In compression moulding, there are limitations with regards to size of die, effective heat transfer, and ability to mould intricate parts. Transfer moulding overcomes many of these limitations. The charge is preheated in transfer chamber, a pot which may sometimes form part of mould. The fluidised material from the pot is transferred to mould cavity due to plunging action of plunger through heated flow channels. This permits moulding of large and intricate parts, as the melted polymer flows easily. It is also possible to include inserts into the article. The mould itself is maintained at high temperature to facilitate curing of set resin in the mould. Thick sections are uniformly cured so that dimensional accuracies are maintained within limits.

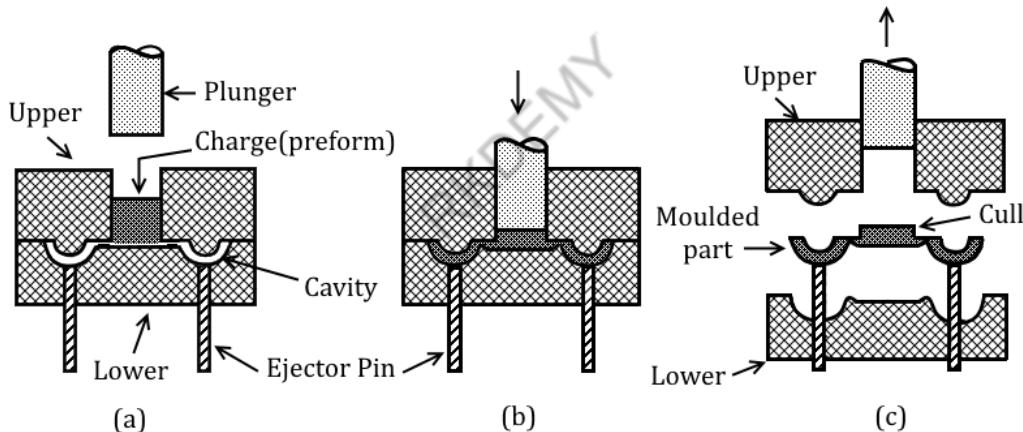


Fig. 5.7 Fabrication by Transfer moulding[The processes is (a) charge is loaded into pot; (b) softened polymer is pressed into mold cavity and cured; and (c) part is ejected.]

Cycle times in the case transfer moulding are shorter than those of compression moulding as the initial charge is in fluidised state and the mould is maintained at right temperature for proper curing. Thick portions and mechanically strong section can be fabricated by transfer moulding technique.

Examples of articles made by transfer moulding are complicated shape and delicate designs.

5.7.3. INJECTION MOULDING TECHNIQUE

This technique is used for high, speed moulding of thermoplastic resins. The machine consists of two parts - injection unit and the clamping unit which carries the mould. The injection unit is a hollow cylindrical device fitted inside with screw conveyor or plunger. The end attached to mould narrows down to form the nozzle.

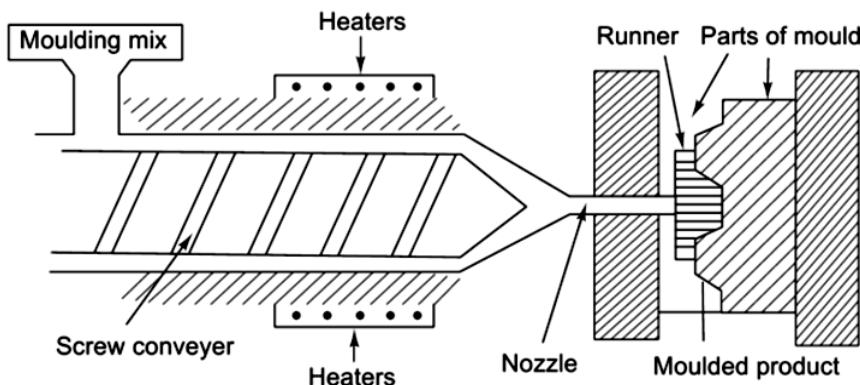


Fig. 5.8 Fabrication through injection moulding

Part of the forward section carries electrical heaters which heat the charge as it moves along the cylinder length. The movement of screw conveyer pushes the charge forward where it gets heated and melts. The temperature at the nozzle is between 130-260°C. The molten mass is then pushed through the nozzle into the cold mould. It immediately solidifies to rigid form. The mould is opened to eject the product and again closed and clamped tightly. Since the molten mass is pushed at high pressure, arrangements for keeping the two halves of mould should be secure. High pressure also ensures that molten material is evenly distributed in the mould cavity. Example of articles made by injection moulding are buckets, dustbin, telephone flowerpot, ballpen etc.

5.7.4 EXTRUSION MOULDING

It is mainly used for continuous moulding of thermosoftening plastics. Pipes, rods, hoses, tubes are some of the products manufactured by extrusion process. This method is also used to coat cables with a layer of plastic insulating material. The extruder is designed in such a way that as the raw mix passes along the length of extruder, it melts and flows out at uniform rate towards the die section.

The extruded product is shaped according to die characteristics, into rods, pipes or tubes and carried along a conveyer belt to be cut into specified lengths. Then tubular films are also made by extrusion process. Besides these methods of fabrication, blow moulding and calendering are some of the other methods used extensively for fabrication purposes.

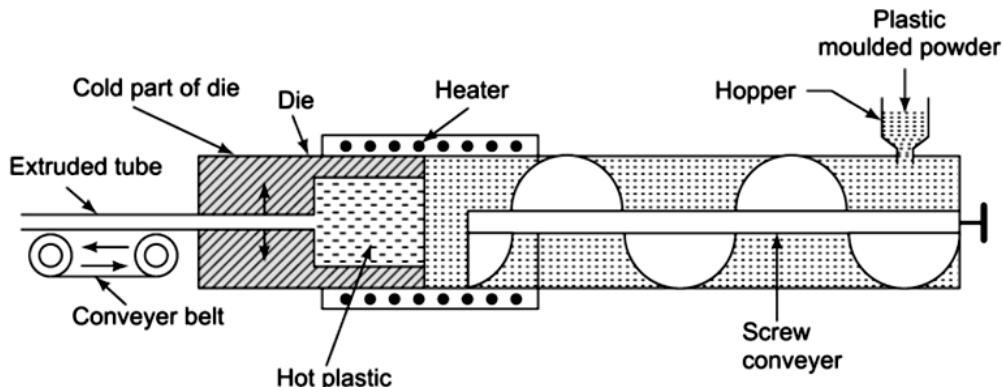
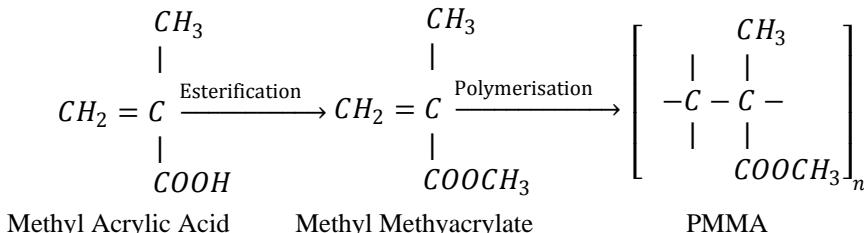


Fig. 5.9 Horizontal extrusion moulding of plastics.

Examples of articles made by extrusion moulding are insulated pipes, rain water pipe, garden hose etc.

5.8 PMMA (POLYMETHYL METHACRYLATE) OR LUCITE

It is prepared by polymerisation of methyl-methacrylate an ester of methyl acrylic acid, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOH}$ in presence of acetyl peroxide. It is an acrylic polymer



PROPERTIES

Colourless thermoplastic, hard, fairly rigid material with high softening temperature 130–140°C, it becomes rubber like above 65°C. It has high optical transparency, high resistance cured conditions. Its refractive index is 1.59. It's most important drawback is low resistance to hot acids and alkalis and low scratch resistance.

USES

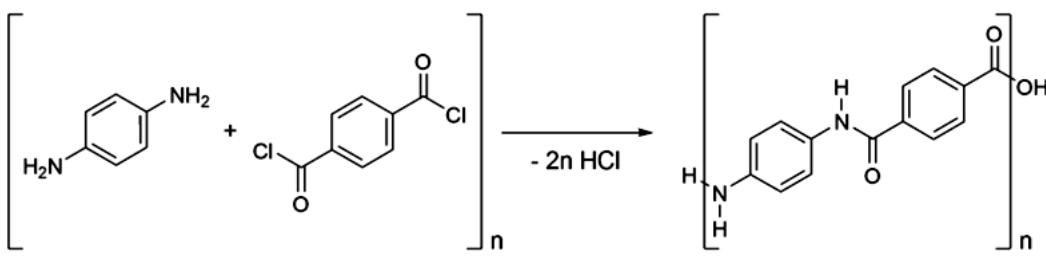
- Mainly used for protective coating and for manufacture of safety glass as it can be moulded easily to almost any shape.
- Emulsions of acrylic resins have been widely used as textile and leather finish, base coats on rubberised surfaces, etc.
- Widely used in industry in making lenses, bumper noses, transport models of complicated mechanisms, artificial eyes, emulsions, paints, adhesives, automobiles, wind screens, TV screens, optical parts of instruments, jewellery, etc.
- Solution polymer in volatile solvents used for adhesive and for heat and fume resistant enamels, luminescent paints, etc.

5.9 KEVLAR

Kevlar is the registered trademark for a para-aramid synthetic fiber, related to other aramids such as Nomex and Technora. Developed at DuPont in 1965, this high strength material was first commercially used in the early 1970s as a replacement for steel in racing tires. Typically it is spun into ropes or fabric sheets that can be used as such or as an ingredient in composite material components.

SYNTHESIS OF KEVLAR

Kevlar is synthesized in solution from the monomers 1,4-phenylenediamine (*para*-amino aniline) and terephthalic acid dichloride by condensation reaction yielding hydrochloric acid as a byproduct. The result has liquid crystalline behavior, and mechanical drawing orients the polymer chains in the fiber's direction. Hexamethyl-phosphoramide (HMPA) was the solvent initially used for the polymerization, but for safety reasons, DuPont replaced it by a solution of *N*-methyl-pyrrolidone and calcium chloride.



p-aminobiphenyl terephthalic acid dichloride

Kevlar

Kevlar production is expensive because of the difficulties arising from using concentrated sulfuric acid, needed to keep the water-insoluble polymer in solution during its synthesis and spinning.

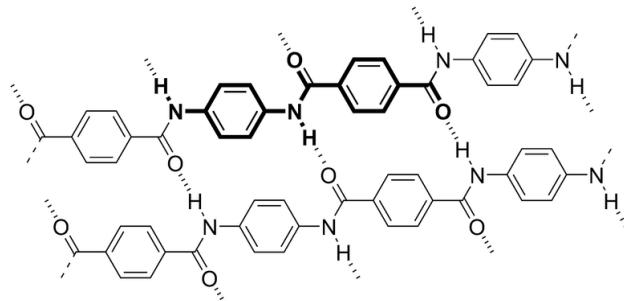
SEVERAL GRADES OF KEVLAR

1. *Kevlar K-29* – in industrial applications, such as cables, asbestos replacement, brake linings, and body/vehicle armor.
2. *Kevlar K49* – high modulus used in cable and rope products.
3. *Kevlar K100* – colored version of Kevlar
4. *Kevlar K119* – higher-elongation, flexible and more fatigue resistant.
5. *Kevlar K129* – higher tenacity for ballistic applications.
6. *Kevlar AP* – has 15% higher tensile strength than K-29.
7. *Kevlar XP* – lighter weight resin and KM2 plus fiber combination.
8. *Kevlar KM2* – enhanced ballistic resistance for armor applications

The ultraviolet component of sunlight degrades and decomposes Kevlar, a problem known as UV degradation, and so it is rarely used outdoors without protection against sunlight.

MOLECULAR STRUCTURE OF KEVLAR

Bold represents a monomer unit, **dashed** lines indicate hydrogen bonds.



PROPERTIES

When Kevlar is spun, the resulting fiber has a tensile strength of about 3,620 MPa, and a relative density of 1.44. The polymer owes its high strength to the many inter-chain bonds. These intermolecular hydrogen bonds form between the carbonyl groups and NH centers. Additional strength is derived from aromatic stacking interactions between adjacent

strands. These interactions have a greater influence on Kevlar than the van der Waals interactions and chain length that typically influence the properties of other synthetic polymers and fibers such as Dyneema. The presence of salts and certain other impurities, especially calcium, could interfere with the strand interactions and caution is used to avoid inclusion in its production. Kevlar's structure consists of relatively rigid molecules which tend to form mostly planar sheet-like structures rather like silk protein.

THERMAL PROPERTIES

Kevlar maintains its strength and resilience down to cryogenic temperatures (-196°C); in fact, it is slightly stronger at low temperatures. At higher temperatures the tensile strength is immediately reduced by about 10–20%, and after some hours the strength progressively reduces further. For example at 160°C (320°F) about 10% reduction in strength occurs after 500 hours. At 260°C (500°F) 50% strength reduction occurs after 70 hours.

APPLICATIONS OF KEVLAR

- (a) **Cryogenics:** Kevlar is used in the field of cryogenics for its low thermal conductivity and high strength relative to other materials for suspension purposes.
- (b) **Armor:** Kevlar is a well-known component of personal armor such as combat helmets, ballistic face masks, and ballistic vests.
- (c) **Personal protection:** Kevlar is used to manufacture gloves, sleeves, jackets, chaps and other articles of clothing designed to protect users from cuts, abrasions and heat.
- (d) **Sports equipment:** It is used as an inner lining for some bicycle tires to prevent punctures. In table tennis, plies of Kevlar are added to custom ply blades, or paddles, in order to increase bounce and reduce weight
- (e) **Shoes:** With advancements in technology, Nike used Kevlar in shoes for the first time.
- (f) **Audio equipment:** Kevlar has also been found to have useful acoustic properties for loudspeaker cones, specifically for bass and midrange drive units.
- (g) **Strings:** Kevlar can be used as an acoustic core on bows for string instruments.
- (h) **Drumheads:** Kevlar is sometimes used as a material on marching snare drums. It allows for an extremely high amount of tension, resulting in a cleaner sound.
- (i) **Woodwind reeds:** Kevlar is used in the woodwind reeds of Fibracell.
- (j) **Fire dancing:** Wicks for fire dancing props are made of composite materials with Kevlar in them.
- (k) **Frying pans:** Kevlar is sometimes used as a substitute for Teflon in some non-stick frying pans.
- (l) **Rope, cable, and sheath:** The fiber is used in woven rope and in cable, where the fibers are kept parallel within a polyethylene sleeve.
- (m) **Electricity generation:** Kevlar was used by scientists at Georgia Institute of Technology as a base textile for an experiment in electricity-producing clothing.
- (n) **Expansion joints and hoses:** Kevlar can be found as a reinforcing layer in rubber bellows expansion joints and rubber hoses, for use in high temperature applications, and for its high strength.

- (o) **Brakes:** The chopped fiber has been used as a replacement for asbestos in brake pads.
- (p) **Particle physics:** A thin Kevlar window has been used by the NA48 experiment at CERN to separate a vacuum vessel from a vessel at nearly atmospheric pressure, both 192 cm in diameter.
- (q) **Smartphones:** The Motorola Droid RAZR has a kevlar backplate, chosen over other materials such as carbon fiber due to its resilience and lack of interference with signal transmission.
- (r) **Composite materials:** Aramid fibers are widely used for reinforcing composite materials, often in combination with carbon fiber and glass fiber.

5.10 GLASS TRANSITION TEMPERATURE

Amorphous polymers when cooled below certain temperature become hard, brittle and glassy, but above this temperature they are soft, flexible and rubbery, this transition temperature of polymer is called '**glass transition temperature**'(T_g).

Glass transition temperature (T_g) is temperature at which internal energy of the molecules of polymer increases to such an extent that the chain segments of polymer molecules leaves their lattice site. The hard brittle state is known as the glassy state and the rubbery is the soft one. All chain motions are completely frozen in the glassy state, these are neither segmental nor molecular motions. When a polymer is heated beyond T_g the polymer passes from glassy state to rubbery state. Only segmental motion while molecular mobility is forbidden is rubbery state. Further heating much above T_g melt polymer starts flowing as each polymer chain eventually obtains sufficient energy.

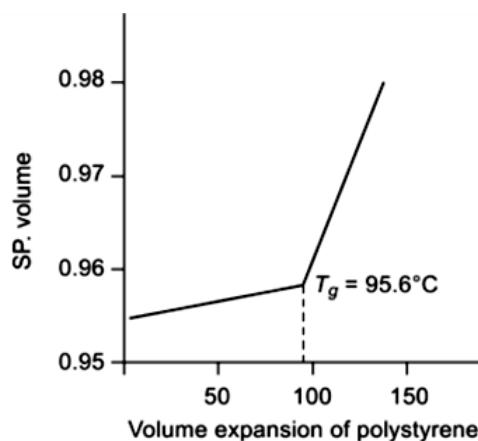
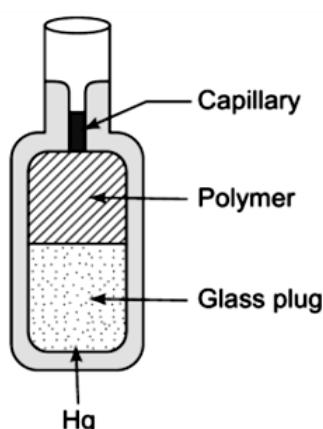
The temperature below which the polymer is in rubbery state and above which it is a liquid is called melting point of polymer (T_m). As no sharp melting points are shown by polymers. The transition temperature at which polymer passes from rubbery state to liquid state is called its flow temperature (T_f).

FACTOR AFFECTING GLASS TRANSITION TEMPERATURE

- (a) T_g depends on Chain length.
- (b) Extent of cross linking i.e. cross linking increases T_g
- (c) Barriers which binding internal rotation around chain links.
- (d) Presence of bulky group increases T_g
- (e) T_g depends on ability of a chain to chain flexibility.
- (f) Addition of plasticizer reduces T_g

DETERMINATION OF GLASS TRANSITION TEMPERATURE

Polymer appropriately contained in bulb at the bottom is kept immersed in a suitable liquid, usually mercury so as to give a column of the liquid in the capillary up to a convenient height for measurement. The positioning of the glass plug, as shown enables heating the test specimen avoiding overheating. The dilatometer placed in an outer bath may be heated at the present rate and pattern. From the rise of the liquid in the capillary on heating and consequent rise in the temperature the change in the volume of the specimens may be conveniently obtained.

**Fig. 5.10 Dilatometer**

T_m and T_g values of some of the polymers.

Polymer	R-unit	T _m °C	T _g °C
Polyethylen (HDPE)	-CH ₂ -CH ₂ -	137	- 90
Polyethylen (LDPE)	-CH ₂ -CH ₂ -	115	- 110
Polystyrene	-CH ₂ -CH-C ₆ H ₅	240	100
Polysiloxane	-OSi(CH ₃) ₂	-85	-123
Polyvinylchloride	-CH ₂ -CH- Cl	212	87

5.11 VISCOELASTICITY

Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Viscous materials, like honey, resist shear flow and strain linearly with time when a stress is applied. Elastic materials strain when stretched and quickly return to their original state once the stress is removed.

Viscoelastic materials have elements of both of these properties and, as such, exhibit time-dependent strain. Whereas elasticity is usually the result of bond stretching along crystallographic planes in an ordered solid, viscosity is the result of the diffusion of atoms or molecules inside an amorphous material. The viscosity of a viscoelastic substance gives the substance a strain rate dependence on time. Purely elastic materials do not dissipate energy (heat) when a load is applied, then removed. However, a viscoelastic substance loses energy when a load is applied, then removed.

Hysteresis is observed in the stress-strain curve, with the area of the loop being equal to the energy lost during the loading cycle. Since viscosity is the resistance to thermally activated plastic deformation, a viscous material will lose energy through a loading cycle. Plastic deformation results in lost energy, which is uncharacteristic of a purely elastic material's reaction to a loading cycle. Specifically, viscoelasticity is a molecular rearrangement, when a

stress is applied to a viscoelastic material such as a polymer, parts of the long polymer chain change positions. This movement or rearrangement is called **creep**.

Polymers remain a solid material even when these parts of their chains are rearranging in order to accompany the stress, and as this occurs, it creates a back stress in the material. When the back stress is the same magnitude as the applied stress, the material no longer creeps. When the original stress is taken away, the accumulated back stresses will cause the polymer to return to its original form. The material creeps, which gives the prefix visco-, and the material fully recovers, which gives the suffix -elasticity.

5.11.1 TYPES OF VISCOELASTICITY

- (a) **Linear viscoelasticity** is when the function is separable in both creep response and load. Linear viscoelasticity is usually applicable only for small deformations.
- (b) **Nonlinear viscoelasticity** is when the function is not separable. It usually happens when the deformations are large or if the material changes its properties under deformations.
- (c) An **anelastic** material is a special case of a viscoelastic material as it will fully recover to its original state on the removal of load.

USES

Viscoelastic materials are used for isolating vibration, dampening noise, and absorbing shock. They give off the energy absorbed as heat.

5.12 CONDUCTING POLYMERS

Initially, organic polymers are normally used as insulators because of their excellent insulating properties. In 1977, Heeger, Macdiand and Shirkawa for the first time showed that electrical conductivity of polyacetylene can be increased by 13 fold of magnitude by doping with electron acceptor and donors. Norman and others have achieved conductivity as high as copper metal in polyacetylene.

Polymers have π backbone when doped results in drastic electrical, electronic, magnetic and optical properties. The important doping reactions are oxidative, reductive and proton acid doping. An organic polymer with highly delocalised π -electron system, having electrical conductance of the order of conductor is called a **conducting polymer**. These compounds have various applications because of flexibility, ease of fabrication, stability, ease of process ability with the low cost.

5.12.1 CLASSIFICATION OF CONDUCTING POLYMERS

The conducting polymers can be classified into the following categories:

1. **Conductive element-filled polymer:** It is a polymer or resin filled with conducting elements such as carbon black, metallic fibres, metal oxides, etc. In this, the polymers acts as the binder to hold the conducting elements together in the solid entity. These polymers possess reasonably good conductivity; and are available at low cost, light in weight, mechanically durable and strong, and easily processed in different forms, shapes, and sizes.
2. **Conjugated π -electrons conducting polymer:** In this polymer backbones or associated groups consist of delocalized electron-pair or residual charge. In an electric field, conjugated π -electrons of the polymer get excited, and thereby can be transported

through the solid polymeric material. Overlapping of orbitals of conjugated π -electrons over the entire backbone results in the formation of valence bands as well as conduction bands, which extend over the entire polymer molecule. Presence of conjugated π -electron in a polymer increases its conductivity.

3. **Doped conducting polymer:** Doped conducting polymer is obtained by exposing a polymer to a charged transfer agent in either gas phase or in solution. In general, doping increases the surface conductivity of the polymer.
4. **Coordination conducting polymer (or inorganic polymer):** Coordination conducting polymer is a charge transfer complex containing polymer obtained by combining a metal atom with a polydentate ligand. Although the degree of polymerization in such polymers is small (18), yet they exhibit corrosion characteristics.
5. **Blended conducting polymer:** Blended conducting polymer is obtained by blending a conventional polymer with a conducting polymer either by physical or chemical change. Such polymers can be easily processed and possess better physical, chemical, and mechanical properties.

Important commercially produced conducting polymers include:

- (a) Polyacetylene polymers, e.g., poly-p-phenylene, polyquinoline, polyphenylene-co-vinylene, poly-m-phenylene sulphide, etc.
- (b) with condensed aromatic rings, e.g., polyanthrylene, polyphenanthrylene, etc.
- (c) With aromatic heteroaromatic and conjugated aliphatic units, e.g., polypyrrole, polythiophene, polyazomethane, polybutadienylene, etc.

QUESTIONS

1. What are polymers? Describe the classification of polymers.
 2. Distinguish between thermoplastics and thermosetting polymers.
 3. Write a note on melting and glass transition temperature .
 4. What is polymerization? Explain the degree of polymerisation.
 5. Discuss various types of polymerisation with suitable examples.
 6. What are advanced polymer materials?
 7. What are plastics? Explain compounding of plastics.
 8. Describe conducting polymers in detail
 9. What are electrical properties of polymers?
 10. What is meant by fabrication of plastics? Mention various methods of fabrication of plastics. Describe two methods of fabrication of plastics.
 11. Write synthesis, properties and uses of
 - (i)Kevler
 - (ii) PMMA
 12. What are the applications of kevler .
 13. Given the following composition –molar mass data for polydisperse polymer mixture

n_i (mol)	0.1	0.2	0.4	0.2	0.1
M_i (kg mol ⁻¹)	1.00	1.20	1.40	1.60	1.80

Calculate \overline{M}_n and \overline{M}_w .

14. A polymer sample has molecules having molecular weight of 1.0×10^5 , 2.0×10^5 , 3.0×10^5 . Calculate the number average molecular weight.
 15. A sample of polymer contains 10, 20, 30 and 40% molecules of the polymer with molecular weights 10000; 12000; 14000 and 16000 respectively. Calculate the number average and weight average molecular weight of the polymers.
 16. In a sample, 25% of molecules have molecular weight of 20000; 30% have molecular weight of 30000 and remaining have molecular weight 50000. Calculate number average molecular and weight average molecular weight and polydispersity index.

RKDEMY

Water

Introduction - Impurities in water, hardness of water- units (no conversions), types and numerical problems, determination of hardness of water by EDTA method and numerical problems. Softening of water by Ion Exchange process and numerical problems, BOD, COD- definition, significance and Numerical problems. Water purification-membrane technology- Electrodialysis, Reverse osmosis, and Ultra filtration.

Water plays a vital role in our life. It is most abundant, wonderful and useful solvent. Although it is the most abundant commodity in nature it is the most misused one also. 80% of the earth's crust is covered with water. The quantity available for actual use in the form of rivers, lakes, wells and ponds is hardly 0.5% of the world's water resources. This is because more than 96% of water is locked in oceans which are too saline to drink or to be used directly for agricultural, industrial or domestic purposes. 2% of the water is locked up in polar ice caps and glaciers.

About 1% is deeply underground and not accessible. Due to rapid industrialization, urbanization and growth in population man has successfully polluted most of the water available on earth. Industrial and domestic waste has caused significant pollution of the aquatic ecosystem (Trivedi and Goel 1986). Hence monitoring and control of pollution is essential for better future.

6.1. SOURCES OF WATER

- (a) **Surface waters:** Water present on the surface is called surface water. River water, stream water (flowing water, moorland surface drainage) as well as water in the ponds, lakes and reservoirs (low and surface drainage) is called surface water.
- (b) **Underground water:** Some part of rain water penetrates through the soil. It goes down and down till it reaches impermeable rocks. If the top of this rock is flat, it stays there. If the layers of rock have slope, water will flow the slope down. We get this water in the form of well or spring water. Water from lower measures of coal mines is also underground water.
- (c) **Rainwater:** it is purest form of water obtained by natural distillation

6.2 CHARACTERISTIC IMPARTED BY IMPURITIES IN WATER

The natural water is contaminated by different types of impurities i.e. physical impurities, chemical impurities and biological impurities.

6.2.1 PHYSICAL IMPURITIES

(a) **Colour:** These kinds of impurities affect the physical properties of water like colour, taste, turbidity and odour. The colour in the water is due to dissolved substances (metallic salts) and substances present as fine colloids. The change in colour of water is not harmful, unless it is associated with any chemical toxic nature.

For e.g. yellowish colour of water is due to presence of chromium salts, yellowish-red colour due to iron salts and red brown colour due to peaty matter.

(b) **Turbidity:** It is due to colloidal suspension such as clay, slit, insoluble substances, finely divided (organic and inorganic) matters and micro-organisms. Turbidity of the water depends up on quantity, size, shape and refractive index of insoluble constituents. It can be remove by sedimentation, followed by coagulation, filtration etc.

(c) **Taste:** It is interlinked directly with odour. The presence of dissolved minerals is responsible to impart undesired taste to the water.

E.g. bitter taste can be due to salts of iron, sulphates, manganese, aluminum or excessive lime. Soapy taste due to sodium bicarbonate, brackish taste is due to unusual amount of salts. Palatable taste is due to presence of dissolve gases (CO_2) and minerals (nitrates). Presence of algae also impart grassy odour to water bodies.

6.2.2 CHEMICAL IMPURITIES

These kinds of impurities affect the chemical properties of water like PH and acidity of water.

(a) **Inorganic and Organic Chemicals:** The various kind of organic and inorganic effluents released from paints, varnishes, dyes, pulp, textiles, detergent, drugs, insecticides, pesticides industries, tanneries etc are responsible to contaminate the water and causes harmful effects.

(b) **Acidity:** It is a power to neutralize hydroxyl ions. Surface and ground water attain acidity from industrial wastes like acids, oils, drainage and pickling liquors. Acidity is also caused by free CO_2 , H_2SO_4 .

(c) **Gases:** The presence of dissolved gasses, nitrogen and nitrogenous compounds and urea are generally found to be present in sewage and polluted water.

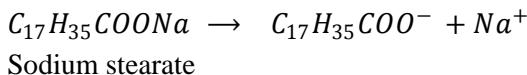
(d) **Mineral matters:** It is impart by rock and industry effluents. These include mineral acid, Ca, Mg, Na, K, Fe, etc.

6.2.3 BIOLOGICAL IMPURITIES

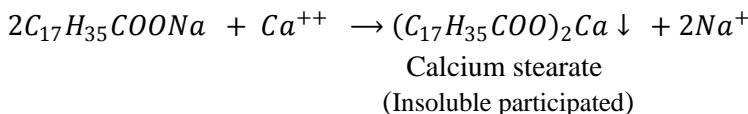
These kinds of impurities include microorganisms like algae, bacteria, fungi, viruses, pathogen, and parasite worms etc which actually come from the domestic discharge, sewage wastes and excreta.

6.3 HARDNESS OF WATER

Hardness can be defined as the soap consuming capacity of water sample. Soaps are sodium salts of fatty acids like oleic acids, palmetic acid and stearic acid. They dissolve readily in water to form lather due to which it has cleansing property.



But compounds of fatty acids with other metals do not dissolve in water. If water contains other metal ions like calcium and magnesium ions, they react with sodium salts of long chain fatty acids to form insoluble soap which we observe as curd.



These other metals ions are responsible for the hardness of water. Most important metal ions which cause hardness to water are calcium and magnesium ions. The hardness of water can be calculated from the amounts of calcium and magnesium ions present in water along with bicarbonates, sulphates, chlorides and nitrates.

The relation between the type of water and degree of hardness is as given below.

Type of water	Hardness as ppm of CaCO_3
Soft	0—75
Moderately hard	75 — 150
Hard	150—300
Very hard	above 300

6.3.1 TYPES OF HARDNESS

Hardness of water is the characteristics property by which it prevents lathering of soap. This is due to the presence certain salts of calcium, magnesium and other heavy metals.

- (a) **Temporary hardness:** “T. H.” is the term applied to the hardness caused by dissolved bicarbonates and carbonates of Ca, Mg and other heavy metal atoms. This is also known as alkaline or carbonate hardness i.e. $\text{Ca}(\text{HCO}_3)_2$, MgCO_3 . When water containing calcium and magnesium bicarbonates is heated, soluble bicarbonates are converted into insoluble carbonates and hydroxide. On filtering of such water, soft water is obtained. The hardness which can be removed by boiling is referred as ‘temporary hardness’ or bicarbonate hardness.
- (b) **Permanent hardness:** ‘Permanent hardness’ is the term applied to the hardness caused by dissolved chlorides, nitrates and sulphates of calcium and magnesium and other heavy metal ions. This hardness cannot be removed by boiling the water sample. Sum of temporary and permanent hardness is referred to as total hardness. Permanent hardness can only be removed by softening methods like lime-soda, ion exchange or zeolite process. It is also known as non carbonate or non alkaline hardness. i.e. MgCl_2 , CaCl_2 .

6.3.2 UNITS OF HARDNESS

Hardness in water is expressed in terms calcium carbonate equivalents as:

- (a) **Parts Per Million (ppm):** It expresses the concentration of hardness causing salt as the number of parts of substance by weight in million parts by weight of water. One part per million, i.e., 1 ppm hardness means one part of CaCO_3 equivalent hardness is present in one million parts of water. For calculation, the units of weight used should be same for the substance and water ($1 \text{ ppm} = 1 \text{ mg/litre}$).
- (b) **Clark's Degree ($^{\circ}\text{Cl}$):** It is the number of grains of CaCO_3 equivalent hardness per gallon of water. It is also expressed as parts of CaCO_3 equivalent hardness per 70,000 parts of water. Thus, 1° Clark is equal to one grain of CaCO_3 equivalent hardness in one gallon of water which is same as 1 part of CaCO_3 equivalent hardness per 70,000 parts of water.
- (c) **Degree French ($^{\circ}\text{Fr}$):** It is the part of CaCO_3 equivalent hardness per 10^5 parts of water. The various units of hardness are inter-convertible and by using the following information, hardness in one unit can be expressed in other units as -

$$\begin{aligned} 1 \text{ ppm} &\equiv 1 \text{ mg/litre} \equiv 0.1^{\circ}\text{Fr} \equiv 0.07^{\circ}\text{Cl} \\ 1^{\circ}\text{Cl} &\equiv 14.3 \text{ ppm} \equiv 14.3 \text{ mg/litre} \equiv 1.43^{\circ}\text{Fr} \\ 1^{\circ}\text{F} &\equiv 10 \text{ ppm} \equiv 10 \text{ mg/litre} \equiv 0.7^{\circ}\text{Cl} \end{aligned}$$

Table 6.1: Calculation of equivalents of CaCO_3

Dissolved impurities	Molar mass	Chemical Equivalent or Equivalent Weight	Multiplication factor for conversion into CaCO_3 equivalents
$\text{Ca}(\text{HCO}_3)_2$	162	81	100/162
$\text{Mg}(\text{HCO}_3)_2$	146	73	100/146
CaSO_4	136	73	100/136
CaCl_2	111	55.5	100/111
MgSO_4	120	60	100/120
MgCl_2	95	47.5	100/95
CaCO_3	100	50	100/100
MgCO_3	84	42	100/84
$\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$	278	139	100/278
$\text{Ca}(\text{NO}_3)_2$	164	82	100/164
$\text{Mg}(\text{NO}_3)_2$	148	74	100/148
$\text{Al}_2(\text{SO}_4)_3$	342	57	100/114
FeCl_2	127	63.5	100/127
Ca^{2+}	40		100/40
Mg^{2+}	24		100/24

* NaCl , Na_2SO_4 , KCl do not contribute hardness in terms of CaCO_3 equivalent.

6.4. EFFECTS OF HARD WATER IN INDUSTRIES

Industries like paper, sugar, chemical textile, pharmaceutical industries, etc. require large amount of water and for steam generation, heat exchangers and condensers. Water free from all kinds of impurities with hardness below 25 ppm is desirable for the industrial purpose.

The pH of the water used in industries should be 7 to 8.0 and free from all types of impurities.

Water of higher hardness causes the following problems in industries.

- (a) In **textile industry** calcium/magnesium soap precipitates adhere to the fabric material and interfere with dyeing process which affects the shades.
- (b) In **boilers** it leads to the formation of scales and sludges which reduces efficiency of boilers.
- (c) In **sugar industry** presence of calcium magnesium salt interfere with the crystallisation of sugar.
- (d) In **paper industry** smooth finish and proper colour cannot be obtained if hard water is used.
- (e) **Pharmaceutical industry:** If hard water is used for preparing pharmaceutical products like drugs, injections, lotions, syrups, etc., then the hardness causing ions in water may react with them to produce undesirable products. This may reduce efficiency of the material or create adverse action.
- (f) **Concrete making:** If the water containing chlorides, sulphates, etc. is used may affect the hydration of compounds in cement and final strength of concrete will be affected.

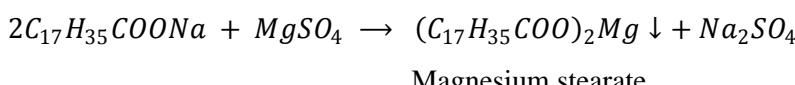
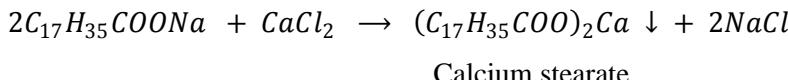
6.5. ESTIMATION OF HARDNESS

Hardness of water can be determined by two methods:

6.5.1. SOAP TITRATION METHOD

Total hardness of water can be determined by titrating a fixed volume of water sample against standard alcoholic soap solution. Formation of stable lather which persists for two minutes is the end point of titration.

In the beginning sodium soap will precipitate all hardness causing ions as their respective stearates.



(Thus, water which readily lathers with soap is called soft water whereas water which forms scum or precipitate and does not form lather immediately is called hard water.)

6.5.2 EDTA METHOD (COMPLEXOMETRIC TITRATION)

Principle: It is based on the fact that hardness causing ions like Ca^{++} , Mg^{++} form unstable complexes with the indicator Eriochrome Black T. However, when such a complex is treated with EDTA, since EDTA has more affinity to form stable complexes with metal ions, it extracts the metal ions from the metal ion-dye complex to form stable metal EDTA complex. The colour of dye-metal complex and dye are different. However, the change in colour is sharper at pH 10.0 than at other pH ranges. The metal-dye complex has wine red colour at pH 10.0 where the dye itself has blue colour at pH 10.0. Hence, by observing the sharp change in colour, the exact end point of reaction involving complete extraction metal ions by EDTA can be determined. The results obtained by this method are more accurate than those obtained by soap titration method.

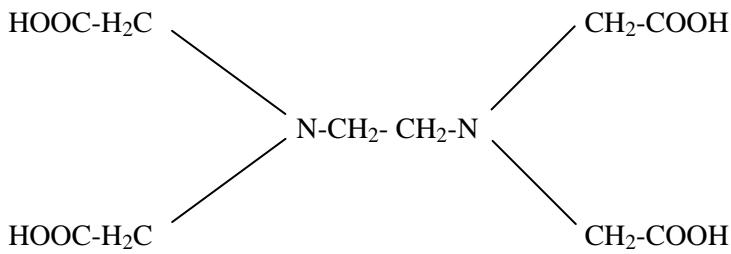
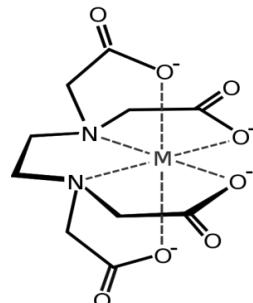


Fig 6.1 (a) Ethylene diamine tetra acetic acid (EDTA)



(b) Metal - EDTA chelate

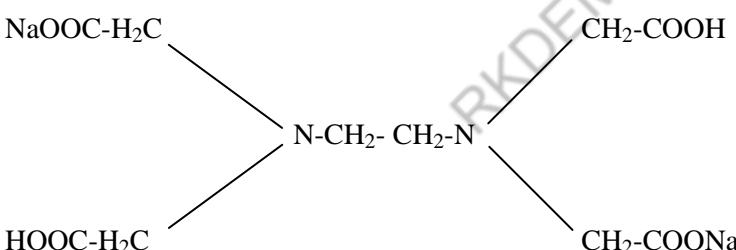
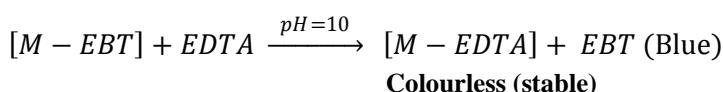
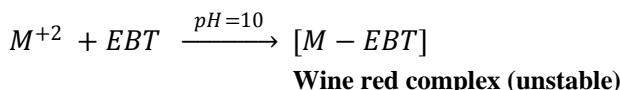


Fig. 6.2 Structure of disodium salt of EDTA



The various steps involved in estimation of hardness by EDTA method are given as below.

PREPARATION OF SOLUTIONS

- (a) **Standard hard water:** 1.0 gm of pure CaCO_3 dissolved in minimum quantity of cone. HCl and diluted to a one litre with distilled water. Each ml contains 1 mg CaCO_3 .
- (b) **EDTA solution:** 4 gm of pure EDTA (disodium salt) is dissolved in one litre of water.
- (c) **Eriochrome Black T Indicator:** 0.5 gm of the dye is dissolved in 100 ml of pure alcohol. Freshly prepared solutions are more suitable in order to obtain more accurate results.

- (d) **Buffer of pH = 10:** 67.5 of NH₄Cl is mixed with 570 ml of liquor ammonia, and diluted upto a litre with distilled water.

ESTIMATION OF HARDNESS

- 50 ml of standard hard water is pipetted out a clean 250 ml conical flask. Add 5 to 10 ml pH 10 buffer solution and mix well. Add 3 to 4 drops of Eriochrome Black T. The colour of solution is wine red.
- Fill the burette with EDTA solution and titrate against standard hard water in flask. Let the volume of EDTA required be 'A' ml when the colour changes to blue.
- Pipette out 50 ml of sample of hard water adds to 10 ml buffer and 3 to 4 drops of indicator and titrate against EDTA from burette. Let the volume be 'B' ml.
- Boil sample of hard water, cool and filter it. Take 50 ml of it and add 5 to 10 ml pH 10 buffer solution, 3 to 4 drops of indicator and titrate against EDTA till the colour changes to blue. Let the volume of EDTA consumed be 'C' ml.

CALCULATIONS

1. Standardization of EDTA

Since standard hard water contains 1 mg/ml of CaCO₃ hardness equivalent,

$$50 \text{ ml of standard hard water} \cong 50 \text{ mg of CaCO}_3 \text{ hardness}$$

$$50 \text{ ml of standard hard water requires} \cong 'A' \text{ ml of EDTA}$$

$$\therefore 'A' \text{ ml of EDTA} \equiv 50 \text{ mg of CaCO}_3 \text{ hardness}$$

$$\therefore 1 \text{ ml of EDTA} \equiv \frac{50}{A} \text{ mg of CaCO}_3 \text{ hardness.}$$

2. Total Hardness

50 ml of water sample requires 'B' ml of EDTA solution

$$\equiv B \times \frac{50}{A} \text{ mg of CaCO}_3 \text{ hardness}$$

$$(\because 1 \text{ ml of EDTA} = \frac{50}{A} \text{ mg of CaCO}_3 \text{ hardness equivalent})$$

$$\therefore 1000 \text{ ml of water sample} \equiv B \times \frac{50}{A} \times \frac{1000}{50} \text{ mg of CaCO}_3, \text{ hardness equivalent.}$$

$$\therefore \text{Total hardness} \equiv \frac{B}{A} \times 1000 \text{ mg of CaCO}_3$$

3. Permanent Hardness

50 ml of water sample after boiling requires 'C' ml of EDTA

$$\equiv C \times \frac{50}{A} \text{ mg of CaCO}_3 \text{ hardness equivalent}$$

$$(\because 1 \text{ ml of EDTA} = \frac{50}{A} \text{ mg of CaCO}_3 \text{ hardness equivalent})$$

$$\therefore 1000 \text{ ml water sample after boiling}$$

$$\equiv C \times \frac{50}{A} \times \frac{1000}{50} \text{ mg of CaCO}_3 \text{ hardness equivalent}$$

$$\equiv 1000 \times \frac{C}{A} \text{ mg of CaCO}_3 \text{ hardness equivalent.}$$

$$\therefore \text{Permanent hardness} = \frac{C}{A} \times 1000 \text{ mg of CaCO}_3$$

4. Temporary Hardness

Temporary hardness = Total hardness - Permanent hardness

$$\begin{aligned} &= \frac{B}{A} \times 1000 - \frac{C}{A} \times 1000 \\ &= 1000 \times \left(\frac{B-C}{A} \right) \text{ mg of CaCO}_3 \end{aligned}$$

Example 6.1: 50 ml of standard and hard water containing 1 mg of pure CaCO_3 per ml consumed 10 ml of EDTA solution. 50 ml of the given water sample required 10 ml of same EDTA solution. Calculate the total hardness of water sample in ppm.

Solution: Strength of Standard hard water 1 mg / ml

$$\therefore 50 \text{ ml of standard hard water} \equiv 50 \text{ mg/ml}$$

$$\therefore 50 \text{ ml of standard hard water} \equiv 10 \text{ ml of EDTA solution}$$

$$\begin{aligned} \therefore 1 \text{ ml of EDTA solution} &\equiv \frac{50}{10} \text{ ml of std hard water} \\ &\equiv \frac{50}{10} \text{ mg of CaCO}_3 \\ &\equiv 5 \text{ mg of CaCO}_3 \text{ equivalent} \end{aligned}$$

$$50 \text{ ml of water sample} \equiv 10 \text{ ml of EDTA solution}$$

$$\equiv 10 \times 5 \text{ mg of CaCO}_3$$

$$\equiv 50 \text{ mg of CaCO}_3 \text{ equivalent}$$

$$50 \text{ ml of water sample} \equiv 50 \text{ mg CaCO}_3$$

$$\therefore 1000 \text{ ml of water sample} \equiv 50 \times \frac{1000}{50}$$

$$\equiv 1000 \text{ mg CaCO}_3$$

$$\text{Hardness of water sample} \equiv 1000 \text{ ppm.}$$

Example 6.2: In the determination of hardness by EDTA method, 50 ml of standard hard water (containing 1 mg of CaCO_3 hardness per ml of solution) required 30 ml of EDTA solution, while 50 ml of the sample of hard water consumed 20 ml of EDTA solution. After boiling 50 ml of the same sample which required 10 ml of EDTA solution. Calculate the various hardness in ppm.

Solution: 1 ml of std. hard water \equiv 1 mg of CaCO_3

$$50 \text{ ml of std. hard water} \equiv 50 \text{ mg of CaCO}_3$$

$$50 \text{ ml of std. hard water} \equiv 30 \text{ ml of EDTA}$$

$$\equiv 50 \text{ mg of CaCO}_3$$

$$\therefore 1 \text{ ml of EDTA} \equiv \frac{50}{30} \text{ mg of CaCO}_3$$

Now 50 ml of sample water \equiv 20 ml of EDTA solution

$$\equiv 20 \times \frac{50}{30} \text{ mg of CaCO}_3$$

$$1000 \text{ ml of sample water } \equiv 20 \times \frac{50}{30} \times 20 \text{ mg of CaCO}_3$$

$$\text{Total hardness } \equiv 664 \text{ mg of CaCO}_3$$

$$\equiv 664 \text{ ppm.}$$

50 ml of boiled water sample \equiv 10 ml of EDTA solution

$$\equiv 10 \times \frac{50}{30} \text{ mg of CaCO}_3$$

$$\therefore 1000 \text{ ml of boiled water sample } \equiv 10 \times \frac{50}{30} \times 20 \text{ mg of CaCO}_3$$

$$\equiv 332 \text{ mg of CaCO}_3$$

i.e. Permanent hardness $\equiv 332 \text{ ppm.}$

i.e. Temporary hardness $\equiv \text{Total} - \text{Permanent}$

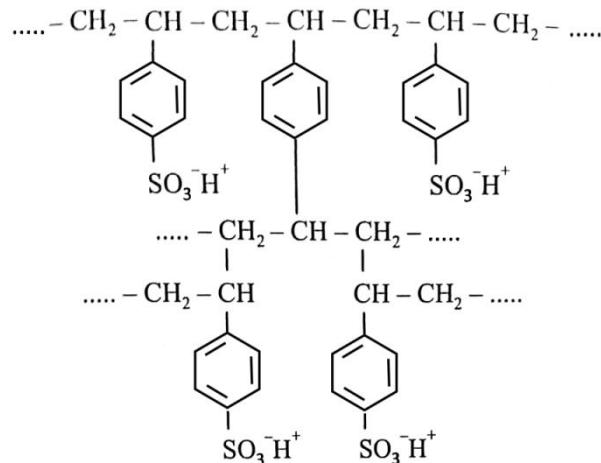
$$\equiv 664 - 332 = 332 \text{ ppm.}$$

6.6 ION EXCHANGE PROCESS

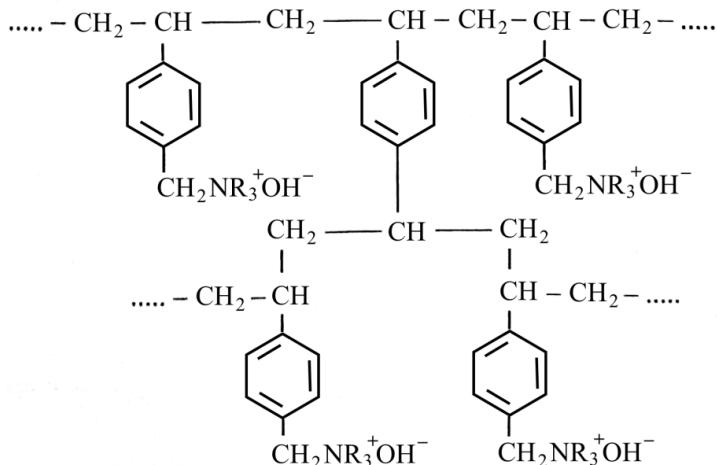
Ion exchange resins are used for softening of water. Ion exchange resins are organic polymers with long chains with cross links and having functional groups through which various ions are exchanged. The resins are porous and insoluble in water.

There are two types of ion exchange resins

(a) Cation exchange resins which exchange their H^+ ions for cations present in water. These resins have functional groups like $-SO_3H^+$, $-COO^-$, H^+ , OH (phenolic) where the H^+ ions get replaced with other cations present in water.



(b) The **anion exchange resins** have functional groups like $-\text{NH}_2$, $=\text{NH}$, $-\text{OH}$ which can be exchanged with anions present in resin.



The principle of ion exchange method is based on ability of the ion exchange resins to exchange their functional group like H^+ with cations like Ca^{++} , M^{++} , Na^+ and $(\text{OH})^-$ with all anions present. The process of softening in the ion exchange process involves passing raw water through cationic exchange resin and followed by passing it through the anion exchange resin.

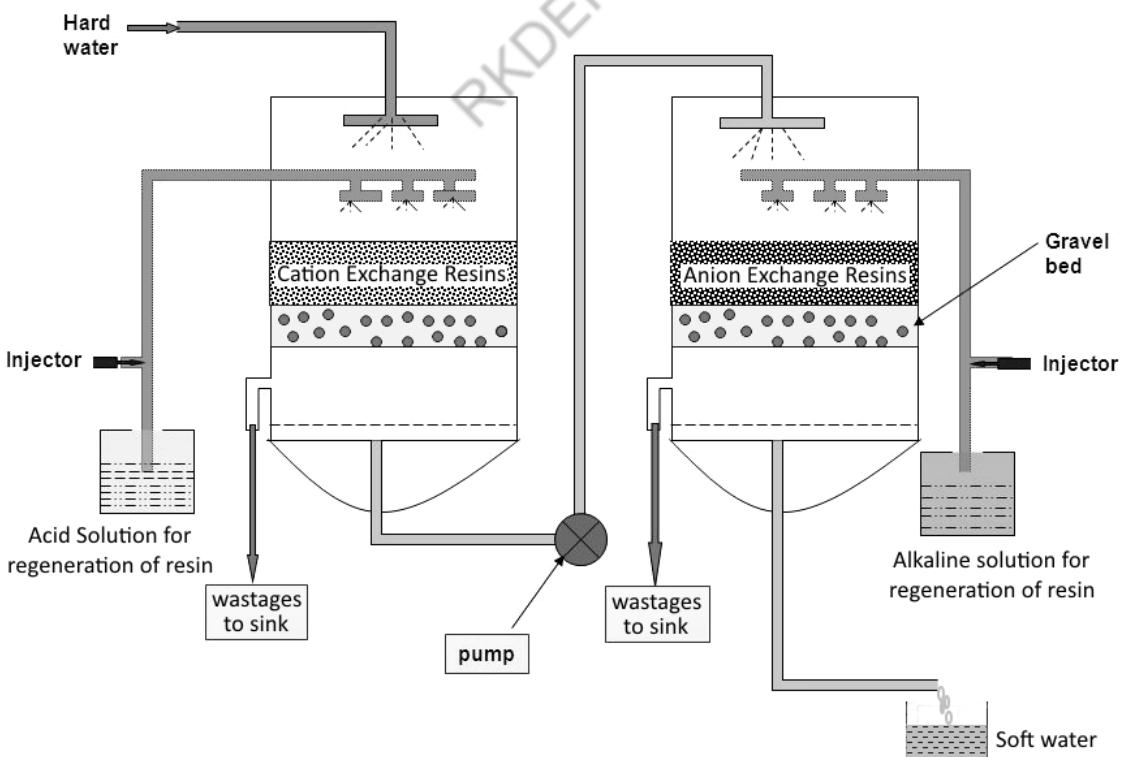


Fig. 6.3 Ion exchange method of softening of water

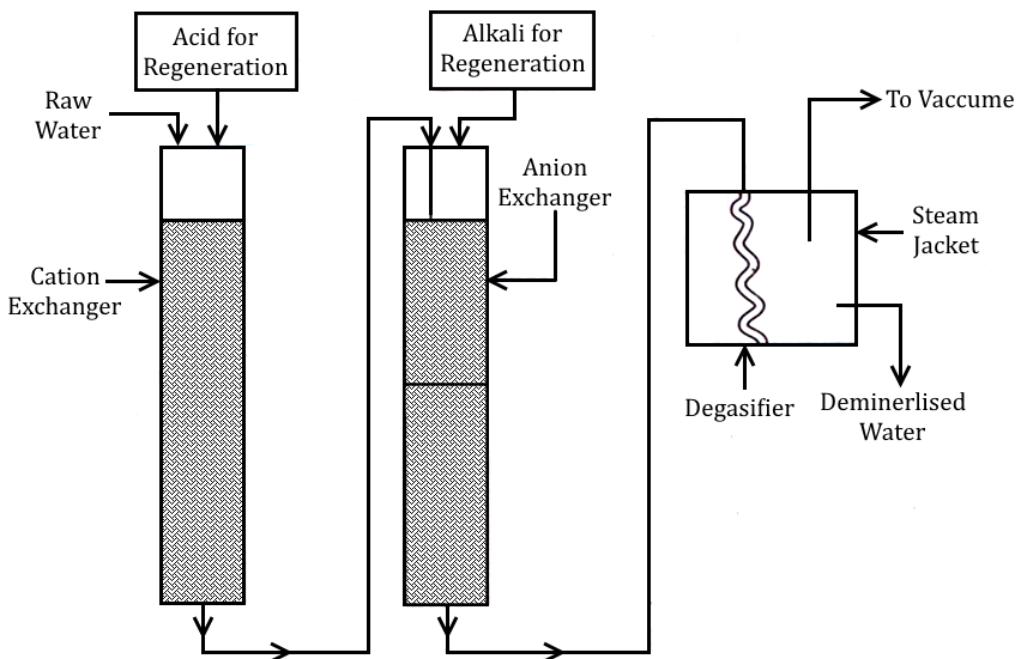
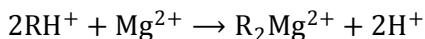
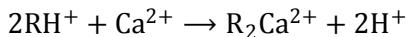


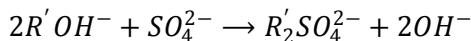
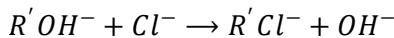
Fig. 6.4 Flow Chart of Ion exchange method

The equipment consists of two cylinders which contain the cation exchange resin and the anion exchange resin. The outlet from cation exchange resin is connected to anion exchange cylinder. Separate outlets are provided for draining purposes. Tanks provided at the top of cylinders contain the regeneration chemicals.

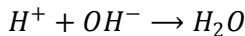
As the raw water passes through the cation exchange resin, Ca^{2+} , Mg^{2+} their ions are exchanged with H^+ ions of the resin.



Thus, sulphates, Chlorides, bicarbonates, get converted into sulphuric, hydrochloric and carbonic acids. The acidic water emerging from the cation exchange bed is passed through the anion exchange bed where the anions are exchanged for the OH^- ions of resin.



H^+ and OH^- ions get combined to produce water molecule

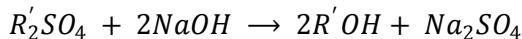
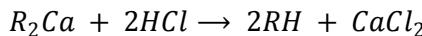


The water emerging from the anion exchange bed is free from both cations and anions and hence completely demineralised. It means it does not have any hardness at all. However water may contain some dissolved gases.

In order to remove the dissolved gases, water is passed through degasifiers where the water is heated, the escaping gases are removed by applying vacuum.

The cation exchange resin and the anion exchange resin are regenerated when they get saturated with cations and anions, they are then said to be exhausted. Cation exchange resins are regenerated by passing dilute acids and anion exchange resins by passing alkali.

REGENERATION REACTION



The regenerated resins can be used for treating further fresh raw water. Thus, the same amount of resins can be used over and again after regeneration. Water obtained from ion exchange softening process has very low residual hardness of less than 2 ppm. It can be safely used for high pressure boilers.

LIMITATIONS DUE TO PRESENCE OF CERTAIN IMPURITIES

Ion exchange resins do not function effectively in the presence of turbidity or suspended matter as they tend to cover the surface of resin and prevent easy exchange of ions. Similarly, very high total solid content in raw water will mean frequent regeneration of the resin. Hence, for efficient performance, raw water is pretreated to reduce the total dissolved solid content.

ADVANTAGES OF ION EXCHANGE PROCESS

1. The process can be used for softening acidic or alkaline waters.
2. Where mineral free water is required as in the case of some pharmaceutical, cosmetics and explosives and other manufacturing processes, ion exchange process of softening is the only process available for getting such pure
3. The residual hardness after treatment is less than 2 ppm and this makes water suitable for high pressure boilers.
4. Continuous supply of softened water can be made available by providing storage facilities and two columns of each resin.

DISADVANTAGES OF THE ION EXCHANGE PROCESS

1. The resins used are costly, the regeneration chemicals like acids and alkalis are costlier.
2. The initial investment in equipment is more.
3. When water is highly turbid and contains a large amount of dissolved matter, pretreatment of such water is essential to get the best results from the ion exchange method.

Example 6.3: For treating 100 litres of hard water in ion exchange method, the cationic resin require 50 litres of 0.1 N HCl and 50 litres of 0.1N NaOH solution. Determine the hardness of water.

Solution: In ion exchange method, all hardness causing cations are removed by cation-exchanger, hence the amount of acid used for regeneration of resin refers to hardness of water.

\therefore Hardness in 100 litres of waters \equiv 50 liters of 0.1N HCl

$$\equiv 50 \text{ litres} \times 0.1\text{N } CaCO_3 \text{ equivalent}$$

$$\equiv 5 \times 1\text{N CaCO}_3 \text{ equivalent}$$

$$\equiv 5 \times 50 = 250 \text{ gms CaCO}_3 \text{ equivalent}$$

$$\therefore \text{Hardness in 1 litre of water} = \frac{250}{100} \text{ gms of CaCO}_3 \text{ equivalent}$$

$$= 2.5 \text{ gm of CaCO}_3 \text{ equivalent}$$

$$\therefore \text{Hardness of water is } = 2.5 \text{ gm/liter} = 2500 \text{ ppm.}$$

Example 6.4: For treating 1,00,000 litres of hard water in ion exchange method, the cationic resin require 150 litres of 0.1 N HCl and 50 litres of 0.1N NaOH solution. Determine the hardness of water.

Solution: In ion exchange method, all hardness causing cations are removed by cation-exchanger, hence the amount of acid used for regeneration of resin refers to hardness of water.

$$\therefore \text{Hardness in 100000 litres of waters} \equiv 150 \text{ liters of 0.1N HCl}$$

$$\equiv 150 \text{ litres} \times 0.1\text{N CaCO}_3 \text{ equivalent}$$

$$\equiv 15 \times 1\text{N CaCO}_3 \text{ equivalent}$$

$$\equiv 15 \times 50 \text{ g} = 750 \text{ gms CaCO}_3 \text{ equivalent}$$

$$\therefore \text{Hardness in 1 litre of water} = \frac{750}{100000} \text{ gms of CaCO}_3 \text{ equivalent}$$

$$= .0075 \text{ gm of CaCO}_3 \text{ equivalent}$$

$$= 7.5 \text{ mg of CaCO}_3 \text{ equivalent}$$

$$\therefore \text{Hardness of water is } = 7.5 \text{ mg/liter} = 7.5 \text{ ppm.}$$

6.7. REVERSE OSMOSIS

When two solutions of different concentrations are separated by a semi permeable membrane, solvent flows from low region concentration to higher one until concentration is equal in both sides. This process is known as osmosis. This technique is used for the removal of dissolved salts from seawater called desalination or desalting of water. Demineralised water is produced by forcing water through semi permeable membrane at high pressure.

PRINCIPLE OF REVERSE OSMOSIS

In this process dissolved salts are separated from water by using semi permeable membrane. When membrane is placed in between water containing dissolved salts and pure water. Water flows through a membrane into salty water due to osmotic pressures.

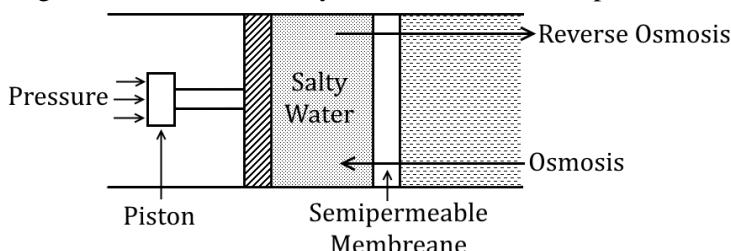


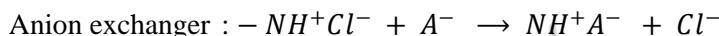
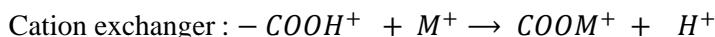
Fig 6.5 Reverse Osmosis

This natural tendency of water may be reversed by applying a higher pressure on the salty water part. This tends to flow water from higher concentrations to lower one. This reverse process of osmosis is called as reverse osmosis. The membranes used are cellulose acetate, cellulose butyrate, etc.

This method is also known as super filtration. This is a single and continuous process, involves no phase changes and needs low energy. This technique is also used for the separation of toxic ions from plating wastes, concentration of radioactive waste and removal of organics from vegetable and animal wastes.

6.8 ULTRA FILTRATION

Ultra filtration is used for removal of larger particle because of the open character of membrane. The productivity is high while the pressure difference is low. Some of the toxic chlorinated organisms are removed by filtering industrial waste with ultra filters. Aldrin, Dieldrin, Endrin, DDT, etc. are removed nearly 99%. Synthetic organic ion exchange resins are very useful for removal of industrial waste chemicals. Styrene-divinyl-benzene copolymer can remove chlorinated pesticides by adsorption at the surface. Ionic dyes from textile mill wastewater can be eliminated by using cation and anionic ion exchange resins.



Ultrafiltration is cross flow filtration techniques. The process can remove particle in the range of 0.0001 to 0.1μ . It is normally operated in the pressure range 1 to 10 bar. It is membrane filtration in which hydrostatic pressure force applied on liquid against a semi-permeable membrane. Suspended solids and solute of high molecular weight are retained while water and low molecular weight solute pass through the membrane.

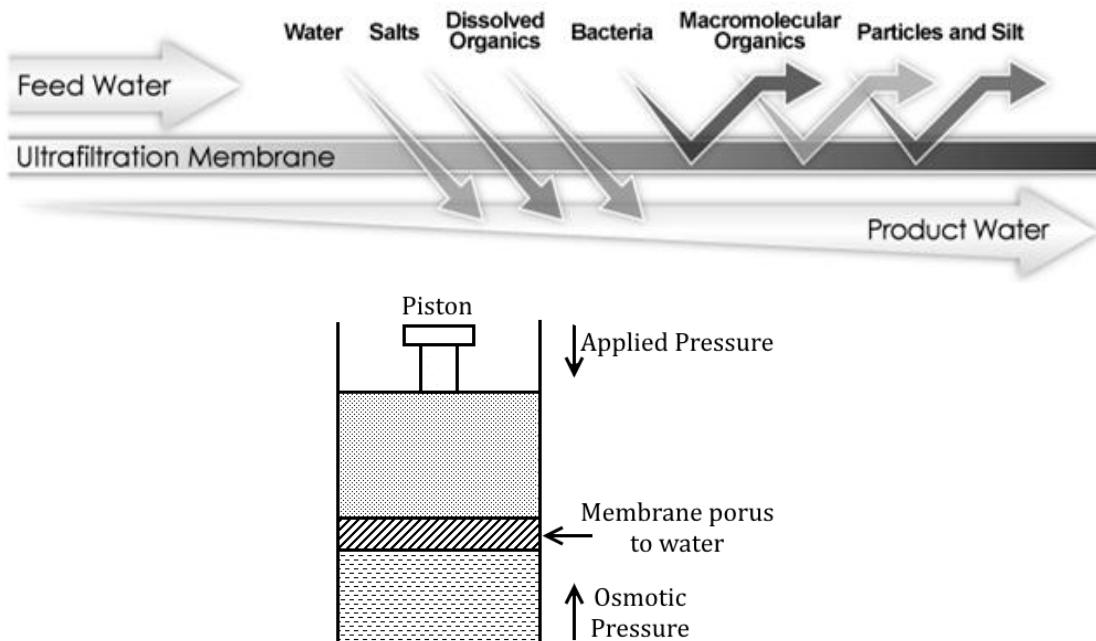


Fig. 6.6 Wastewater purification by ultra filtration (membrane pore size 0.1-0.0001μm)

ADVANTAGES

1. No chemical required
2. Low cost of installation and maintenance.
3. Gives constant product quality
4. Neat and compact plants
5. 90-100% pathogens removal

APPLICATION

1. Use for blood dialysis (process of removing waste and excess water from blood).
2. For purifying and concentrating protein solution.
3. It is used in paint recovery in automobile industry
4. It is used in the fractionation of milk and whey.

6.9 ELECTRODIALYSIS

In the electrodialysis method positive and negative ions are separated out of a flowing current of saline or brackish water when it is allowed to pass through ion exchange membranes under the influence of an electric field. In this a direct current of electricity is passed through a saline water in a series of closely spaced, alternately placed, cation exchanger and anion exchanger membranes.

Cations pass through the cation exchanger membranes and anions through the anion exchanger membranes. As movement of cations and anions result in the salinity decreases in one space and increases in the next space, and so on throughout the stack.

The water containing more salt (increased salinity) is run to waste, while the water containing less salt (decreased salinity) may either be re-circulated through the stack may be passed through a series of stacks in this manner, saline water may be converted into drinking water.

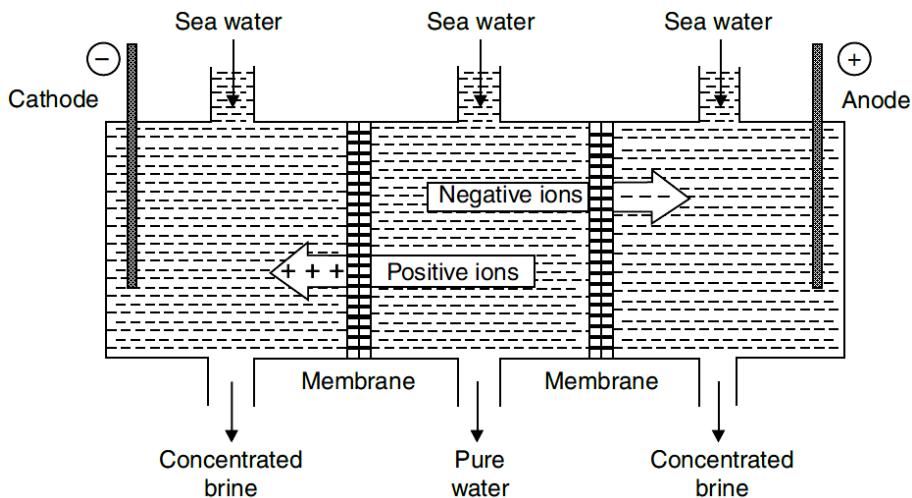


Fig. 6.7 Electrodialysis Method

Completely deminerlised water is not obtained by this method. The method reduces the salinity of **brackish water** so as to make it suitable for drinking and general use. The process is capable at reducing salt contents of brackish water from 2000 to about 300 ppm, but it is very costly.

For more efficient separation, Ion selective membranes, which are permeable to only one kind of ions with specific charge is used. Cation selective membranes is permeable to cation only and anion selective membranes are permeable to anions only.

The permeability of permeable ions, inside the membrane pores. The ion selective membrane pores and designed with fixed charge which exclusively allows one type of charged ions to pass through its pores and does not allow oppositely charged ions to flow.

6.10 CHEMICAL OXYGEN DEMAND (COD)

Method to determine extent of water pollution. Unpolluted water has 5 to 7mg/L of dissolved oxygen (DO). This level of DO is essential for supporting aquatic lives including micro organism. If DO decreases due to water pollution, gases are formed and smell starts coming.

Chemical oxygen demand (COD) is the amount of oxygen used while oxidising organic matter by means of strong oxidising agent. All organic matters are converted into CO_2 and H_2O . In chemical oxidation both biologically oxidisable organic matter like starch, sugar, inert materials like cellulose, etc. are oxidised and hence COD values are always higher than BOD. COD can be determined in 11/2 hours.

The wastewater sample is refluxed with a known excess of potassium dichromate in a dilute sulphuric acid in the presence of silver sulphate as a catalyst or HgSO_4 . The organic matter of the sample is oxidised to water, carbon dioxide and ammonia. The unreacted excess of dichromate remaining is titrated with standard solution of ferrous ammonium sulphate (FAS) with indicator ferroin. The end point is determined by colour change blue to wine red. COD is 4 times BOD.

$$\text{COD} = \frac{(x - y) \times 8 \times N}{v} \times 1000 \text{ mg/l}$$

x = Volume of ferrous ammonium sulphate required for blank

y = Volume of ferrous ammonium sulphate required for test

N = Normality of ferrous ammonium sulphate

v = Volume of the sewage sample taken.

Example: 6.5. 25 ml of waste water required 20.3 ml of 0.001 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution for complete oxidation. The blank titration reading was 29.7 ml. calculate COD of water sample.

Solution: x = blank titration reading = 29.7 ml

y = back titration reading = 20.3 ml

N = normality of ferrous amm. Sulphate = 0.001 M

v = volume of waste water = 25 ml

$$\begin{aligned}
 COD &= \frac{(x - y) \times 8 \times N \times 1000}{v} \text{ mg of oxygen} \\
 &= \frac{(29.7 - 20.3) \times 8 \times 0.001 \times 1000}{25} \\
 &= 3.008 \text{ mg of oxygen}
 \end{aligned}$$

Example: 6.6. 25 ml of waste water is mixed with 25 ml of acidified potassium dichromate and refluxed. The unreacted potassium dichromate required 10.1 ml of 0.1 N ferrous amm. sulphate. The blank titration reading was 20.2 ml calculate COD of water sample.

Solution: x = blank titration reading = 20.2 ml

y = back titration reading = 10.1 ml

N = normality of ferrous amm. Sulphate = 0.1 M

v = volume of waste water = 25ml

$$\begin{aligned}
 COD &= \frac{(x - y) \times 8 \times N \times 1000}{v} \text{ mg of oxygen} \\
 &= \frac{(20.2 - 10.1) \times 8 \times 0.1 \times 1000}{25} \\
 &= 323.2 \text{ mg of oxygen}
 \end{aligned}$$

If an inorganic substances like chlorides, nitrates and organic substances like benzene pyridine are present in wastewater they interfere as they are also oxidised by dichromate and create an inorganic COD. Chloride interference can be eliminated by adding mercuric sulphate prior to the addition of other reagents and nitrite interference by adding sulphuric acid to the dichromate solution.

COD is much more useful than the BOD for estimating amount of oxygen in industrial wastes. Ratios of BOD/COD can be employed to get an indication of the degree of the bio-treatability of the waste. 0.8 or higher ratio indicates wastes are highly amenable to biological treatment, while lower ratios indicate that the wastes is not favourable to biological treatment. COD is important in calculating the efficiency of treatment plants and proposing standards for discharge of domestic effluents.

Sewage: Water containing domestic or municipal waste is called sewage, which contains nearly 99.95% water and 0.05% waste materials. Strength of sewage is expressed in terms of Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD).

6.11 BIOLOGICAL OXYGEN DEMAND (BOD)

Is the quantity of dissolved oxygen required by bacteria for the oxidation of organic matter under aerobic conditions or it is a measure of the oxygen utilised by micro organisms during the oxidation of organic materials. The demand for oxygen is directly proportional to the amount of organic wastes which has to be broken down. Hence, BOD is a direct measure of oxygen requirement and an indirect measure of biodegradable organic matter. Greater BOD greater is the pollution.

A known volume of sewage sample is diluted with known volume of dilution water. This diluted sample is taken in two stoppered bottles of 300 ml. The dissolved oxygen (DO) content of one of the bottles is immediately determined by Winkler's method (blank).

Another bottle is incubated at 20°C for a period of 5 days. Then unused oxygen is determined. The difference in the dissolved oxygen of blank and back sample is BOD of water sample.

$$\text{BOD} = (\text{D}_{\text{Ob}} - \text{D}_{\text{Os}}) \times \text{dilution factor}$$

D_{Ob} = dissolved oxygen present in the blank.

D_{Os} = dissolved oxygen of sewage after incubation

BOD is expressed in mg/l.5 days BOD of wastewater can be obtained in 2.5 days if the temperature is 35°C rather than 20°C. BOD enables us to determine the degree of pollution hence it has special significance in pollution control.

BOD values are useful generally in process design and loading calculations, measurement of treatment efficiency and operation, self pollution control and in determination of self purifying capacity of a stream.

Difference between BOD and COD

S. N.	BOD	COD
1	The biological oxygen demand (BOD) is defined as amount of free oxygen required for the biological oxidation of the organic matter under aerobic condition at 20°C for a period of five days.	The chemical oxygen demand (COD) is defined as the measure of the oxygen equivalent to that portion of organic matter present in waste water sample that is susceptible to oxidation by potassium dichromate.
2	It is the basic parameter to determine the level of organic matter which can be oxidized biologically.	It is the basic parameter to determine the level of organic matter which can be oxidized chemically.
3	It measures the oxidation of carbon and nitrogenous compounds possibly in the waste water.	It measures the oxidation of carbon only in the waste water.
4	It is the measures of only consumed oxygen by micro organisms to oxidize the organic matter only.	It is the measures of only consumed oxygen by micro organisms to oxidize both the organic as well as inorganic matter.
5	BOD is always less than COD Allowed limit for BOD is 30 ppm	COD is greater than BOD Allowed limit for COD is 250 ppm
6	This test require 5 days	It is a rapid test carried out within three hours with oxidizing agents.

Example 6.7: A sample of water found to contain following impurities in mg/litre. $Mg(HCO_3)_2 = 73$ mg, $MgSO_4 = 120$ mg, $CaCl_2 = 222$ mg, $Ca(NO_3)_2 = 164$ mg. Calculate Temp., Permanent & Total Hardness.

Solution: Conversion of the impurities in $CaCO_3$ equivalent.

T/P	Substance	Quantity (mg/litre)	Conversion Factor	$CaCO_3$ equivalent (mg/litre)
T	$Mg(HCO_3)_2$	73	$\frac{100}{146}$	$\frac{100}{146} \times 73 = 50$
P	$MgSO_4$	120	$\frac{100}{120}$	$\frac{100}{120} \times 120 = 100$
P	$CaCl_2$	222	$\frac{100}{111}$	$\frac{100}{111} \times 222 = 200$
P	$Ca(NO_3)_2$	164	$\frac{100}{164}$	$\frac{100}{164} \times 164 = 100$

1. Temporary hardness in water = hardness due to $Mg(HCO_3)_2$
= 50 mg/litre
2. Permanent hardness in water = hardness due to $MgSO_4$, $CaCl_2$ and $Ca(NO_3)_2$
= $100 + 200 + 100 = 400$ mg / litre
3. Total hardness = Temp. Hardness + Perm. Hardness = $50 + 400 = 450$ mg/l

Example 6.8: A water sample contains following impurities per litre. $Ca(HCO_3)_2 = 81$ mg, $Mg(HCO_3)_2 = 73$ mg, $CaSO_4 = 68$ mg, $MgSO_4 = 60$ mg, $KCl = 100$ mg. Calculate (a) Temporary hardness and permanent hardness in water.

Solution: Conversion of the impurities in $CaCO_3$ equivalent.

T/P	Substance	Quantity (mg/litre)	Conversion Factor	$CaCO_3$ equivalent (mg/litre)
T	$Ca(HCO_3)_2$	81	$\frac{100}{162}$	$\frac{100}{162} \times 81 = 50$
T	$Mg(HCO_3)_2$	73	$\frac{100}{146}$	$\frac{100}{146} \times 73 = 50$
P	$CaSO_4$	68	$\frac{100}{136}$	$\frac{100}{136} \times 68 = 50$
P	$MgSO_4$	60	$\frac{100}{120}$	$\frac{100}{120} \times 60 = 50$

1. Temporary hardness in water = hardness due to $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$
= $50 + 50 = 100$ mg / litre.
2. Permanent hardness in water = hardness due to $CaSO_4$ and $MgSO_4$
= $50 + 50 = 100$ mg / litre.
3. Total hardness = Temp. Hardness + Perm. Hardness = $100 + 100 = 200$ mg/l.

Example 6.9: Calculate the different type of hardness present in water containing the following salts in ppm. $\text{Ca}(\text{HCO}_3)_2 = 162 \text{ ppm}$, $\text{MgCl}_2 = 9.5 \text{ ppm}$, $\text{Fe}_2\text{O}_3 = 100 \text{ ppm}$, $\text{NaCl} = 58.5 \text{ ppm}$, $\text{SiO}_2 = 25 \text{ ppm}$, $\text{MgSO}_4 = 60 \text{ ppm}$, $\text{CaCO}_3 = 100 \text{ ppm}$.

Solution: Conversion of the impurities in CaCO_3 equivalent.

T/P	Salt	Amount in ppm	Conversion Factor	CaCO_3 equivalent ppm
T	$\text{Ca}(\text{HCO}_3)_2$	162	$\frac{100}{162}$	$\frac{100}{162} \times 162 = 100$
P	MgCl_2	9.5	$\frac{100}{95}$	$\frac{100}{95} \times 9.5 = 10$
-	Fe_2O_3	100 ppm		does not contributes to hardness
-	NaCl	58.5 ppm		-
-	SiO_2	25 ppm		-
P	MgSO_4	60	$\frac{100}{120}$	$\frac{100}{120} \times 60 = 50$
T	CaCO_3	100	$\frac{100}{100}$	$\frac{100}{100} \times 100 = 100$

- Temporary hardness in water = hardness due to $\text{Ca}(\text{HCO}_3)_2$ and CaCO_3
 $= 100 + 100 = 200 \text{ ppm}$.

- Permanent hardness in water = hardness due to MgCl_2 and MgSO_4
 $= 10 + 50 = 60 \text{ ppm}$.

- Total hardness = Temp. Hardness + Perm. Hardness = $200 + 60 = 260 \text{ ppm}$.

Example 6.10: Calculate the Temp. and Perm. Hardness of water containing $\text{Ca}(\text{HCO}_3)_2 = 30.2 \text{ ppm}$, $\text{Mg}(\text{HCO}_3)_2 = 20.8 \text{ ppm}$, $\text{CaCl}_2 = 28.1 \text{ ppm}$, $\text{MgCl}_2 = 8.7 \text{ ppm}$, $\text{CaSO}_4 = 35.0 \text{ ppm}$, $\text{MgSO}_4 = 6.7 \text{ ppm}$. (At. wt. for H = 1, C = 12, O = 16, Na = 23, Mg = 24)

Solution: Conversion of the impurities in CaCO_3 equivalent.

T/P	Impurity	amount in ppm	conversion factor	CaCO_3 equivalent in ppm
T	$\text{Ca}(\text{HCO}_3)_2$	30.2	$\frac{100}{162}$	$\frac{100}{162} \times 30.2 = 18.64$
T	$\text{Mg}(\text{HCO}_3)_2$	20.8	$\frac{100}{146}$	$\frac{100}{146} \times 20.8 = 14.24$
P	CaCl_2	28.1	$\frac{100}{111}$	$\frac{100}{111} \times 28.1 = 25.31$
P	MgCl_2	8.7	$\frac{100}{95}$	$\frac{100}{95} \times 8.7 = 9.15$
P	CaSO_4	35	$\frac{100}{136}$	$\frac{100}{136} \times 35 = 25.73$
P	MgSO_4	6.7	$\frac{100}{120}$	$\frac{100}{120} \times 6.7 = 5.58$

- Temporary hardness in water = hardness due to $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$
 $= 18.64 + 14.24 = 32.88 \text{ ppm.}$
- Permanent hardness in water = hardness due to CaCl_2 , MgCl_2 , CaSO_4 and MgSO_4
 $= 25.31 + 9.15 + 25.73 + 5.58 = 65.77 \text{ ppm.}$
- Total hardness = Temp. Hardness + Perm. Hardness = $32.88 + 65.77 = 98.07 \text{ ppm.}$

Example 6.11: Calculate temporary and permanent hardness of water sample containing $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/L}$, $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/L}$, $\text{MgCl}_2 = 9.5 \text{ mg/L}$, $\text{CaSO}_4 = 13.6 \text{ mg/L}$.

Solution: Conversion of the impurities in CaCO_3 equivalent.

Types of hardness	Constituents	Quantity in mg/L	Multiplication factor	CaCO_3 equivalent (mg/L)
T	$\text{Mg}(\text{HCO}_3)_2$	7.3	100/146	$7.3 \times \frac{100}{146} = 5$
T	$\text{Ca}(\text{HCO}_3)_2$	16.2	100/162	$16.2 \times \frac{100}{162} = 10$
P	MgCl_2	9.5	100/95	$9.5 \times \frac{100}{95} = 10$
P	CaSO_4	13.6	100/136	$13.6 \times \frac{100}{136} = 10$

- Temporary hardness = Hardness due to $\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2$
 $= 5 + 10$
 $= 15 \text{ mg/L}$
- Permanent hardness = Hardness due to $\text{MgCl}_2 + \text{CaSO}_4$
 $= 10 + 10$
 $= 20 \text{ mg/L}$

Example 6.12: Calculate the hardness in a given hard water sample having the following data.
(a) 50 ml of standard hard water containing 1 mg of CaCO_3 per ml consumed.
(b) 25 ml of EDTA using eriochrome black T as indicator.
(c) 50 ml of water sample consumed 40 ml EDTA using the same indicator.
(d) 50 ml water sample after boiling consumed 25 ml of EDTA using the same indicator.

Solution: 50 ml of std. hard water \equiv 25 ml of EDTA

1 mg CaCO_3 per ml is strength

\therefore 50 mg of $\text{CaCO}_3 \equiv$ 25 ml of EDTA

\therefore 1 ml of EDTA $\equiv \frac{50}{25}$ mg of CaCO_3

Now 50 ml of sample water \equiv 40 ml of EDTA solution

$\equiv 40 \times \frac{50}{25}$ mg of CaCO_3

$$1000 \text{ ml of sample water} \equiv \frac{1000}{50} \times \frac{50}{25} \times 40 \text{ mg of CaCO}_3$$

$$\text{Total hardness} \equiv 1600 \text{ mg of CaCO}_3$$

$$\equiv \mathbf{1600 \text{ ppm.}}$$

$$50 \text{ ml of boiled water sample} \equiv 25 \text{ ml of EDTA solution}$$

$$\equiv 25 \times \frac{50}{25} \text{ mg of CaCO}_3$$

$$\therefore 1000 \text{ ml of boiled water sample} \equiv 25 \times \frac{50}{25} \times \frac{1000}{50} \text{ mg of CaCO}_3$$

$$\equiv 1000 \text{ mg of CaCO}_3$$

$$\text{i.e. Permanent hardness} \equiv \mathbf{1000 \text{ ppm.}}$$

$$\text{i.e. Temporary hardness} \equiv \text{Total} - \text{Permanent hardness}$$

$$\equiv 1600 - 1000$$

$$\equiv \mathbf{600 \text{ ppm.}}$$

Example 6.13: 50 ml of hard water Sample required 8 ml of 0.05 N EDTA solution for titration. 30 ml of the same water sample after boiling required 5 ml of 0.02 EDTA solution for titration. Calculate the hardness of water.

$$\text{Solution: } 1000 \text{ ml of 1N EDTA} \equiv 50 \text{ gm CaCO}_3$$

$$1 \text{ ml of 1N EDTA} \equiv 50 \text{ mg CaCO}_3$$

$$\text{Now 50 ml of hard water sample} \equiv 8 \text{ ml of 0.05 N EDTA solution}$$

$$\equiv (8 \times 0.05) \text{ ml of 1N EDTA solution}$$

$$\equiv (8 \times 0.05 \times 50) \text{ mg CaCO}_3$$

$$\equiv 20 \text{ mg CaCO}_3$$

$$1000 \text{ ml of hard water sample} \equiv \frac{20}{50} \times 1000 \text{ mg of CaCO}_3$$

$$\equiv 400 \text{ mg CaCO}_3$$

$$\text{Total hardness} \equiv 400 \text{ mg of CaCO}_3$$

$$\equiv \mathbf{400 \text{ ppm.}}$$

$$30 \text{ ml of boiled water sample} \equiv 5 \text{ ml of 0.02N EDTA solution}$$

$$\equiv (0.02 \times 5) \text{ ml of 1N EDTA}$$

$$\equiv (0.02 \times 5 \times 50) \text{ mg of CaCO}_3$$

$$\therefore 1000 \text{ ml of boiled water sample} \equiv \frac{0.02 \times 5 \times 50}{30} \times 1000 \text{ mg of CaCO}_3$$

$$\equiv 166.6 \text{ mg of CaCO}_3$$

i.e. Permanent hardness $\equiv 166.6$ ppm.

i.e. Temporary hardness \equiv Total - Permanent hardness

$$\equiv 400 - 166 = 234 \text{ ppm.}$$

Example 6.14: A standard hard water sample contains 0.20 mg of CaCO_3 per ml. 100 ml of this water consumed 25ml 0.02 N EDTA. 25ml sample water consumed 12ml of 0.05N EDTA. The sample water is boiled and filtered, 50ml of this water sample consumed 4ml of 0.01N EDTA. Calculate the hardness of water.

Solution: Given: 100 ml of std. hard water (0.2mg/ml of CaCO_3)

$$\equiv 25 \text{ ml of } 0.02\text{N EDTA mg of } \text{CaCO}_3$$

$$25 \text{ ml of sample water} \equiv 12 \text{ ml } 0.02 \text{ N EDTA}$$

$$50 \text{ ml of boiled hard water} \equiv 4 \text{ ml of } 0.01\text{N EDTA}$$

$$\therefore 25 \text{ ml of } 0.02\text{N EDTA} \equiv (100 \times 0.20) \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of } 1\text{N EDTA} \equiv \frac{100 \times 0.20}{25 \times 0.02} \text{ mg of } \text{CaCO}_3$$

$$\equiv 40 \text{ mg of } \text{CaCO}_3$$

Now 25 ml of sample water \equiv 12 ml of 0.02 N EDTA solution

$$\equiv 12 \times 0.02 \text{ ml of } 1\text{N EDTA}$$

$$\equiv 12 \times 0.02 \times 40 \text{ mg of } \text{CaCO}_3$$

$$\equiv 9.60 \text{ mg of } \text{CaCO}_3$$

$$\text{Total hardness} \equiv 9.60 \times \frac{100}{25} \text{ mg of } \text{CaCO}_3$$

$$\equiv 384 \text{ mg/litre}$$

$$\equiv 384 \text{ ppm.}$$

50 ml of boiled water sample \equiv 4 ml of 0.01N EDTA solution

$$\equiv (4 \times 0.01) \text{ ml of } 1\text{N EDTA solution}$$

$$\equiv 40 \times 4 \times 0.01 \text{ mg of } \text{CaCO}_3$$

$$\equiv 1.6 \text{ mg } \text{CaCO}_3$$

$$\therefore 1000 \text{ ml of boiled water sample} \equiv 1000 \times \frac{1.6}{50} \text{ mg of } \text{CaCO}_3$$

$$\equiv 32 \text{ mg of } \text{CaCO}_3$$

i.e. Permanent hardness $\equiv 32$ ppm.

i.e. Temporary hardness \equiv Total - Permanent

$$\equiv 384 - 32 = 352 \text{ ppm.}$$

QUESTIONS

1. Define soft and hard water,
2. What are temporary hardness and permanent hardness?
3. What are different impurities present in water.
4. Distinguish between temporary and permanent hardness
5. What is the principle involved in the estimation of hardness of water by EDTA titration method?
6. Describe EDTA method for hardness determination.
7. Why water is required to be softened? Mention the methods available for softening.
8. Draw well labeled diagram for Ion exchange method.
9. Explain in detail the demineralization process. State advantages and disadvantages.
10. Give reactions involved in ion exchange process.
11. Describe the process of Ion exchange method of softening of water. Mention its advantages and disadvantages.
12. Explain regeneration reactions of Ion exchange method.
13. What is reverse osmosis? Explain in details.
14. What is ultra filtration? Write its industrial applications.
15. Write short note on:
 - (a) BOD
 - (b) COD
16. Calculate the hardness of water sample whose 100 ml required 20 ml EDTA, 20 ml of calcium chloride solution (whose strength is equivalent to 4.5 gm of Calcium carbonate per litre) required 30 ml of the same EDTA. (Ans: 600 ppm)
17. 0.5 gm of CaCO_3 are dissolved in dilute HCl and diluted to 500 ml, 25 ml of this solution required 24.0 ml of EDTA using Eriochrom black T as indicator. 50 ml of hard water sample required 22.5 ml of the same EDTA, 100 ml of the water sample after boiling required 12.0 ml of the said EDTA. Calculate the hardness in sample.
(Total hardness = 468.75 ppm, permanent hardness = 125 ppm)
18. A sample of water has hardness 304 ppm CaCO_3 equivalent. Find the hardness in terms of degree clark, degree French and mg/litre.
19. 50 ml of standard hard water (1.2 gm CaCO_3 /litre) requires 32 ml of EDTA solution. 100 ml of water sample consumes 14 ml EDTA solution. 100 ml of the boiled and filtered water sample consumes 8.5 ml of EDTA solution. Calculate temporary hardness of this sample.
20. 25 ml of waste water is mixed with 25 ml of acidified potassium dichromate solution and refluxed. The unreacted potassium dichromate required 11.8 ml of 0.1N ferric ammonium sulphate. The blank titration reading was 20.2 ml. calculate COD of water.
21. 25 ml of waste water require 18.1 ml of 0.001M potassium dichromate solution for complete oxidation. The blank titration reading was 26.2 ml. calculate COD of water.