Chapter

1

Chemical Bonding and Solid State Chemistry

KEY-TERMS

- **Anion:** A negatively charged ion; that is, an ion in which the atom or group of atoms has more electrons than protons.
- **Binary compound:** A compound consisting of two elements; may be ionic or covalent.
- **Bond dissociation energy:** The stabilization of a bonded pair of atoms compared to the same atoms when separated; the energy required to break the bonding between a pair of atoms.
- **Bonding pair:** A pair of electrons involved in a covalent bond. Also called shared pair.
- **Bond length:** The distance between the centers (nuclei) of two bonded atoms.
- **Cation:** A positively charged ion; that is, an ion in which the atom or group of atoms has fewer electrons than protons.
- **Chemical bond:** Attractive forces that hold atoms together in elements and compounds.
- **Covalent bond:** A chemical bond formed by the sharing of one or more electron pairs between two atoms.
- **Duet Rule:** A term describing the distribution of valence electrons when hydrogen atoms—which end up with only two valence electrons—experience chemical bonding with other atoms. Most other elements follow the octet rule.
- **Lewis Structure:** A means of showing schematically how valence electrons are distributed among the atoms in a molecule. Also known as the electron-dot system, Lewis structure represents pairs of electrons with a symbol rather like a colon, which—depending on the situation—can be placed above, below, or on either side of the chemical symbol. In the Lewis structure, the pairs of electrons involved in chemical bonds are usually represented by a dashed line.

INTRODUCTION

A chemical bond may be in general defined as the force of attraction that binds the constituent particles (atom, ion) together in various chemical species. Atoms enter into chemical combination to form the molecules because by doing so they attain a state of lowest energy or maximum stability. Based on this basic idea, the formation of different kinds of bonds like ionic, covalent, etc. takes place.

The concept of covalent bond formation based on sharing of electrons (Lewis concept) was purely a qualitative approach. The above basis could not offer satisfactory answer regarding the forces of attractive interactions in a molecule. In order to offer a reasonable explanation, the modern researchers proposed two theories:

(1) Valence Bond Theory (VBT)

(2) Molecular Orbital Theory (MOT)

REVIEW OF VALENCE BOND THEORY (VBT)

This approach was put forward by Heitler and London in 1927 and was later developed by Linus Pauling who emphasized the participation of valence electrons in the formation of chemical bond.

Salient features of this theory are summed up below:

1. According to this theory, atoms retain their individuality even in a molecule and bond is formed by the interaction of half filled orbitals belonging to the valence shell of the participating atoms.
2. The overlapping atomic orbitals must contain electrons of opposite spin.
3. The strength of bond depends upon the extent of overlapping. The greater the overlap, the stronger is the bond.
4. The stability of the molecule is further explained in terms of exchange of electrons between the atoms participating on bond formation.

5. The valency of the element is equal to the number of half filled orbitals in the valence shell of its atoms.

The theory successfully explained the formation of hydrogen molecule. Besides, the application of these ideas were extended to molecules such as F_2, NH_3, H_2O, CH_4, C_2H_2, etc. Though the theory could reasonably explain the shapes and bonding of many molecules, yet it failed to explain the magnetic properties of some molecules. For example, it could not explain why oxygen is paramagnetic in nature. However, the theory fails to explain the bonding in electron deficient molecules as well as metals and intermetallic compounds.

The second approach of Molecular Orbital Theory can explain the bonding in covalent molecules more satisfactorily.

MOLECULAR ORBITAL THEORY (MOT)

Molecular Orbital Theory was put forward by Hund and Mulliken in 1932. The theory is modern and more rational. It assumes that in molecules, atomic orbitals lose their identity and electrons in molecules are present in new orbitals called molecular orbitals which are not associated with particular atom and belong to a molecule as a whole.

The salient features of this theory are given below:

1. In molecules, the electrons are present in new orbitals called molecular orbitals. Molecular orbitals like atomic orbitals are characterized by a set of quantum numbers.
2. Molecular orbitals are formed by the combination of atomic orbitals of nearly same energies and same symmetry.
3. Molecular orbitals are not associated with a particular atom but belong to the nuclei of all the atoms constituting the molecule. Nuclei of different atoms in a molecule behave as a polycentric nucleus. Thus, the atomic orbital is monocentric and molecular orbital is polycentric.
4. The number of molecular orbitals formed is equal to the number of atomic orbitals undergoing combination. Among the new molecular orbitals formed, half are of lower energy than combining atomic orbitals (bonding molecular orbitals) and half are of higher energy than combining atomic orbitals (anti-bonding molecular orbitals).
5. The shapes of the molecular orbitals depend upon the shape of combining atomic orbitals.
6. The molecular orbitals are filled in increasing order of their energies, starting with the orbital of least energy (Aufbau principle).
7. The molecular orbital like atomic orbital can accommodate only two electrons and these electrons must have opposite spin (Pauli's principle).
8. While filling molecular orbitals of equal energy, pairing of electrons does not take place until all such orbitals are singly occupied (Hund's rule).

Similarities between Valence Bond Theory and Molecular Orbital Theory

Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT) have the following common features:

1. The basic principle is same in both the theories. Both involve distribution of electrons. Thus, whether it is atomic or molecular cannot have more than two electrons.
2. Both the theories include the sharing of electrons by the nuclei.
3. According to both the theories, the energy of overlapping orbitals must be comparable and there must be similarities in their symmetry.

Dissimilarities between VBT and MOT

Valence Bond Theory (VBT)	Molecular Orbital Theory (MOT)
Bonds are localized to two atoms not molecules.	Bonds are localized to two atoms as well as molecules.
Valence orbital theory was first proposed by W. Heitler and F. London in 1927.	Molecular orbital theory was proposed by F. Hund and R.S. Mulliken in 1932.
Orbitals of bonded atoms cannot lose their identity.	Orbitals of bonded atoms lose their identity.
Atomic orbitals are monocentric.	Molecular orbitals are polycentric.
Resonance plays an important role in this theory.	There is no place of resonance in this theory.
It explains that inert gases have orbitals already spin paired, so they have no tendency to form any linkage.	Molecular orbital theory explains the non-existence of molecules of inert gases, since number of bonding and anti-bonding electrons are equal.
There is no explanation of paramagnetic character of oxygen.	Satisfactory explanation of paramagnetic character of oxygen.
Calculations are simpler.	Calculations are very tedious.

LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

Molecular orbitals are formed by the combination of atomic orbitals of bonded atoms. In wave mechanics, atomic orbitals are expressed by wave functions (ψ). The wave functions are obtained as the solutions of Schrodinger wave equation. Just like atomic orbitals, Schrodinger wave equation can be written to describe the behaviour of the electron in molecules also. However, because of the complex nature of the Schrodinger wave equation, it may not be easy to solve it for molecules. Thus, in view of it, for the sake of convenience, an approximate technique to obtain the wave functions for molecular orbitals was applied. This approximate method is known as Linear Combination of Atomic Orbitals Method (LCAO Method).

Let us apply this theory to homo-nuclear diatomic molecules such as hydrogen molecule. Let us consider two atoms of hydrogen in the molecule as A and B. Each hydrogen has one electron in 1s orbital in the ground state. These atomic orbitals may be represented by wave functions ψ_A and ψ_B. Then according to LCAO method, the molecular orbitals in H_2 molecule are given by linear combination (addition or subtraction of wave functions of individual atoms) of ψ_A and ψ_B as shown below:

$$\psi_{MO} = \psi_A \pm \psi_B$$

$$\psi_b = \psi_A + \psi_B$$

$$\psi_a = \psi_A - \psi_B$$

The molecular orbital ψ_b formed by the addition overlap (constructive interference of waves) of atomic orbitals is called bonding molecular orbital and the molecular orbital ψ_a formed by subtraction overlap (destructive interference of waves) of atomic orbitals is called anti-bonding molecular orbital.

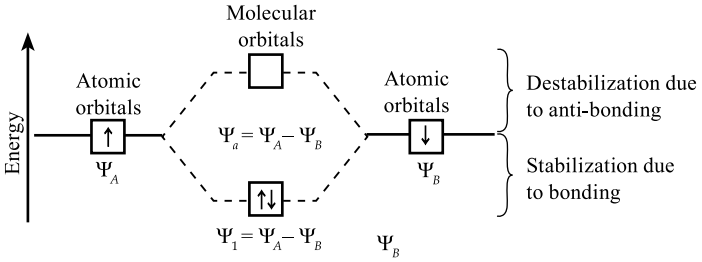


Figure 1: Formation of bonding (σ) and anti-bonding (σ*) molecular orbitals by the linear combination of atomic orbitals ψ_A and ψ_B centred on two atoms A and B respectively.

The formation of bonding and anti-bonding orbitals can be interpreted in terms of sign of wave functions of the orbitals which interact. Such a wave possesses a crest and a trough, therefore, the positive and negative signs are arbitrarily assigned to the crest and trough respectively. Now if the crest of one wave overlaps with the crest of the other, the two waves interact in a constructive interference and therefore the new resulting wave is reinforced i.e., add up or there is in-phase overlap, hence, bonding orbitals result by overlap of atomic orbitals with the same sign. On the contrary, if crest of one overlaps with the trough of the other two, waves interact in a destructive manner or out of phase overlap or subtraction overlap and thus, the resulting wave gets weakened. Therefore, the anti-bonding orbitals result from atomic orbitals with opposite sign.

The combination of 1st orbitals of hydrogen atoms to form molecular orbitals has been shown in Figure 2.

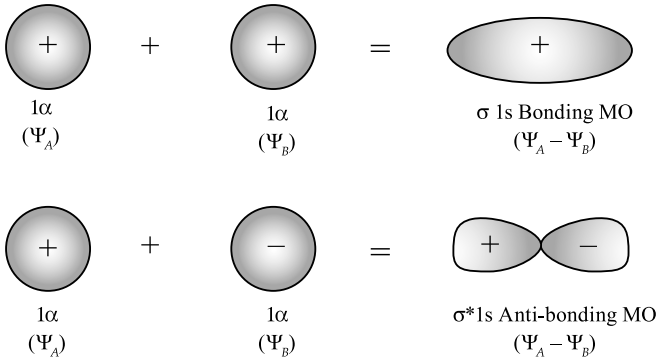


Figure 2: Molecular orbitals formed by combination of two 1s orbitals.

As is clear from the figure, in the bonding molecular orbital, the electron density is mainly concentrated in between the nuclei, so the electrons feel greater force of attraction in the orbital. Hence, bonding molecular orbital is of lower energy as compared to atomic orbitals. On the other hand, in anti-bonding molecular orbital, the electron density is mainly concentrated away from the nuclei; in between the nuclei, there is a node. So the electrons feel less force of attraction in this orbital and hence anti-bonding molecular orbital is of higher energy as compared to atomic orbitals. It may be noted that bonding molecular orbital is stabilised almost to the same extent as the anti-bonding molecular orbital is destabilised relative to atomic orbitals.

Table: Differences between Bonding and Anti-bonding Molecular Orbitals

Bonding Molecular Orbital	Anti-bonding Molecular Orbital
Bonding molecular orbital is formed by the addition overlap of atomic orbitals.	Anti-bonding molecular orbital is formed by the subtraction overlap of atomic orbitals.
It may or may not have a node.	It always has a node in between the nuclei of bonded atoms.
It has lower energy than the AOs from which it is formed.	It has higher energy than the AOs from which it is formed.

The electron charge density in between the nuclei is high and hence the repulsion between the nuclei is very low. This results in stabilisation of BMO. In other words, the electrons in the BMO favour stable bond formation.	The electron charge density in between the nuclei is less and hence the repulsion between the nuclei is high. This results in de-stabilisation of anti-bonding MO. In other words, the electron in the ABMO opposes bond formation.

CONDITIONS FOR THE COMBINATION OF ATOMIC ORBITALS

For atomic orbitals to combine, resulting in the formation of molecular orbitals, the main conditions are:

1. The combining atomic orbitals should have almost the same energies. For example, in the case of diatomic molecules, 1s orbital of one atom can combine with 1s orbital of the other atom, but 1s orbital of one atom cannot combine with 2s orbital of the other atom.
2. The extent of overlap between the atomic orbitals of the two atoms should be large.
3. The combining atomic orbitals should have the same symmetry about the molecular axis. For example, $2p_x$ orbital of one atom can combine with $2p_x$ orbital of the other atom but not with $2p_z$ orbital.

Note: It may be noted that Z-axis is taken as the inter-nuclear axis according to modern conventions.

Combination of s-Atomic Orbitals

The molecular orbitals which are cylindrically symmetrical around inter-nuclear axis are called σ - molecular orbitals. The molecular orbital formed by the addition of 1s orbitals is designated as σ1s and the molecular orbital formed by subtraction of 1s orbitals is designated as σ*1s. Similarly, combination of 2s orbital results in the formation of two 2s molecular orbitals designated as σ2s and σ*2s. They differ from σ 1s and σ* 1s MOs with regard to their size only.

Combination of p-Atomic Orbitals

There are three p-atomic orbitals represented as p_x, p_y and p_z. As a convention, the z-axis is taken as the inter-nuclear axis. The x and y axes would then be perpendicular to the nuclear line. The combination of two p_z atomic orbitals belonging to different nuclei would give a sigma bonding molecular orbital, represented as $\sigma 2p_z$ and sigma anti-bonding molecular orbital σ^*2p_z. The combination of two p_x atomic orbitals or two p_y atomic orbitals on the other hand would give rise to π-bonding molecular orbitals represented as: $\pi 2p_x$ and $\pi 2p_y$ and π-*anti-bonding* molecular orbitals represented as: π^*2p_x and π^*2p_y. The region of overlapping of π- MOs is at right angles to the molecular axis i.e., z-axis.

The formation of $\sigma\ 2p_z$ BMO by linear additive combination of two p_z atomic orbitals is represented in Figure 1.3.

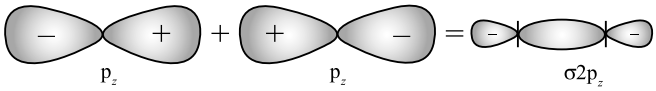


Figure 3 *Formation of $\sigma 2p_z$ BMO by the linear additive combination of two p_z atomic orbitals*

In this combination, the positive lobes of two AOs overlap so that the electron charge density between the two nuclei is enhanced. The nuclei are thus well shielded from each other since the repulsion between the nuclei in such case is minimum. The energy of the MO is lower than the energy of any atomic orbitals which have gone into its formation.

The corresponding ABMO is obtained by the linear subtractive combination of two p_z atomic orbitals, as represented in Figure 4.

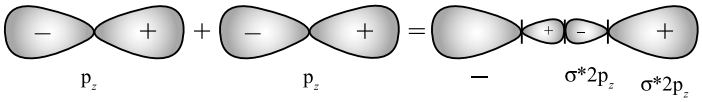


Figure 4: Overlapping of two p_z atomic orbitals by the linear subtractive combination to form an σ^*2p_z ABMO

Combination of p_x and p_y Orbitals

Suppose a p_x orbital of an atom overlaps with a p_x orbital of another atom. The overlap would be positive, but it would be side to side and not end to end as in the case of p_z orbitals. The resulting molecular orbitals will thus be called π-molecular orbitals. The formation of the BMO is designated as $\pi 2p_x$ and is shown in Figure 5.

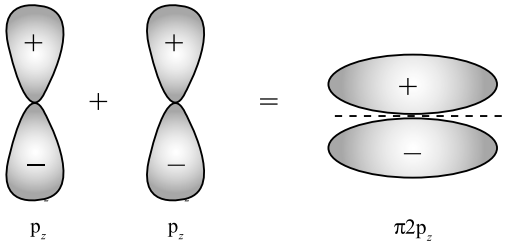


Figure 5: Overlapping of two p_x AO's formed by linear additive combination to give $\pi 2p_x$ BMO

The corresponding ABMO formed by linear subtractive combination of p_x AOs designated as π^*2p_x is shown in Figure 6.

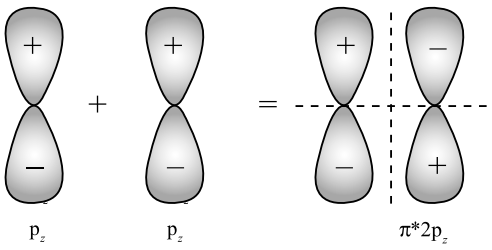


Figure 6: Overlapping of two p_x AO's by linear subtractive combination to give π^*2p_x ABMO

The energy of the anti-bonding molecular orbital would be high because the similarly charged nuclei are not effectively screened by the electronic charge and therefore repel each other considerably.

The formation of $\pi 2p_y$ BMO and $\pi^* 2p_y$ ABMOs is similar to the formation of $\pi 2p_x$ and $\pi^* 2p_x$ MOs. The only difference is that the AOs which combine and MOs which are formed now lie perpendicular to the plane of the paper.

Energy Level Diagram for Molecular Orbitals

Energy levels of such molecular orbitals have been found out experimentally by spectroscopic studies. The order of rising energy in case of the diatomic homo-nuclear molecules of first and second period of the periodic table is as shown below:

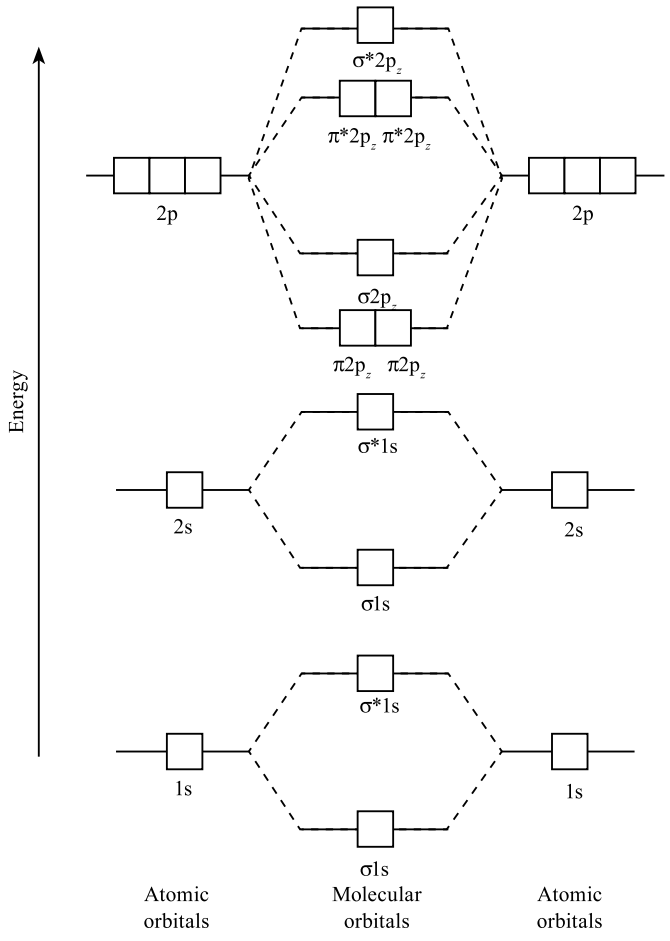


Figure 7: Molecular orbital energy level diagram for diatomic homo-nuclear molecules of first and second period (i.e., except O_2, F_2 and so on)

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

This order of energies of different molecular orbitals is valid for molecules or ions such as, H_2, H_2^+, He_2^+, He_2 (i.e., hypothetical), Li_2, Be_2 (i.e., hypothetical), B_2, C_2 and N_2 molecules. The above energy diagram for the molecular orbitals is as shown in figure below. Though, experimental proof for oxygen and heavier diatomic molecules have shown in the above sequence of energy levels of MOs is not accurate. In case of these elements, the order of energy levels of σ_{2pz}, π_{2px} and π_{2py} is reversed that is, σ_{2pz} has lesser energy than π_{2px} and π_{2py}. Therefore, the order of rising energy of MOs for these molecules is as shown below.

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

This order of energies of different MOs is valid for molecules or ions such as O_2, O_2- (i.e., super oxide ion), O_2^{2-} (i.e., peroxide ion), F_2 and Ne_2 (i.e., hypothetical). This energy level diagram for MOs is as shown in Figure 8.

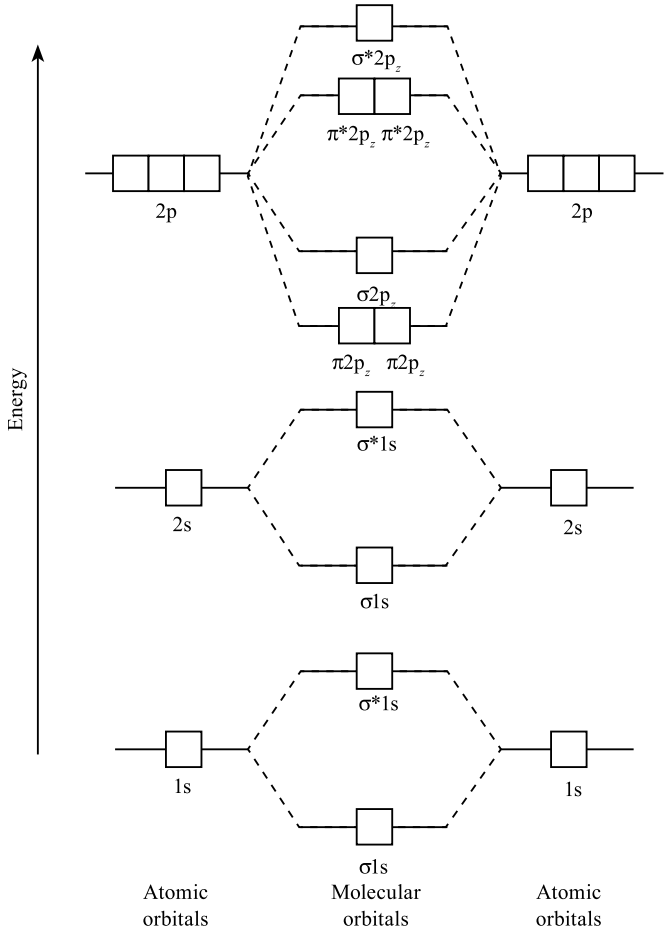


Figure 8: Molecular orbital energy level diagram for diatomic homo-nuclear molecules of O_2 and other heavier elements.

Now the question arises that why the order of energy of molecular orbitals is different for molecules lighter than F_2 (N_2, C_2, B_2). This can be explained as follows:

(i) In case of homo-nuclear diatomic molecules of second row elements, if the energy difference between 2s and 2p atomic orbital is large, then the 2s orbital of one atom interacts very slightly with the $2p_z$ orbital of other atom. Though the symmetry is proper for overlap, the energy difference is very high and the overlap is not effective. This is true for diatomic molecules such as O_2 and F_2. Thus, the σs MO's are composed of two 2s atomic orbitals and the order of energy is as shown in Figure 1.9.

(ii) In case of elements upto nitrogen, in the second row, the energy difference between 2s and 2p atomic orbitals is small. As the two orbitals are of same symmetry, their overlap cannot be ignored. As a result of interaction between s orbital of one atom with the p orbital of the other and vice versa, σ2s and σ*2s do not retain their pure *s* character and $\sigma 2p_z$ and $\sigma^* 2p_z$ do not retain their pure *p* character.

(iii) Due to this mixing, the energies of all the four MO's change in such a way that resulting MOs σ2s and σ*2s which also contain some *p* character, become more stable and thus lowered in energy.

(iv) Similarly, MOs $\sigma 2p_z$ and $\sigma^* 2p_z$ which also contain some s character become less stable and their energy is raised. Thus, there is an upward displacement of $\sigma 2p_z$ so that it lies above $\pi 2p_x$ and $\pi 2p_y$.

(v) Since π2p orbitals are not involved in mixing, the energies of $\pi 2p_x$ and $\pi 2p_y$ remain unchanged.

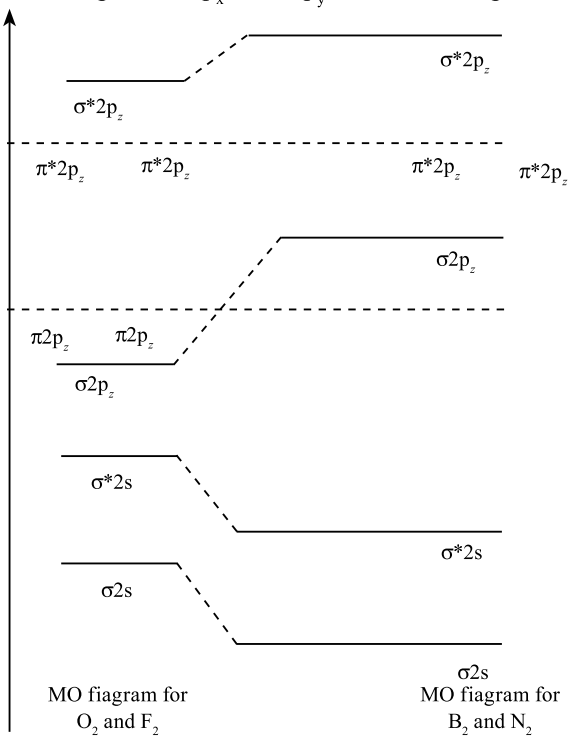


Figure 9: Change in energies of MOs due to the mixing of orbitals of same symmetry

BOND ORDER

Bond order calculation is useful as they allow us to predict the number of bonds a diatomic molecule is likely to have. The most common bond orders are 1, 2 and 3, which represent single, double and triple bonds.

The following equation is used to calculate bond orders, when used in conjunction with the principles of Molecular Orbital theory.

$$Bond\ order = \frac{N_b - N_a}{2}$$

N_b = Number of electrons in bonding MO's

N_a = Number of electrons in anti-bonding MO's

Information given by bond order:

$$\text{Stability} \propto \frac{1}{Bond\ length} \propto \frac{1}{Reactivity}$$

HOMO-NUCLEAR DIATOMIC MOLECULES

Hydrogen molecule, H_2

Each hydrogen molecule contains one electron and hence there are two electrons in the molecule, occupying the lowest energy level. Thus, the electronic configuration of H_2 is $\sigma 1s^2$.

$$Bond\ order = \frac{2-1}{2} = 1$$

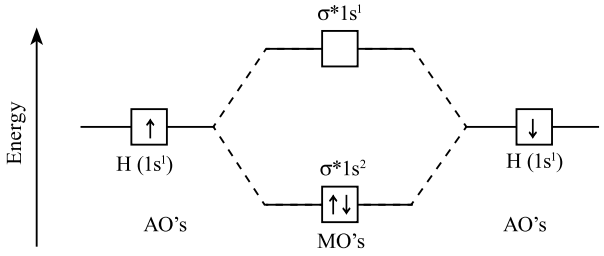


Figure 10: Energy level diagram of H_2 molecule

Helium Molecule Ion, He_2^+

This may be considered to be formed from He atom and a He^+ ion. In the molecular ion, there are three electrons which are arranged as $\sigma 1s^2$, $\sigma^* 1s^1$. Thus, He molecular ion can exist, but is not very stable.

$$Bond\ order = \frac{9-4}{2} = 2.5$$

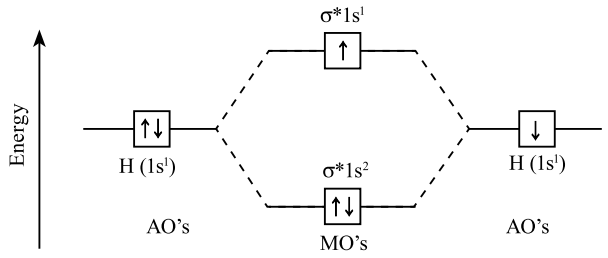


Figure 11: Energy level diagram of He_2^+ molecule

Helium Molecule, He_2

The electronic configuration of helium atom is $1s^2$. In helium molecule, there are four electrons which are arranged as $\sigma 1s^2$, $\sigma^* 1s^2$. Thus, stabilizing effect of bonding orbitals is cancelled out by the destabilizing effect of anti-bonding orbitals and the molecule does not exist.

$$Bond\ order = \frac{2-1}{2} = 1$$

Lithium Molecule, Li_2

Electronic configuration of lithium atom: $1s^2$, $2s^1$

Total number of electrons in lithium molecule: 6

MO configuration of lithium molecule: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$

$$Bond\ order = \frac{2-1}{2} = 1$$

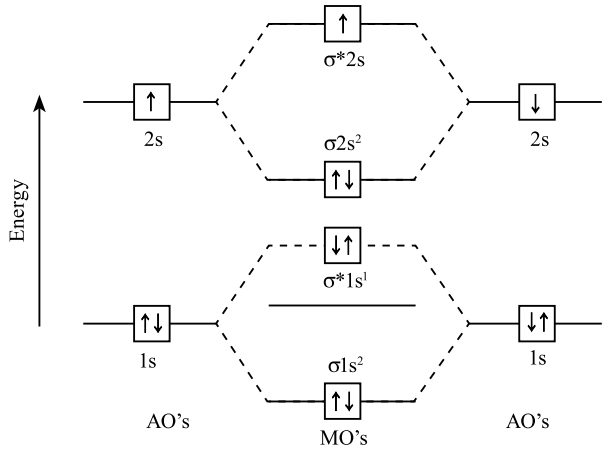


Figure 12: Energy level diagram of Li_2 molecule

Beryllium Molecule, Be_2

Electronic configuration of beryllium atom: $1s^2$, $2s^2$

Total number of electrons in beryllium molecule: 8

MO configuration of beryllium molecule: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$

$$Bond\ order = \frac{2-1}{2} = 1.$$ This molecule does not exist.

Boron Molecule, B_2

Electronic configuration of boron atom: $1s^2$, $2s^2$, $2p^1$

Total number of electrons in boron molecule: 10

MO configuration of boron molecule: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2p_x^1 = \pi 2p_y^1$

$$Bond\ order = \frac{2-1}{2} = 1.$$ It is paramagnetic in nature as it has two unpaired electrons in molecular orbitals.

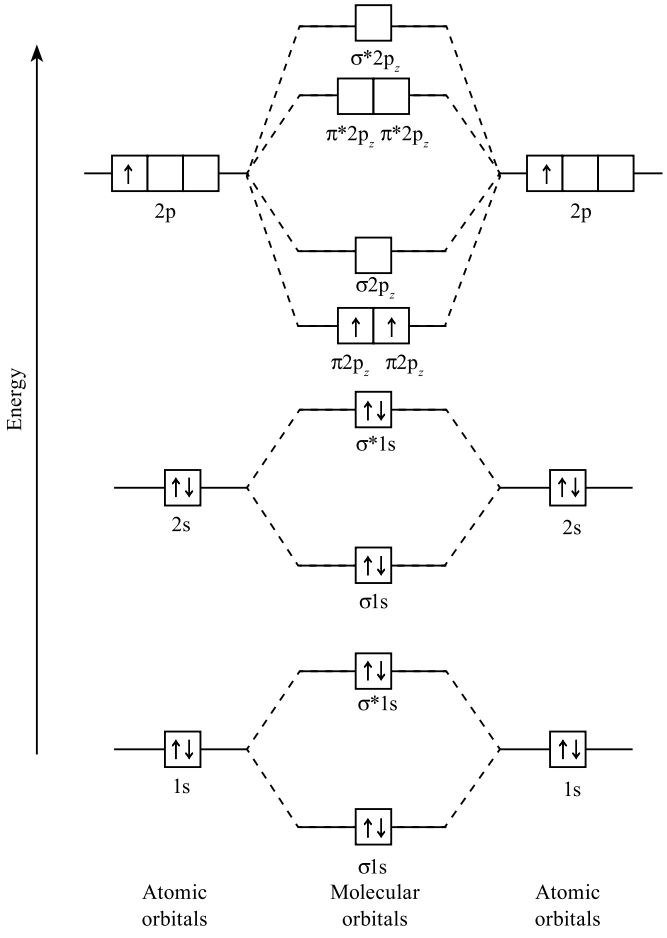


Figure 13: Energy level diagram for B_2 molecule

Nitrogen Molecule, N_2

Electronic configuration of nitrogen atom: $1s^2$, $2s^2$, $2p^3$

Total number of electrons in nitrogen molecule: 14

MO configuration of nitrogen molecule: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2p_x^2 = \pi 2p_y^2$, $\sigma 2p_z^2$

$Bond\ order = \frac{10-8}{2} = 1$. It contains a triple bond and is a highly stable molecule. It is diamagnetic in nature as it has all paired electrons in molecular orbitals.

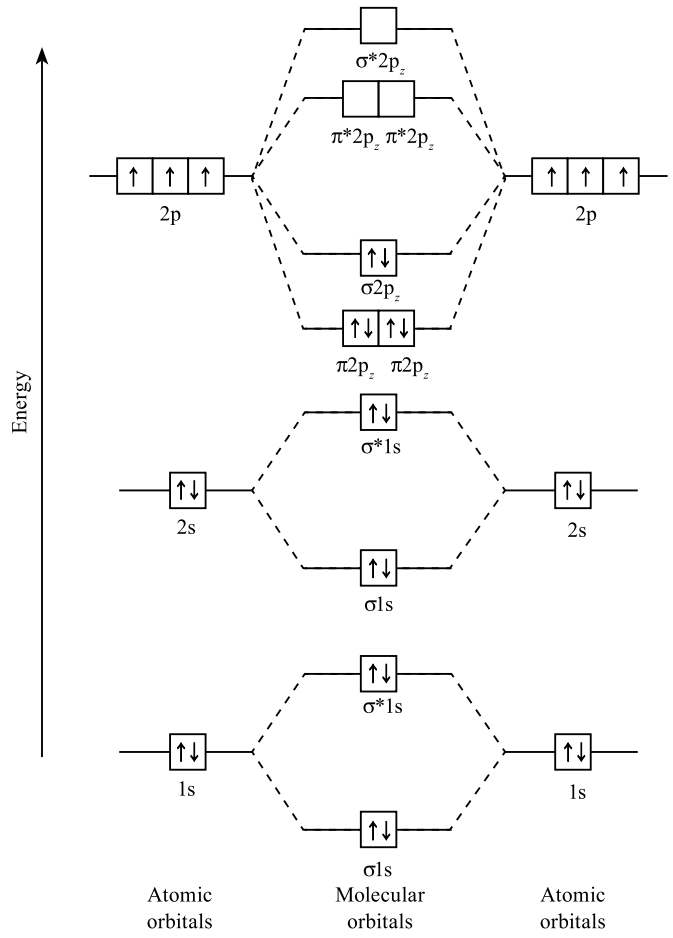


Figure 14: Energy level diagram for N_2 molecule

N_2^+ ion: N_2^+ has one electron less than N_2 molecule. This electron will be lost from $\sigma 2p_z$ orbital.

Hence, the MO configuration will be: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2p_x^{\ 2} = \pi 2p_y^{\ 2}$, $\sigma 2p_z^{\ 1}$

$$Bond\ order = \frac{9-4}{2} = 2.5.$$

The ion is paramagnetic due to the presence of one unpaired electron and is less stable than N_2 molecule.

N_2^- ion: N_2^- has one electron more than N_2 molecule. This electron will be added in $\pi^* 2p_x$ orbital.

Hence, the MO configuration will be: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2p_x^{\ 2} = \pi 2p_y^{\ 2}$, $\sigma 2p_z^{\ 2}$, $\pi^* 2p_x^{\ 1}$

$$Bond\ order = \frac{10-5}{2} = 2.5.$$

The ion is paramagnetic due to the presence of one unpaired electron and is less stable than N_2 molecule.

Oxygen Molecule, O_2

Electronic configuration of oxygen atom: $1s^2$, $2s^2$, $2p^4$

Total number of electrons in oxygen molecule: 16

MO configuration of oxygen molecule: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\sigma 2p_z^{\ 2}$, $\pi 2p_x^{\ 2} = \pi 2p_y^{\ 2}$ $\pi^* 2p_x^{\ 1} = \pi^* 2p_y^{\ 1}$

$$Bond\ order = \frac{10-8}{2} = 1$$

.

It contains a double bond and is a highly stable molecule. It is paramagnetic in nature as it has two unpaired electrons in molecular orbitals.

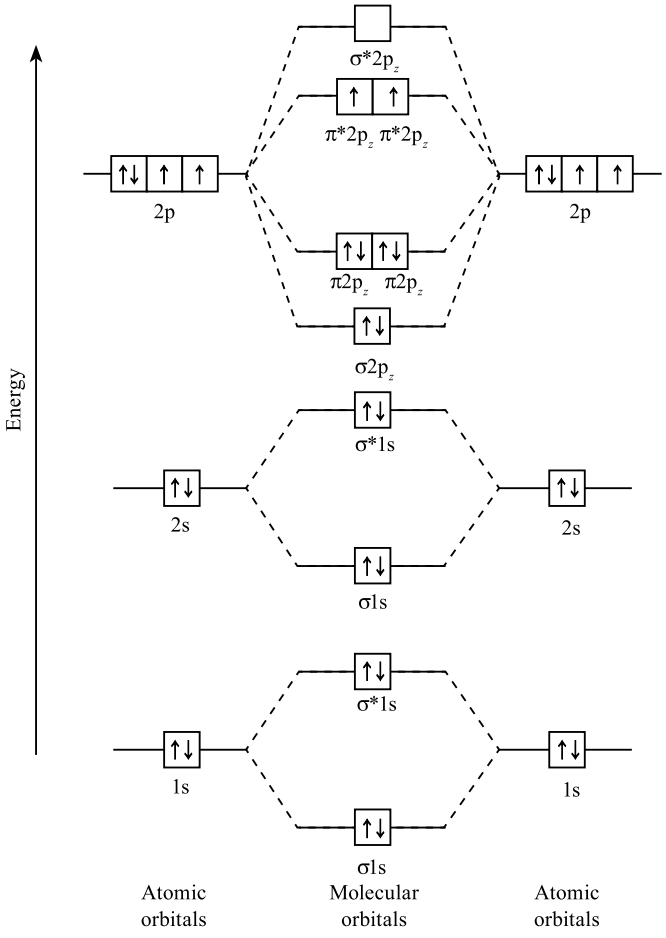


Figure 15: Energy level diagram for O_2 molecule

O_2^+ ion: O_2^+ has one electron less than O_2 molecule. This electron will be lost from $\pi^* 2p$ orbital.

Hence, the MO configuration will be: $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\sigma 2p_z^{\ 2}$, $\pi 2p_x^{\ 2} = \pi 2p_y^{\ 2}$, $\pi^* 2p_x^{\ 1}$

$$Bond\ order = \frac{10-5}{2} = 2.5.$$

The ion is paramagnetic due to the presence of one unpaired electron and is more stable than O_2 molecule.

O_2^- ion: O_2^- has one electron more than O_2 molecule. This electron will be added in π^*2p_x orbital.

Hence, the MO configuration will be: $\sigma 1s^2$, σ^*1s^2, $\sigma 2s^2$, σ^*2s^2, $\sigma 2p_z^2$, $\pi 2p_x^2 = \pi 2p_y^2$ $\pi^*2p_x^2 = \pi^*2p_y^1$

$$Bond\ order = \frac{10-5}{2} = 2.5.$$

O_2^{2-} ion: This ion has 18 electrons. Hence, the MO configuration will be: $\sigma 1s^2$, σ^*1s^2, $\sigma 2s^2$, σ^*2s^2, $\sigma 2p_z^2$, $\pi 2p_x^2 = \pi 2p_y^2$ $\pi^*2p_x^2 = \pi^*2p_y^2$

$$Bond\ order = \frac{10-8}{2} = 1.$$

HETERO-NUCLEAR DIATOMIC MOLECULES

To draw the MO diagrams for hetero-nuclear diatomic molecules, we face a new problem: Where do we place the atomic orbitals on an atom relative to atomic orbitals on other atoms? For example, how can we predict whether a fluorine 2s or a hydrogen 1s orbital is lower in energy? The answer comes from our understanding of electronegativity. Fluorine is more electronegative than hydrogen. Then electrons are more stable, i.e., lower in energy, when they are lone pairs on fluorine rather than on hydrogen. The more electronegative element's orbitals are placed lower on the MO diagram than those of the more electropositive elements. Therefore, the MO diagram of hetero-nuclear diatomic molecules is not symmetrical.

Moreover, since there is energy difference between the two sets of atomic orbitals, they interact less strongly and the energy lowering as a result of overlap is less pronounced in hetero-nuclear molecules than in homo-nuclear molecules.

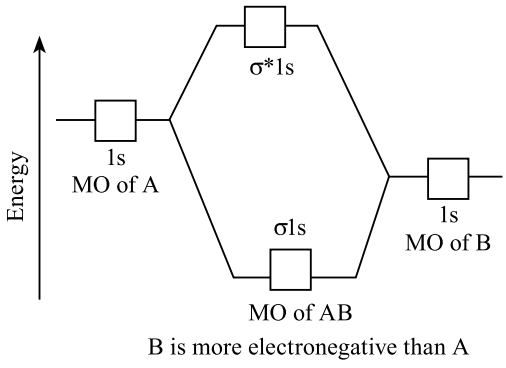


Figure 16: Energy level diagram for hetero-nuclear molecule

Hydrogen Fluoride Molecule, HF

The electronic configurations of hydrogen and fluorine atoms are:

$H = 1s^1$

$F = 1s^2\ 2s^2\ 2p^5$

The formation of HF molecule takes place by linear combination of H (1s) atomic orbital with $2p_z$ orbital of fluorine. Spectroscopic evidence shows that the energies of 1s and 2s electrons of fluorine are very low and they do not take part in bonding. Out of the three 2p orbitals, only $2p_z$ orbital is able to combine with s-orbital because of symmetry reasons.

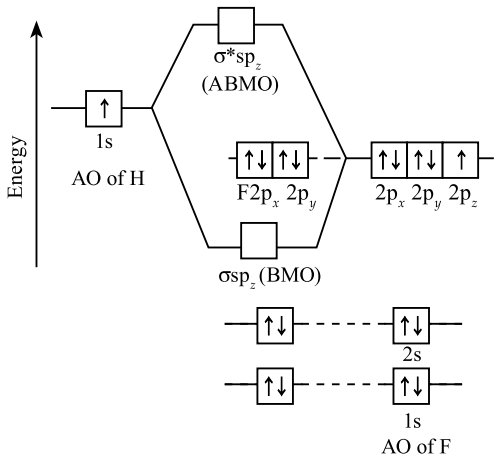


Figure 17: Energy level diagram for HF molecule

MO configuration of HF: $1s^2$, $2s^2$, σsp_z^2, $2p_x^2 = 2p_y^2$, $\sigma^*sp_z^0$

It may be noted that σsp_z is the only MO formed in HF molecule and bonding MO contains two electrons.

In case of hetero-nulcear HF molecule, the electrons are no longer shared equally between the two nuclei. The F ($2p_z$) atomic orbital is contributing more than the H (1s) orbital to the molecular orbital. The MO has the energy which lies closer to that of $2p_z$ orbital of fluorine than to that of 1s orbital of hydrogen.

$$Bond\ order = \frac{2-1}{2} = 1$$

Nitric Oxide Molecule, NO

The electronic configurations of N and O atoms are:

$N = 1s^2\ 2s^2\ 2p^3$

$O = 1s^2\ 2s^2\ 2p^4$

There are total of 15 electrons to be accommodated in the MO's of the molecule. The bonding MO's are closer to oxygen and anti-bonding MO's are closer to nitrogen because oxygen is more electronegative than nitrogen.

MO configuration of NO:

$\sigma\ 1s^2$, σ^*1s^2, $\sigma\ 2s^2$, $\sigma^*\ 2s^2$, $\pi 2p_x^2 = \pi 2p_y^2$, $\sigma\ 2p_z^2$, $\pi^*2p_x^1 = \pi^*2p_y^0$

$$Bond\ order = \frac{10-5}{2} = 2.5$$

NO is paramagnetic as it contains one unpaired electron.

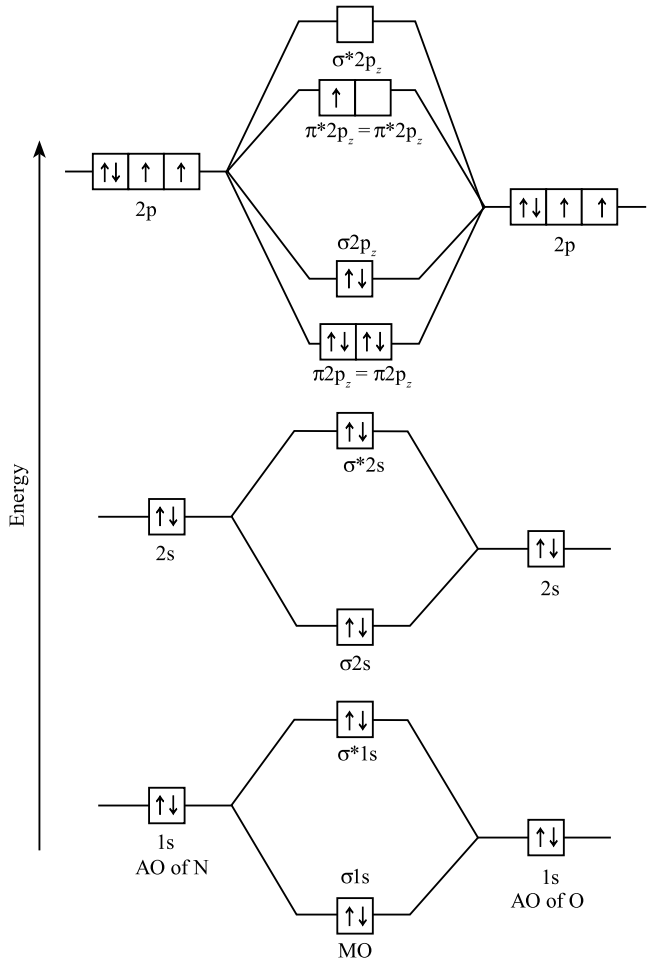


Figure 18: Energy level diagram for NO molecule

MO configuration of NO:

$$\sigma\ 1s^2, \sigma^*1s^2, \sigma\ 2s^2, \sigma^*\ 2s^2, \pi 2p_x^{\ 2} = \pi 2p_y^{\ 2}, \sigma\ 2p_z^{\ 2}, \pi^*2p_x^{\ 1} = \pi^*2p_y^{\ 0}$$

$$Bond\ order = \frac{10-5}{2} = 2.5$$

NO is paramagnetic as it contains one unpaired electron.

METALLIC BONDING

Metallic bonding is the bonding between atoms within metals. It is the electrostatic attractive forces between the delocalized electrons, called conduction electrons and the positively charged metal ions. Metallic bonding accounts for many physical properties of metals, such as strength, malleability, ductility, thermal and electrical conductivity, opacity and luster.

There are theories to explain most of the properties of metals. These theories do not involve directional bond formation.

Free Electron Theory or Electron Sea Model for Metallic Bonding

Lorentz developed this theory to explain the properties of metals.

The main features of this model are:

1. A metal atom is supposed to consist of two parts, valence electrons and the remaining part (nucleus and inner shells) which is called kernel.
2. The metallic crystal consists of closely packed metal atoms in three dimensions. The kernels of the metal atoms occupy the fixed positions called lattice sites while the space between the kernels is occupied by valence electrons. The arrangement of kernels and valence electrons is shown in Figure 1.19.

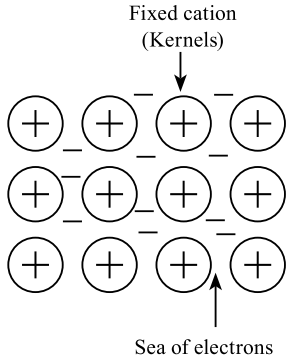


Figure 19: Electron sea model of metals

3. Due to smaller ionization energies, the valence electrons of metal atoms are not held very firmly by nucleus. Therefore, they can leave the field of influence of one kernel and enter the field of another. This movement can take place through the vacant valence orbitals. Thus, the valence electrons are not localized but are mobile or delocalized. As the movement of electrons in metallic crystal is just like the gas molecules, hence this model is called electron gas model.
4. The simultaneous force of attraction between the mobile electrons and positive kernels is responsible for holding the metal atoms together and is called metallic bond.

The metallic bond is non-directional and weaker than covalent bond.

Band Theory for Metallic Bonding

The band theory of metals is based on molecular orbital theory. Overlapping of atomic orbitals of metal atoms give rise to molecular orbitals. This can be explained by taking an example of a sodium metal. Sodium atom has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^1$ and a sodium crystal is formed by gradual addition of sodium atoms.

In case of Na_2, one bonding molecular orbital with two electrons and one anti-bonding molecular orbital without electron is formed.

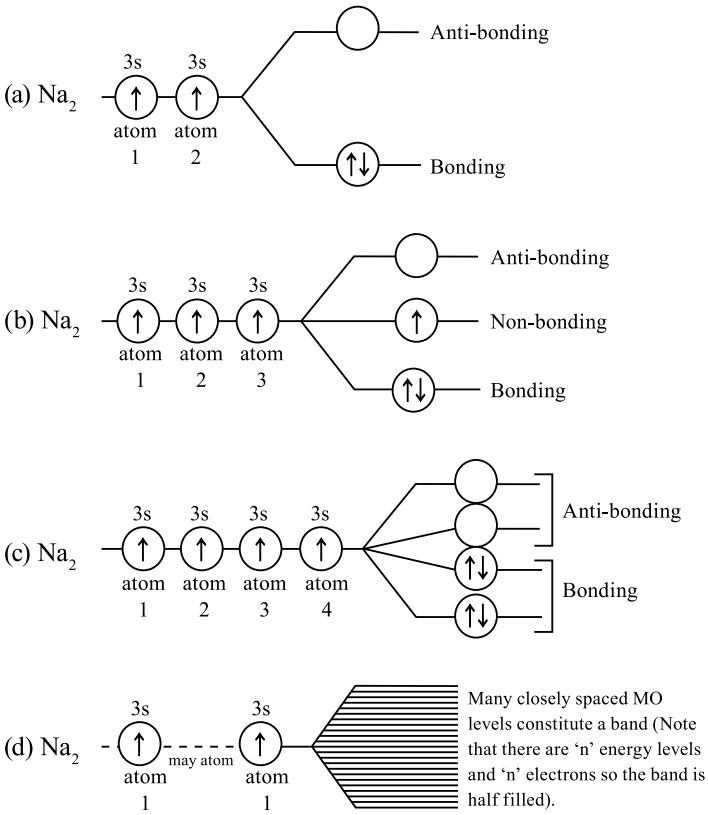


Figure 20: Molecular orbital model of sodium

For Na_3, three molecular orbitals, one bonding, one non-bonding and one anti-bonding are formed as shown in Figure 1.20. For Na_4, two bonding (each with two electrons) and two anti-bonding (empty) orbitals are formed.

For Na_n, n/2 bonding and n/2 anti-bonding molecular orbitals are formed. All n-valence electrons of sodium (Na_n) are accommodated in bonding molecular orbitals while n/2 anti-bonding molecular orbitals are vacant.

It has been observed that the separation of molecular orbitals decreases as the number of sodium atoms increases which are seen as closely spaced bands. So the theory is called the band theory.

The band formed by valence electrons (*i.e.,* $3s^1$) is called valence band and that formed by 2p (vacant) of sodium is called conduction band. The energy gap between valence band and conduction band is negligible (sometimes overlapped).

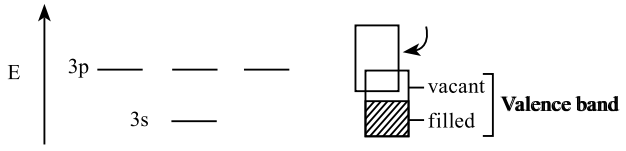


Figure 21: Energy bands in sodium

Different metals will produce different combinations of filled and half filled bands.

- In Na, the 3s band is 1/2 full.
- In Mg, the 3s band is full and 3p band is vacant.
- In Al, the 3s band is full and the 3p band is 1/2 full... and so on.

Note: The lowest unoccupied band is called the conduction band and the highest occupied band is called the valence band. Conduction occurs when electrons are promoted from the valence band to the conduction band, where they can move throughout the solid. The energy separation between the valence and conduction bands is known as the band gap energy.

Band Theory in Solids

Depending upon the energy gap between the valence band and conduction band (band theory), solids can be classified into three categories: Insulators, Semiconductors and Conductors.

Insulators

In insulators, the band gap (5-10 eV) between the valence band and the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band.

Semiconductors

Semiconductors have a small energy gap (0.7-1.0 eV) between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors. This energy gap leads to insulation at ordinary conditions, but on heating or by doping with certain elements (B or As), it functions as conductor.

Conductors

Metals are conductors. There is no band gap between their valence and conduction bands, since they overlap. There is a continuous availability of electrons in these closely spaced orbitals. Hence, electrons are easily transferred from valence band to conduction band.

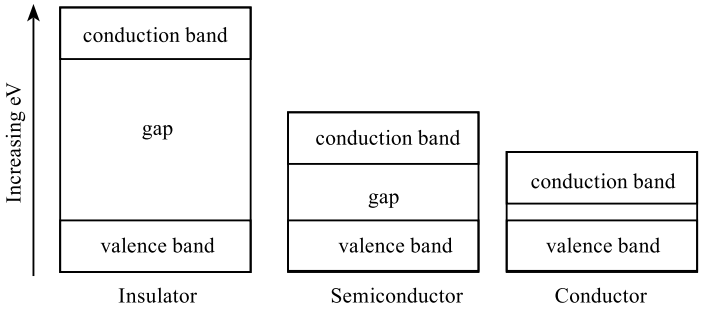


Figure 22: Energy bands in solids (Insulator, Semiconductor and conductor)

LIQUID CRYSTALS

Liquid crystal materials were first discovered in 1888 by an Austrian botanist, F. Renitzer. However, those liquid crystals

were not suitable for any commercial usage and it is only 25 years ago since the first material suitable for electronically driven displays, was developed.

The term "liquid crystal" is used to describe a substance which is in a state between a liquid and a crystal but exhibits properties similar to both. Molecules in liquid crystals tend to arrange themselves until they all point in the same general direction but, at the same time, the whole mass can flow like a liquid.

Normally, we consider matter to have three distinct states: solid, liquid and gas. However, there are states of matter which do not meet the necessary requirements of any of these three categories. For example, a substance such as mayonnaise is somewhere between a liquid and a solid.

Liquid crystals can be considered to be crystals which have lost some or all of their positional order, while maintaining full order of orientation. For example, imagine a large number of toothpicks put into a rectangular box and shaken. When you open the box, the toothpicks will be facing in about the same direction, but will have no definite spatial organization. They are free to move, but like to line up in about the same direction. "Liquid crystal" is an accurate description of both the observed state transitions of many substances and the arrangement of molecules in some states of these substances. Many substances can exist in more than one state.

For example, water can exist as a solid (ice), liquide or gas (water vapour). The state of water depends on its temperature. Below 0°C, water is a solid. As the temperature rises above 0°C, ice melts to liquid water. When the temperature rises above 100°C, liquid water vaporizes completely. The difference between these three states can be attributed to temperature. Temperature is a measure of randomness of the molecules and therefore, the higher the temperature, the less order exists and the increasing temperature will cause the transition from solid to liquid state through the intermediate liquid crystal state.

Liquid crystals are substances that exhibit a phase of matter that has properties between those of conventional liquid and solid crystal.

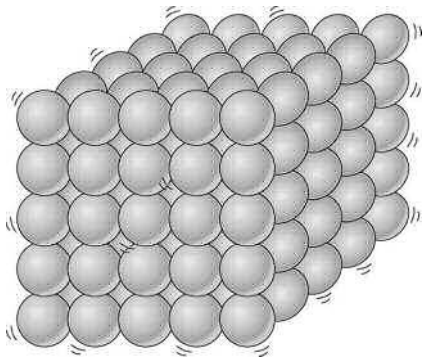


Figure 23: Arrangement of molecules in a solid crystal.

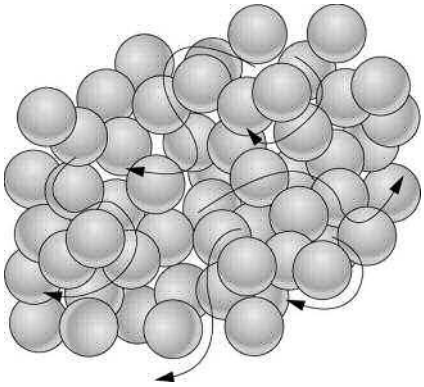


Figure 24: Arrangement of molecules in a liquid

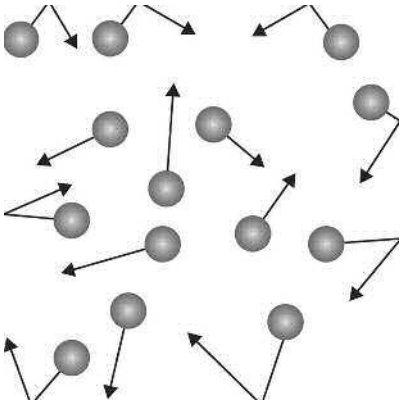


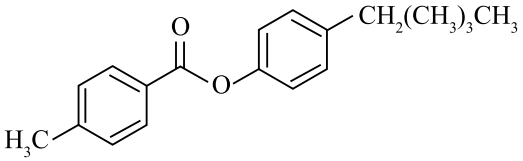
Figure 25: Arrangement of molecules in a gas crystal

"Liquid crystal" also accurately describes the arrangement of molecules in this state. In the crystalline solid state, as represented in Figure 23, the arrangement of molecules is regular, with a regularly repeating pattern in all directions. (Molecules of substances with a liquid crystal state are generally oblong and rigid, that is, rod-shaped.) The molecules are held in fixed positions by intermolecular forces.

As the temperature of a substance increases, its molecules vibrate more vigorously. Eventually, these vibrations overcome the forces that hold the molecules in place, and the molecules start to move. In the liquid state, this motion overcomes the intermolecular forces that maintain a crystalline state, and the molecules move into random positions, without pattern in location or orientation, as represented in Figure 24. In materials that form liquid crystals, the intermolecular forces in the crystalline solid are not the same in all directions; in some directions, the forces are weaker than in other directions. As such a material is heated, the increased molecular motion overcomes the weaker forces first, but its molecules remain bound by the stronger forces. This produces a molecular arrangement that is random in some directions and regular in others. The arrangement of molecules in one type of liquid crystal is represented in Figure 25.

STRUCTURE OF LIQUID CRYSTALS

Typically, a liquid-crystalline molecule consists of a rigid moiety and one or more flexible parts. The rigid part aligns molecules in one direction, whereas the flexible parts induce fluidity in the liquid crystal. This rigid part is referred to as mesogen and it plays a crucial role in the molecule. The optimum balance of these two parts is essential to form liquid-crystalline materials.



4-Pentylphenyl 4-methylbenzoate

Calamitic and Discotic Liquid Crystals

Calamitic, i.e., rod-shaped molecules show a large difference in length and breadth, thus delivering the required anisotropy. A typical calamitic mesogen consists of a rigid core unit, ensuring the anisotropic character, together with flexible side chains, which provide stabilising effects within the liquid crystal phases. The rigid core is mostly aromatic, but can also be alicyclic. Polar end groups are also very common. The physical properties can be widely influenced by the nature of the core and the side chains, allowing designing molecules for a specific purpose.

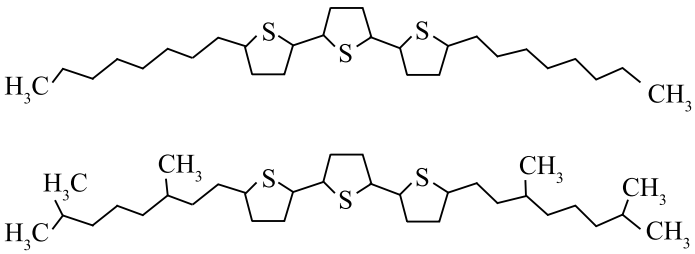


Figure 26: Calamitic liquid crystals: Unsymmetrical oligothiophenes

Discotic molecules also show a great difference between lengths, in this case, the height of the disc and breadth, the diameter. They usually consist of a rigid, flat core unit and flexible side chains, which are surrounding this core. The core unit is mostly but not necessarily aromatic, for example, triphenylene or phthalocyanine. To ensure the disc-shaped geometry of the molecule, the core is often symmetric and an appropriate number of side chains is used. Similarly to the calamitic mesogens, the physical properties can be influenced over a wide range by variation of the core and/or the side chains.

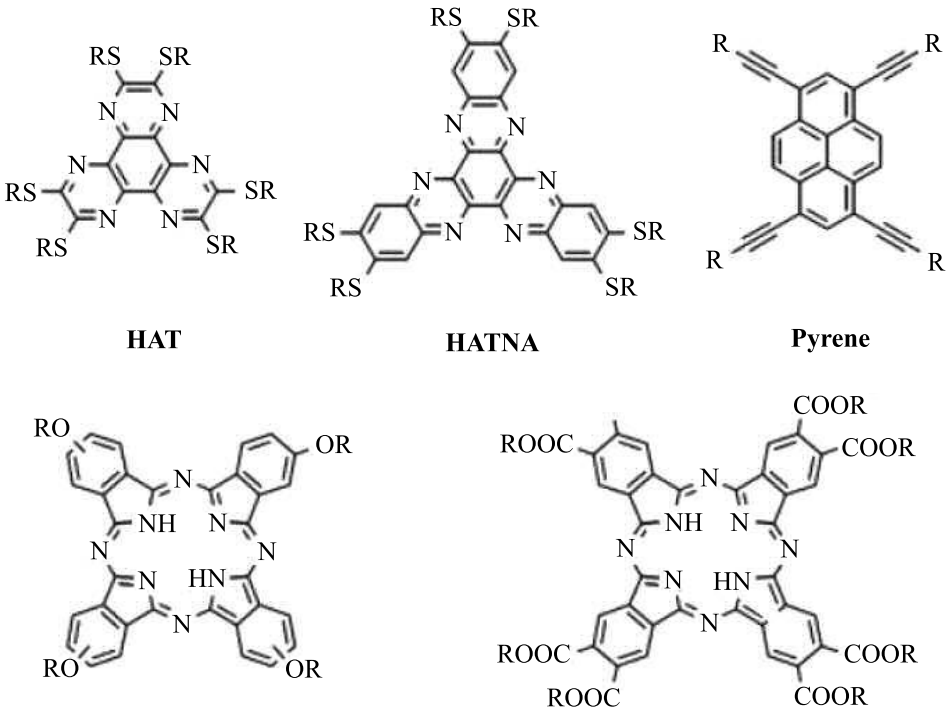


Figure 27: Examples of some discotic liquid crystals HAT: Hexazatriphenylenes, HATNA: Hexazatrinaphthylene

CLASSIFICATION OF LIQUID CRYSTALS

Liquid crystals are classified into two types: Thermotropic and Lyotropic.

1. **Thermotropic Liquid Crystals:** The phase transition is governed by change in the temperature and hence it is called thermotropic. Thermotropic liquid crystals can be subdivided into following categories:

   (i) Isotropic Phase: In this phase, the molecules are randomly aligned and exhibit no longer range order. The isotropic phases have a low viscosity and will often appear to be crystal clear.

   (ii) Nematic Phase: It is characterized by a high degree of orientation but no translational order. They are subdivided into the ordinary nematic and the chiral-nematic (or cholesteric). The molecules in the ordinary nematic structure maintain a parallel or nearly parallel arrangement to each other along the long molecular axes. They are mobile in three directions and can rotate about one axis. This structure is one-dimensional. When the nematic structure is heated, it is generally transformed into the isotropic liquid where the completely disordered motion of the molecules produces a phase in which all directions is equivalent. The nematic structure is the highest-temperature mesophase in thermotropic liquid crystals. The energy required to deform a nematic liquid crystal is so small that even the slightest perturbation caused by a dust particle can distort the structure considerably. In the chiral-nematic structure, the direction of the long axis of the molecule in a given layer is slightly displaced from the direction of the molecular axes of the molecules in an adjacent layer. If a twist is applied to this molecular packing, a helical structure is formed. The helix has a pitch that is temperature sensitive. The helical structure serves as a diffraction grating for visible light.

   (iii) Smectic Phase: The term smectic includes all thermotropic liquid crystals that are not nematic. Smectic phase has orientation order and also have small amount of positional order. In most smectic structures, the molecules are free to bounce around randomly; but they tend to point along a specific direction and arrange themselves in layers, either in neat rows or randomly distributed. The molecules can move in two directions in the plane and rotate about one axis. Smectic liquid crystals may have structured or unstructured strata. Structured smectic liquid crystals have long range order in the arrangement of molecules in layers to form a regular two-dimensional lattice. Depending upon it, we can classify as given further.

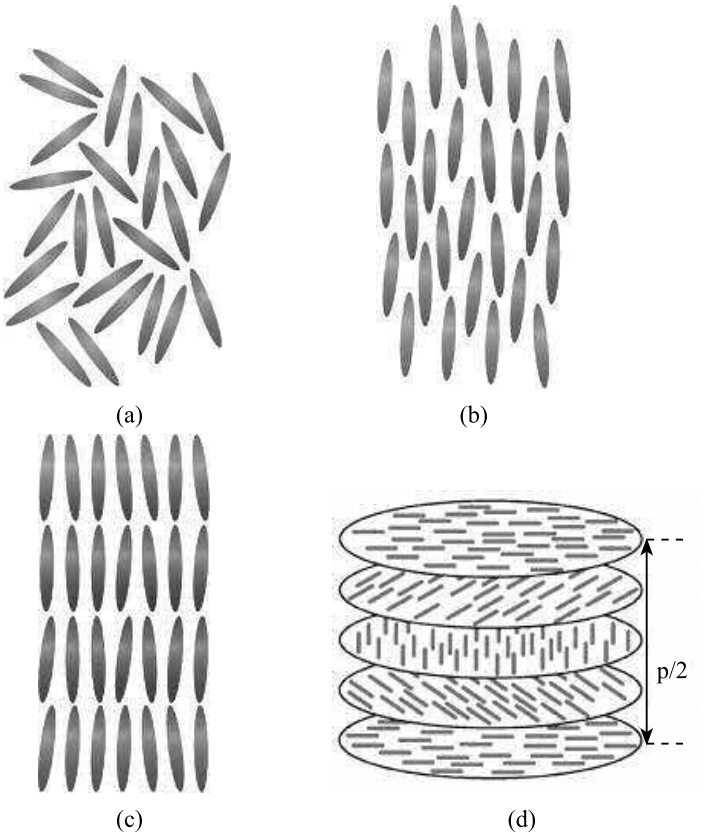


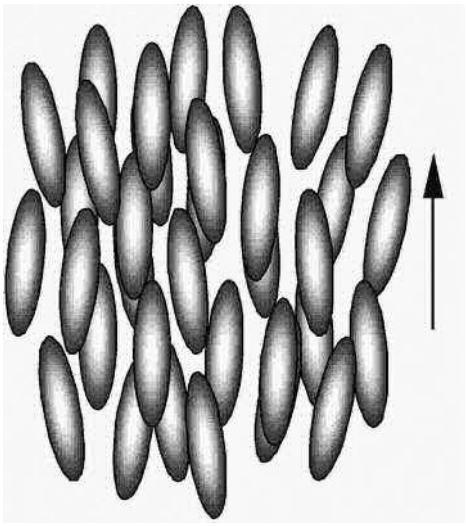
Figure 28: (a) Isotropic phase, (b) Nematic phase, (c) Smectic phase, (d) Chiral nematic

Smectic A. In the smectic A structure, molecules are also packed in strata, but the molecules in a stratum are randomly arranged. The long axes of the molecules in the smectic A structure lie perpendicular to the plane of the layers. They are optically active.

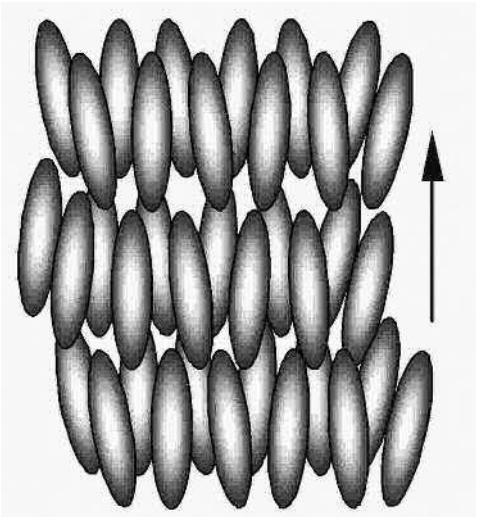
Smectic B. Smectic B is the most common of the structured liquid crystals. Molecular layers are in well-defined order, and the arrangement of the molecules within the strata is also well ordered. The long axes of the molecules lie perpendicular to the plane of the layers. The layers of Smectic B are not flexible. They are the most ordered of the three major phases A, B and C.

Smectic C. Molecular packing in a smectic C is the same as that in smectic A, except the molecules in the stratum are tilted at an angle to the plane of the stratum. The smectic C phase is optically biaxially.

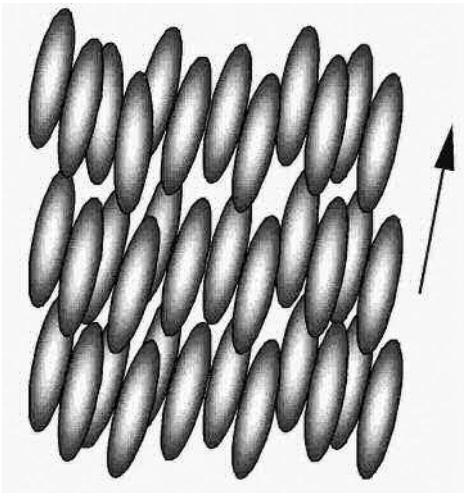
2. **Lyotropic Liquid Crystals:** The phase transition depends upon temperature and concentration. Lyotropic liquid crystals are formed by amphiphilic molecules. These usually have one part, which is hydrophilic and lipophobic, and another one which is just the opposite, lipophilic and hydrophobic.



Smectic A



Smectic B



Smectic C

Figure 29: Types of smectic phase

Due to the fact that the anisotropy is based on the different solubility properties of different ends of the molecules, a solvent is required in order to generate lyotropic liquid crystals. Typical examples for this kind of molecules are soaps. These consist of a polar, hydrophilic head group and an unpolar, hydrophobic tail. Depending on both the temperature and the concentration of the surfactant, different types of liquid crystals can form in contact with a solvent, e.g. water. If the concentration of the surfactant is very low, the molecules diffuse randomly. Once a certain concentration, called the critical micelle concentration (CMC), is reached, the amphiphilic molecules arrange themselves to spherical or rod-shaped micelles, assembling the tails together and exposing the polar heads to the water. With increasing concentration, the single micelles organise themselves to lose lattices. Spherical micelles preferably form cubic arrangements, whereas rod-shaped micelles usually show a hexagonal arrangement of the cylindrical rods. If the concentration is increased even more, sandwich-shaped bilayers are formed, with the hydrophobic tails pointing to the inside and the heads to the outside. These bilayers can also be shaped into a three-dimensional tube-like structure, which is then called vesicle. The lamellar arrangement is particularly important for phospholipids, which are also amphiphilic, because it is the basis for the biological cell membranes.

APPLICATIONS OF LIQUID CRYSTALS

Liquid crystal technology has had a major effect on many areas of science and engineering as well as device technology. Applications for this special kind of material are still being discovered and continue to provide effective solutions to many different problems.

Liquid Crystal Displays

The most common application of liquid crystal technology is liquid crystal displays (LCDs). This field has grown into a multi-billion dollar industry and many significant scientific and engineering discoveries have been made.

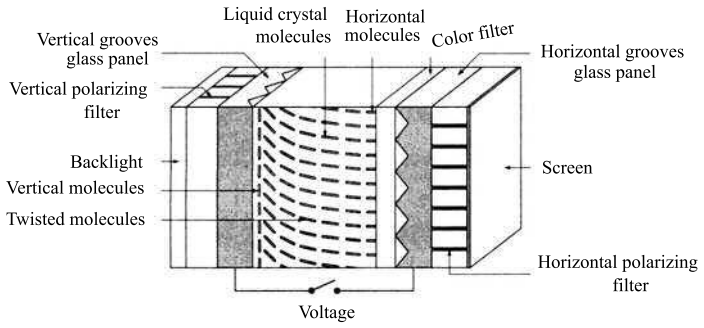


Figure 30: Schematic diagram of liquid crystal display

Working of LCD Display

LC molecules have rod like structure and rotate the direction of polarized light based on their alignment. By applying an electric field, the alignment of the molecules can be controlled.A twisted nematic liquid crystal display cell is made up of the following (as shown in the Figure 30):

- Two bonding glass plates, each with transparent conductive coating of ITO (indium tin oxide) that acts as an electrode.
- Spacers to control the cell gap precisely.
- Two cross polarizers.
- A nematic liquid crystal material.

In a display, the liquid crystal material is sealed between the two glass plates, each of which has a polarizer on its outside. Light passing through one of the polarizers has its polarization rotated with the alignment direction of the liquid crystal. As the light reaches the second analyzer, it can be passed or blocked, depending on the extend of rotation. The transparent conductor on the inner surface of the glass field are used to control the electric field on the cell, and thus the direction of the liquid molecules.

When the voltage is applied to the electrodes, the liquid crystal tends to align with the resulting electric field and the optical wave property of the cell is lost. The cell is dark as it would be without the LC. When the electric field is turned off, the molecules relax back to their twisted state and the cell becomes transparent again.

Liquid Crystal Thermometers

As we know that chiral nematic (cholesteric) liquid crystals reflect light with a wavelength equal to the pitch. Because the pitch is dependent upon temperature, the colour reflected is also dependent upon temperature. Liquid crystals make it possible to accurately gauge temperature just by looking at the colour of the thermometer. By mixing different compounds, a device for practically any temperature range can be built. The “mood ring”, a popular novelty a few years ago, took advantage of the unique ability of the chiral nematic liquid crystal. More important and practical applications have been developed in such diverse areas as medicine and electronics. Special liquid crystal devices can be attached to the skin to show a “map” of temperatures. This is useful because often physical problems, such as tumours, have a different temperature than the surrounding tissue. Liquid crystal temperature sensors can also be used to find bad connections on a circuit board by detecting the characteristic higher temperature.

Medical or Clinical Thermography

Clinical thermography is a non-evasive, diagnostic imaging procedure involving the detection and recording of a patient’s skin surface thermal patterns, using instruments which can provide visual and quantitative documentation of these temperature measurements. Thermography is an imaging technology which provides information on normal and abnormal functioning of the sensory and sympathetic nervous systems, vascular dysfunction, myofascial trauma and local inflammatory processes.

Liquid crystals can be used as a safe and effective means for evaluation of complex pain states associated with arthritis, soft tissue injuries and back pain diseases. It facilitates identification of the damage to the nervous system.

Optical Imaging

An application of liquid crystals that is only now being explored is optical imaging and recording. In this technology, a liquid crystal cell is placed between two layers of photoconductor. Light is applied to the photoconductor, which increases the material’s conductivity. This causes an electric field to develop in the liquid crystal corresponding to the intensity of the light.

The electric pattern can be transmitted by an electrode, which enables the image to be recorded. This technology is still being developed and is one of the most promising areas of liquid crystal research.

Polymer Composite Material

If a polymer is extruded in the liquid crystal phase, the anisotropic ordering of molecules confer an extremely high strength polymer. Kevlar is a good example of such high strength liquid crystal polymer, used in bullet proof vests and car body panels.

Other Liquid Crystal Applications

Liquid crystals have a multitude of other uses. They are used for non-destructive mechanical testing of materials under stress. This technique is also used for the visualization of RF (radio frequency) waves in waveguides. They are used in medical applications where, for example, transient pressure transmitted by a walking foot on the ground is measured. Low molar mass (LMM) liquid crystals have applications including erasable optical disks, full colour “electronic slides” for computer-aided drawing (CAD) and light modulators for colour electronic imaging.

As new properties and types of liquid crystals are investigated and researched, these materials are sure to gain increasing importance in industrial and scientific applications.

SOLID STATE CHEMISTRY

A solid is defined as that form of matter which possesses rigidity and hence possesses a definite shape and a definite volume. Unlike gases and liquids in which the molecules are free to move about and hence constitute fluid state, in solids, the constituent particles are not free to move but oscillate about their fixed positions.

CLASSIFICATION OF SOLIDS

Broadly speaking, solids can be divided into two classes: Crystalline Solids and Amorphous Solids.

A crystalline solid is a substance whose constituent particles possess regular orderly arrangement e.g. sodium chloride, sucrose, diamond, etc.

Crystalline substances have the following properties:

- They have orderly arranged units and are practically incompressible. They show definite melting point and pass sharply from solid to liquid state.
- They have different physical properties in different directions. This phenomenon is known as anisotropy.
- They have definite geometries.

An amorphous solid is a substance whose constituent particles do not possess a regular orderly arrangement e.g. glass, plastics, rubber, starch and proteins. Though amorphous solids do not possess long range regularity, in some cases, they may possess small regions of orderly arrangement. These crystalline parts of an otherwise amorphous solid are known as crystallites.

Amorphous substances have the following properties:

- They do not possess a sharp melting point. They undergo liquefication over a broad range of temperature. The amorphous solids do not possess any characteristic heat of fusion.
- When an amorphous solid is cut with the help of sharp edged knife, it results in an irregular cut.
- Amorphous substances are also sometimes referred to as super cooled liquids because they possess disorderly arrangement like liquids. In fact many amorphous solids such as glass are capable of flowing.
- Their physical properties are same in all the directions so they are said to have isotropic properties.
- They do not have definite geometries.

Distinction Between Crystalline and Amorphous Solids

Crystalline Solids	Amorphous Solids
The internal arrangement of particles is regular so they possess definite and regular geometry.	The internal arrangement of particles is irregular. Thus, they do not have any definite geometry.
They have sharp melting points.	They do not have sharp melting points.
Crystalline solids give a regular cut when cut with a sharp edged knife.	Amorphous solids give irregular cut.
They have characteristic heat of fusion.	They do not have characteristic heat of fusion.
They are rigid and their shape is not distorted by mild distorting forces.	They are not very rigid. These can be distorted by bending or compressing forces.
They are regarded as true solids.	They are regarded as super cooled liquids or pseudo solids.
They are anisotropic. This implies that physical properties such as refractive index, conductivity, thermal expansion, etc. are different in different directions. This is due to orderly arrangement of particles.	They are isotropic in nature. This implies that various physical properties are same in all the directions. This is because of random arrangement of particles.

Depending upon the nature of acting interatomic forces, all solids may be subdivided into six main types: Ionic, Metallic, Network Atomic, Atomic, Molecular and Amorphous Solids.

1. Ionic Solids

Ionic solids form when electrostatic attraction sticks together anions and cations to form a crystal lattice. In an ionic crystal, each ion is surrounded by ions having an opposite charge. Ionic crystals are extremely stable since considerable energy is required to break ionic bonds.

Example: Sodium chloride

2. Metallic Solids

Positively charged nuclei of metal atoms are held together by valence electrons to form metallic solids. The electrons are considered to be "delocalized" because they are not bound to any particular atoms, as in covalent bonds. Delocalized electrons can move throughout the solid. This is the "electron sea model" of metallic solids. Positive nuclei float in a sea of negative electrons. Metals are characterized by high thermal and electrical conductivity and are typically hard, shiny and ductile.

Example: Almost all metals and their alloys, such as gold, brass, steel, etc.

3. Network Atomic Solids

This type of solid is also known simply as a network solid. These solids are huge crystals consisting of atoms held together by covalent bonds. Many gemstones are network atomic solids.

Example: Diamond, ruby

4. Atomic Solids

Atomic solids form when weak London dispersion forces bind atoms of cold noble gases.

Example: These solids are not seen in everyday life, since they require extremely low temperatures. An example would be solid krypton or solid argon.

5. Molecular Solids

Covalent molecules are held together by intermolecular forces to form molecular solids. While the intermolecular forces are strong enough to hold the molecules in place, molecular solids typically have lower melting and boiling points than metallic, ionic or network atomic solids, which are held together by stronger bonds.

Example: Water ice

6. Amorphous Solids

Unlike all of the other types of solids, amorphous solids do not exhibit a crystal structure. This type of solid is characterized by having an irregular bonding pattern. Amorphous solids may be soft and rubbery when they are formed by long molecules, tangled together and held by intermolecular forces. Glassy solids are hard and brittle, formed by atoms irregularly joined by covalent bonds.

Examples: Plastic, glass

SPACE LATTICE OR CRYSTAL LATTICE

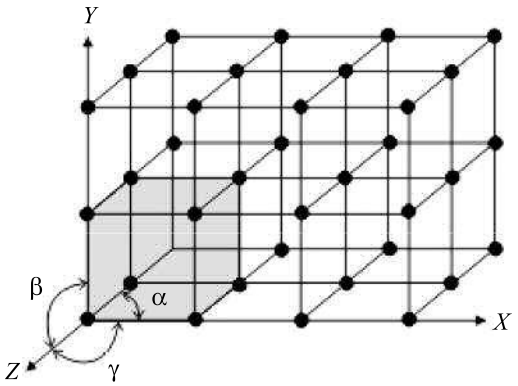
All crystals consist of regularly repeating array of atoms, molecules or ions which are the structural units (or basic units). It is much more convenient to represent each unit of pattern by a point, called lattice point, rather than drawing the entire unit of pattern. This results in a three dimensional orderly arrangement of points called a space lattice or a crystal lattice.

Thus, a space lattice may be defined as a regular three dimensional arrangement of identical points in space or it can be defined as an array of points showing how molecules, atoms or ions are arranged at different sites in three dimensional space.

It must be noted that

(a) Each lattice point has the same environment as that of any other point in the lattice.

(b) The constituent particles have always to be represented by a lattice point, irrespective of whether it contains a single atom or more than one atoms.

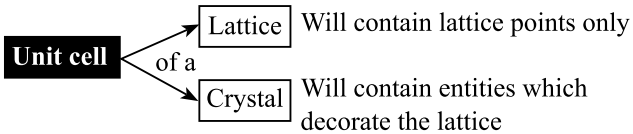


A crystal or space lattice. The shaded portion represents the unit cell

Figure 31: Space lattice and unit cell

Unit Cell

A unit cell is the smallest repeating unit in space lattice which when repeated over and over again results in a crystal of the given substance. Unit cell may be defined as a three dimensional group of lattice points that generate the whole lattice on repetition.



Types of Unit Cell

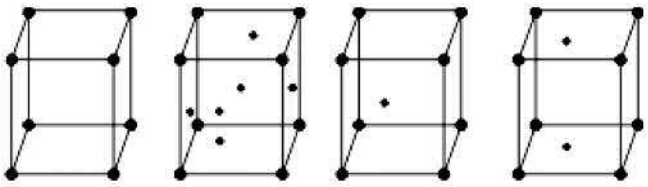
A unit cell is obtained by joining the lattice points. The choice of lattice points to draw a unit cell is made on the basis of the external geometry of the crystal and symmetry of the lattice. There are four different types of unit cells. These are:

(1) PRIMITIVE OR SIMPLE CUBIC (SC): Atoms are arranged only at the corners of the unit cell.

(2) BODY CENTRED CUBIC (BCC): Atoms are arranged at the corners and at the centre of the unit cell.

(3) FACE CENTRED CUBIC (FCC): Atoms are arranged at the corners and at the centre of each faces of the unit cell.

(4) END CENTRED: Atoms are arranged at the centre of only one set of faces in addition to the atoms at the corner of the unit cell.



Primitive unit cell | Face centred unit cell | Body centred unit cell | End centred unit cell

Figure 32: Types of unit cell

Number of Atoms Per Unit Cell

There are eight atoms at the corners. Each corner atom makes 1/8 contribution to the unit cell.

$\therefore$ No. of atoms present in the unit cell = $1/8 \times 8 = 1$

Simple Cubic

Body Centred Cubic (BCC)

BCC has 8 atoms at the corners and one atom within the body. Each corner atom makes 1/8 contribution and the contribution of atom within the body = 1.

$\therefore$ No. of atoms present in BCC = $1/8 \times 8$ (at corner) + 1 (at the body centre)

$= 1 + 1 = 2$

Face Centred Cubic (FCC)

FCC has 8 atoms at the corners and 6 atoms on the faces (one on each face).

Contribution by atoms at the corners = 1/8 × = 1

Contribution by atom on the face = 1/2 × 6 = 3

∴ Number of atoms present in FCC unit cell = 1 + 3 = 4

End Centred

End centred unit cell has 8 atoms at the corners and 2 atoms on any two opposite faces.

Contribution by atoms at the corners = 1/8 × 8 = 1

Contribution by atom on the face = 1/2 × 2 = 1

∴ Number of atoms present in end centred unit cell = 1 + 1 = 2

Example 1: A compound formed by elements A and B has a cubic structure in which A atoms are at the corners of the cube and B atoms are at face centres. Derive the formula of the compound.

Solution:

As 'A' atoms are present at the 8 corners of the cube,

∴ Number of atoms of A in the unit cell = 1/8 × 8 = 1

As B atoms are present at the face centres of the cube,

∴ Number of atoms of B in the unit cell = 1/2 × 6 = 3

Hence, the formula of compound is AB_3.

Example 2: Potassium crystallizes in a body centred cubic lattice. What is the approximate number of unit cells in 4.0 g of potassium? Atomic mass of potassium = 39.

Solution:

In BCC unit cell, there are 8 atoms at the corners of the cube and one atom at the body centre.

∴ Number of atoms per unit = 8 × 1/8 + 1 = 2

Number of atoms in 4 g of potassium = $4/39 \times 6.023 \times 10^{23}$

∴ No. of unit cells in 4.0 g of potassium = $4/39 \times 6.023 \times 10^{23} / 2 = 3.09 \times 10^{22}$.

Example 3: An ionic compound made up of atoms A and B has a face-centred cubic arrangement in which atoms A are at the corners and atoms B are at the face centres. If one of the atoms is missing from the corner, what is the simplest formula of the compound?

Solution:

Number of atoms of A at the corners = 7 (because one A is missing)

∴ Contribution atoms of A towards unit cell = 7 × 1/8 = 7/8

Number of atoms B at face centres = 6

∴ Contribution of atom B towards unit cell = 6 × 1/2 = 3

Ratio of A : B = 7/8 : 3 = 7 : 24

∴ Formula is A_7B_{24}.

Calculation of Density of Unit Cell

Let the edge length of the cube = a cm

∴ Volume of unit cell = a^3 cm^3

$$\therefore \quad Density\ of\ unit\ cell = \frac{Mass\ of\ unit\ cell}{Volume\ of\ unit\ cell} \qquad (1)$$

Mass of unit cell = Number of atoms per unit cell × Mass of each atom

$$= Z \times m \qquad (2)$$

where Z = No. of atoms per unit cell

m = Mass of each atom

But $$m = \frac{Atomic\ mass}{Avogadro's\ number}$$

$$m = \frac{M}{N_0} \qquad (3)$$

From eqns. (2) and (3)

$$Mass\ of\ Unit\ cell = Z \times \frac{M}{N_0} \qquad (4)$$

From eqns. (1) and (4)

$$Density\ of\ Unit\ cell\ (\rho) = \frac{Z \times M}{a^3 \times N_0} \qquad (5)$$

If the edge length is expressed in picometer (pm), then

Edge length = $a \times 10^{-12}$ m = $a \times 10^{-10}$ cm

∴ Volume of unit cell = $a^3 \times 10^{-30}$ cm^3

∴ Eqn. (5) becomes

$$Density\ of\ Unit\ cell\ (\rho) = \frac{Z \times M}{a^3 \times 10^{-30} \times N_0}\ gcm^{-3}$$

Note: Density of the unit cell is same as the density of the substance

Example 4: An element having atomic mass 60 has face centred cubic unit cell. The edge length of the unit cell is 400 pm. Find out the density of the element.

Solution:

Unit cell edge length = 400 pm = 400×10^{-10} cm

Volume of unit cell = $(400 \times 10^{-10})^3 = 64 \times 10^{-24}$ cm^3

Mass of the unit cell = No. of atoms in the unit cell × Mass of each atom

Number of atoms in FCC unit cell = 8 × 1/8 + 6 × 1/2 = 4

∴ Mass of unit cell = $4 \times 60 / 6.023 \times 10^{23}$

Density of unit cell = Mass of unit cell / Volume of unit cell

= $4 \times 60 / 6.023 \times 10^{23} \times 64 \times 10^{-24} = 6.2$ g/cm^3

Example 5: An element has a body centred cubic (BCC) structure with a cell edge of 288 pm. The density of the element is 7.2 g/cm^3. How many atoms are present in 208 g of the element?

Solution:

Volume of unit cell = $(288 \times 10^{-10})^3$ cm^3 = 2.39×10^{-23} cm^3

Volume of 208 g of the element = Mass / Density

= 208 / 7.2 = 28.88 cm^3

Number of unit cells in this volume = $28.88 / 2.39 \times 10^{-23}$

= 12.08×10^{23}

Since each BCC unit cell contains 2 atoms,

$\therefore$ Number of atoms in 208 g = $2 \times 12.08 \times 10^{23}$

= 24.16×10^{23} atoms.

Example 6: Calculate the value of Avogadro's number from the following data: Density of NaCl = 2.165 g/cm^3. Distance between Na^+ and Cl^-=281 pm.

Solution:

A unit cell of NaCl contains 4 NaCl units,

therefore, Z = 4, M = 23 + 35.5 = 58.5 g mol^{-1}

ρ = 2.165g/cm^3

As the distance between Na^+ and Cl^-=281 pm

Edge length of the unit cell = 2 × 281 = 562 pm

Substituting the values in the expression

$$Density\ of\ unit\ cell(\rho) = \frac{Z \times M}{a^3 \times 10^{-30} \times N_0}$$

$$2.165\ g\ cm^{-3} = \frac{4 \times 58.5\ g\ mol^{-1}}{(562)^3 \times 10^{-30} \times N_0}$$

$N_0 = 6.09 \times 10^{23}$ mol^{-1}.

Example 7: A compound formed by elements X and Y, crystallizes in the cubic structure, where X is at the corners of the cube and Y is at the six face centers. What is the formula of the compound? If side length is 5A°, estimate the density of the solid assuming atomic weight of X and Y as 60 and 90 respectively.

Solution:

From eight corner atoms, one atom (X) contributes to one unit cell.

From six face centres, three atoms (Y) contributes to one unit cell.

So, the formula of the compound is XY_3.

As we know that,

$$\rho = \frac{Z \times M}{a^3 \times N_0}$$

Here, Z = 1, a = 5Å = 5×10^{-8} cm

Molar mass of XY_3: M = 60 + 3 × 90 = 330 g

$$\rho = \frac{1 \times 330}{(5 \times 10^{-8})^3 \times 6.023 \times 10^{23}}\ gcm$$

= 4.38 gm/cm^3.

Example 8: An FCC structure of an element has density 10.3 gcm^{-3} and has an edge length 314 pm. Calculate the atomic mass of the element.

Solution:

Given that

Density = 10.3 g/cc

Edge length = 314 pm = 310×10^{-10} cm = 3.14×10^{-8} cm

Volume = $(3.14 \times 10^{-8})^3$ cm^3

Number of atoms in FCC unit cell = 8 × 1/8 + 6 × 1/2 = 4

Let the atomic mass = M

$$Density = \frac{Number\ of\ atoms\ per\ unit\ cell \times Atomic\ mass}{Volume\ of\ unit\ cell \times Avogadro's\ number}$$

$$10.3 = \frac{4 \times M}{(3.14 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$$

$$M = \frac{10.3 \times (3.14 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{4} = 48.01.$$

Example 9: The density of NaCl is 2.165g/cm^3. Calculate the edge of its cubic cell assuming that the four molecules of NaCl are associated per unit cell.

Solution:

Edge length of cube = a cm

Volume = a^3 cm^3

M = 23 + 35.5 = 5 8.5 g

Unit cell of NaCl contains 4 NaCl units,

therefore, Z = 4,

ρ = 2.165g/cm^3

$N_0 = 6.023 \times 10^{23}$

Substituting the values in the expression

$$Density\ of\ unit\ cell(\rho) = \frac{Z \times M}{a^3 \times N_0}$$

$$2.165 = \frac{4 \times 58.5}{a^3 \times 6.023 \times 10^{23}}$$

$$a^3 = \frac{4 \times 58.5}{2.165 \times 6.023 \times 10^{23}}$$

$\therefore$ a = 5.64×10^{-8} cm.

IMPERFECTIONS IN SOLIDS: DEFECTS IN CRYSTALS

Atomic imperfections/point defects:

When deviations exist from the regular (or periodic) arrangements around an atom or a group of atoms in a crystalline substance, the defects are called point defects.

Type of point defects

Point defects in a crystal may be classified into three types: (1) Stoichiometric defects, (2) Non-stoichiometric defects, and (3) Impurity defects.

(1) Stoichiometric defects:

The compounds in which the number of cation and anions are exactly in the same ratio as represented by their chemical formula are called stoichiometric compounds. The defects that do not disturb the ratio of cations and anions are called stoichiometric defects.

These are of two types: Schottky and Frenkel defects.

(i) Schottky defect

If in an ionic crystal of the type $A^+ B^-$, equal number of cations and anions are missing from their lattice, it is called Schottky defect. An example is given below:

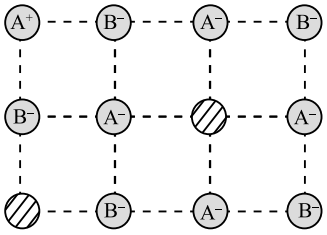


Figure 33: Schottky defect

This type of defect is shown by highly ionic compounds which have

- High coordination number
- Small difference in the sizes of cations and anions.

A few examples of ionic compounds exhibiting Schottky defect are NaCl, KCl, KBr and CsCl.

Consequences of Schottky Defects

- As the number of ions decreases as a result of this defect, the mass decreases whereas the volume remains the same. Hence, density of the solid decreases.
- The crystal begins to conduct electricity to a small extent by ionic mechanism.
- The presence of too many voids lowers lattice energy and the stability of the crystal.

(ii) Frenkel defect

If an ion is missing from its correct lattice sites (causing a vacancy or a hole) and occupies an interstitial site, electrical neutrality as well as stoichiometry of the compounds is maintained. This type of defect is called Frenkel defect. Since cations are usually smaller, it is more common to find the cations occupying interstitial sites.

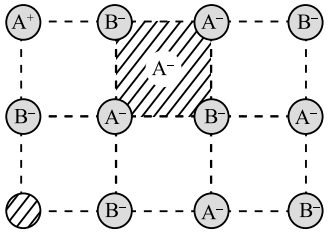


Figure 34: Frenkel defect

This type of defect is present in ionic compounds which have

- Low coordination number
- Larger difference in size of cation and anions
- Compounds having highly polarising cation and easily polarisable anion.

A few examples of ionic compounds exhibiting this defect are AgCl, AgBr, AgI, ZnS, etc.

Consequences of Frenkel Defects

- As no ions are missing from the crystal lattice as a whole, therefore, density of the solid remains the same.
- The closeness of like charges tends to increase the dielectric constant of the crystal.
- The crystal conducts electricity to a small extent by ionic mechanism.

(2) Non-Stoichiometric Defects

If as a result of imperfection, the ratio of number of cation to anion becomes different from that indicated by the ideal chemical formula, the defects are called non-stoichiometric defects. These defects arise either due to excess of metal atoms or non-metal atoms or presence of impurities/foreign particles.

(i) Metal excess defects due to anion vacancies

A compound may have excess metal ion if a negative ion is absent from its lattice site leaving a hole which is occupied by electron to maintain neutrality.

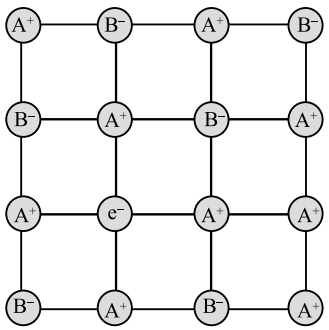


Figure 35: Metal excess defects due to anion vacancy

The holes that are occupied by electrons are called 'F' centres (or colour centres) and are responsible for the colour of the compound and many interesting properties.

(ii) Metal excess defects due to interstitial cations

Metal excess may also be caused by an extra cation (positive ion) present in an interstitial site. Electrical neutrality is maintained by presence of an electron in another interstitial site. This defect is similar to Frenkel defect and is found in crystals having Frenkel defects.

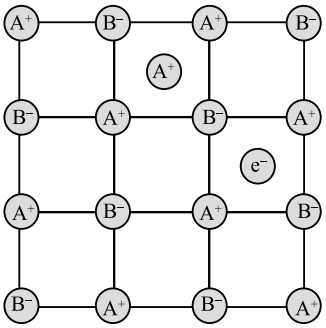


Figure 36: Metal excess defect due to interstitial cation

(iii) Metal deficiency due to cation vacancies

The non-stoichiometric compounds may have metal deficiency due to the absence of a metal from its lattice site. The charge is balanced by an adjacent ion having higher positive charge. This type of defects are generally shown by compounds of transition elements.

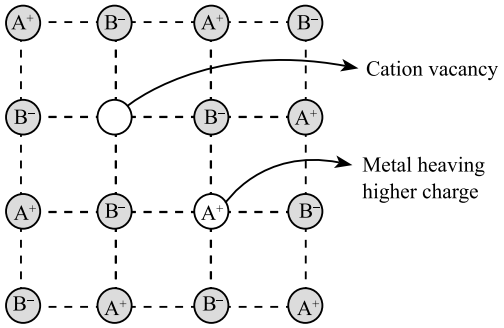


Figure 37: Metal deficiency due to action vacancy

(3) Point defects due to the presence of foreign atoms

These defects arise when foreign atoms are present at the lattice site (in place of host atoms) or at the vacant interstitial sites. In the former case, we get substitutional solid solutions. The formation of former depends upon the electronic structure of impurity while that of later on the size of impurity.

GRAPHITE

Carbon has two natural crystalline allotropic forms: graphite and diamond. Each has its own distinct crystal structure and properties.

Graphite is a soft greyish-black greasy substance. The word 'graphite' comes from a Greek word meaning 'to write'. Graphite is also crystallized carbon. The carbon atoms of graphite form a crystal pattern that differs from that of the carbon atoms in diamond.

Occurrence of Graphite

Natural graphite is mined in Bihar, Andhra Pradesh, Jammu and Kashmir, Odisha, Rajasthan, Tamil Nadu and Uttar Pradesh. Other than India, it is found in Sri Lanka and Russia also. In the United States, it is mined in New York and Pennsylvania. Synthetic graphite is made from hard coal or coke in an electric furnace.

Structure of Graphite

In graphite, each carbon atom is covalently bonded to three carbon atoms to give trigonal geometry. Bond angle in graphite is 120°. Each carbon atom in graphite is sp^2 hybridized. Three out of four valence electrons of each carbon atom are used in bond formation with three other carbon atoms while the fourth electron is free to move in the structure of graphite.

Basic trigonal units unite together to give basic hexagonal ring. In hexagonal ring, C-C bond length is 0.14 nm. In graphite, these rings form flat layers. These layers are arranged in parallel, one above the other. These layers are 0.34 nm apart and are held together by weak Van der Waals forces only. These layers can slide over one another. Thus, it is very soft. Fourth electron of each carbon atom forms delocalized π-bonds which spread uniformly over all carbon atoms. Due to this reason, graphite conducts electricity.

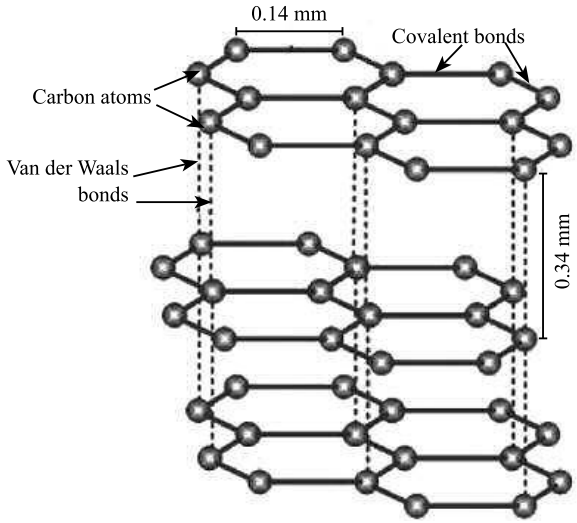


Figure 38: Structure of graphite

Properties of Graphite

1. Graphite is a soft, slippery, greyish-black substance. It has a metallic luster and is opaque to light.

2. Specific gravity of graphite is 2.3.
3. Graphite is a good conductor of heat and electricity.
4. Although graphite is a very stable allotrope of carbon but at a very high temperature, it can be transformed into artificial diamond.
5. Chemically, graphite is slightly more reactive than diamond.

Uses of Graphite

1. The major use of graphite is in making lead pencils of different hardness, by mixing it with different proportions of clay. The weakly held layers of carbon atoms in graphite easily slide over each other and are left behind on paper as black marks.
2. Due to its slippery nature, graphite is used as a dry lubricant in machine parts.
3. Being resistant to chemicals and having a high melting point and also because it is a good conductor of heat, graphite is used to make crucibles.
4. The presence of free electrons makes graphite a good conductor of electricity and it is used to make electrodes.
5. Graphite has the ability to absorb fast-moving neutrons, thus, it is used in nuclear reactors to control the speed of the nuclear fission reaction.

FULLERENES

A third newly discovered allotrope of carbon (after graphite and diamond) is Buckminster fullerene named in the honour of the American architect Buckminster Fuller, the designer of geodesic dome. The shape of C60 resembles with the domes designed by Fuller. Fullerenes were discovered as an unexpected surprise during laser spectroscopy experiments at Rice University in September 1985. The 1996 Nobel Prize in Chemistry was awarded to Professors Robert F. Curl, Jr. Richard E. Smalley and Sir Harold W. Kroto for their discovery.

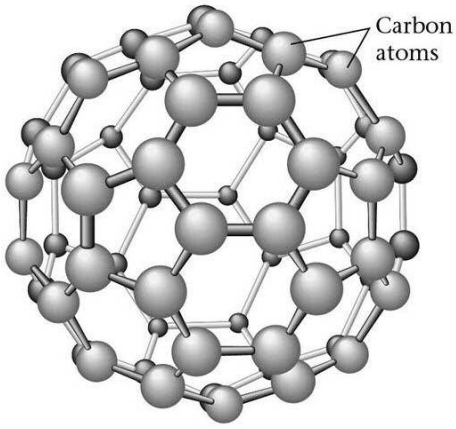


Figure 39: Buckminster fullerene

Types of Fullerenes

Fullerenes are a family of carbon allotropes, molecules entirely composed of carbon, in the form of hollow, sphere, ellipsoid, tube or plane. Thus, fullerenes are of the following types:

1. Spherical fullerenes: They look like a soccer ball and are often called bucky balls.
2. Cylindrical fullerenes: These are called carbon nanotubes or bucky tubes.
3. Planar fullerenes: Graphene is an example of planar fullerene sheet.

Preparation of Fullerenes

Fullerenes are prepared by vaporizing a graphite rod in a helium atmosphere. Mixtures of fullerenes like C_{60}, C_{70}, etc. are formed which are separated by solvent extraction. C_{60} is isolated from this mixture by column chromatography using alumina/hexane as a solvent system.

Structure

Fullerenes are a class of closed-cage carbon molecule, C_n, characteristically containing 12 pentagons and a variable number of hexagons.

C_{60} is a spherical crystal of carbon atoms with an arrangement of even number of sp^2 atoms over the surface of a closed hollow cage. Each atom is trigonally linked to its three neighbouring atoms by bonds and thus forms a polyhedral network. The C_{60} molecule has a truncated icosahedron structure.

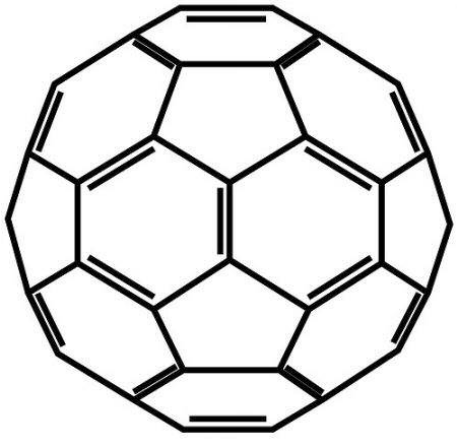


Figure 40: Structure of C_{60}

An icosahedron is a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. A carbon atom is present at each vertex. The valencies of each carbon atom are satisfied by two single and one double bond. The molecule has several resonating structure and is aromatic. The fused ring aromatic system bends around and closes to form a soccer shaped molecule (a bucky ball).

Other fullerenes have also been discovered. C_{70} is elongated like a rugby ball. Richard E. Smalley of Rice University predicts that a 'Russian doll' molecule can be made by trapping C_{60} molecule inside a very large C_{240} fullerenes. Giant fullerenes with at least 600 atoms also seen to form and appear to have interesting polyhedral shapes. The smallest member of fullerene family is C_{20}.

Properties of Fullerenes

The bucky ball has certain unique properties:

1. It exists as a discrete molecule.
2. C_{60} is a mustard coloured solid. When the thickness of the film increases, it appears brown to black.
3. It is moderately soluble in the common organic solvents, especially aromatic hydrocarbons.
4. It dissolves in benzene forming a deep magenta solution.
5. It is very tough. It can be accelerated to 1500 miles/hour and can be pushed against a tough surface without damaging it.
6. Highest tensile strength of any known 2D structure or element.
7. Highest packing density of all known structures.
8. Impenetrable to all elements under normal circumstances, even to a helium atom with energy of 5 eV.
9. It can be compressed to lose 30% of its volume without destroying its cage like structure.
10. It is thermally stable upto 600°C. It undergoes sublimation under vacuum at 600°C.

Derivatives of Fullerenes

Fullerenes readily participate in a number of chemical reactions. Its reactivity is very good, therefore, a number of fullerene derivatives can be prepared:

1. Up to 24 methyl groups can be added to C_{60} polyanions.
2. Polychlorinated and polybrominated derivatives have been produced.
3. Charge transfer complexes such as $[Fe(C_2H_5)_2]2C_{60}$ and exohedral organometallic derivatives (Os, Pt, In) are some of the good examples of fullerene derivatives.
4. Superconducting fullerides: C_{60} is a poor conductor of electricity. When fullerene reacts with good electron donors like alkali metals, its conductivity increases. Alkali-fullerene compounds such as K_3C_{60} are superconducting. This compound has critical temperature (T_c) 19.2K. The potassium atoms occupy the octahedral sites in the cubic cell. Some other fullerides are $PbCs_2C_{60}$, Rb_3C_{60} and Ca_5C_{60}.
5. Magnetic donors: Organic electron donors like tetrakis dimethyl amino ethylene (TDAE) reduces C_{60} and form solid $(TDAE)C_{60}$. It is ferromagnetic solid with a curie temperature of 16K.

Applications of Fullerenes

The fullerene derivatives have been found to exhibit amazing conducting, magnetic, optical and mechanical properties.

1. Fullerenes can easily accept electrons, therefore, they may be used as charge carrier in batteries.
2. Fullerenes can be used as organic photovoltaics.
3. Alkali metal fullerides are superconductors.
4. It can also be used as a soft ferromagnet (e.g. TDAE-C_{60}).
5. Its spherical structure makes it suitable for the use as lubricant.
6. Due to their extremely resilient and sturdy nature, fullerenes are being considered for use in combat armor.
7. Researchers have found that water-soluble derivatives of fullerenes inhibit the HIV-1 protease (enzyme responsible for the development of virus) and are therefore useful in fighting the HIV that leads to AIDS.
8. Fullerenes are powerful antioxidants, reacting readily and at a high rate with free radicals, which are often the cause of cell damage or death. Fullerenes hold great promise in health and personal care applications where prevention of oxidative cell damage or death is desirable, as well as in non-physiological applications where oxidation and radical processes are destructive (food spoilage, plastics deterioration, metal corrosion). Major pharmaceutical companies are exploring the use of fullerenes in controlling the neurological damage of such diseases as Alzheimer's disease and Lou Gehrig's disease (ALS), which are a result of radical damage. Drugs for atherosclerosis, photodynamic therapy and anti-viral agents are also in development.
9. Fullerenes and fullerenic black are chemically reactive and can be added to polymer structures to create new copolymers with specific physical and mechanical properties. They can also be added to make composites. Much work has been done on the use of fullerenes as polymer additives to modify physical properties and performance characteristics.
10. They are used as catalyst as they have marked ability to accept and to transfer hydrogen atoms, hydrogenation and hydro-dealkylations. They are highly effective in promoting the conversion of methane into higher hydrocarbons.

BRAGG'S EQUATION: STRUCTURE DETERMINATION BY X-RAYS

The German physicist *M Von Laue* in 1913 suggested the possibility of diffraction of X-rays by crystals. The reason for this suggestion was that the wavelength of X-rays was of about the same order as the inter-atomic distances in a crystal. Then

if these X-rays were allowed to strike the crystal, the rays will penetrate into the crystal and will be scattered by the electrons of the atoms or the ions of the crystal.

The rays reflected from different layers of the atoms due to wave nature will then undergo interference (constructive and destructive) to produce a diffraction pattern just as it happens in case of light passing through a grating containing a large number of closely spaced lines. In other words, crystals should act as a three dimensional grating for X-rays. Bragg applied this fact in determining structure and dimensions of crystal.

W.L. Bragg and his father *W.H. Bragg* determined the cubic structure of NaCl using X-rays. According to Bragg, a crystal (composed of series of equally spaced atomic planes) could be employed not only as a transmission grating (as suggested by Laue) but also as a reflection grating. In Bragg's treatment, the X-rays strike the crystal at angle θ, these penetrates into the crystal and are reflected by different parallel layers of particles in the crystal.

A strong reflected (constructive) beam will result only if all the reflected rays are in phase. The reflected waves by different layer planes will be in phase with one another only if the difference in the path length of the waves reflected from the successive planes is equal to an integral number of wavelengths.

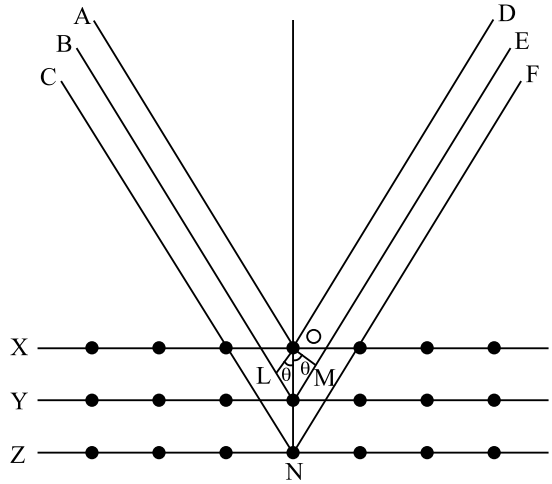


Figure 41: X-Ray reflection from crystals

It may be noted from Figure 41 that the beams of X-rays which are reflected from deeper layers travel more to reach the detector. Two X-ray waves in phase are shown to be approaching the crystal. One wave is reflected from the first layer of atoms while the second wave is reflected from the second layer of atoms. The wave reflected from the second layer travels more distance before emerging from the crystal than the first wave. The extra distance travelled is equal to LN + NM. For constructive interference to take place, the extra distance travelled by the more penetrating beam must be on integral multiple of the wavelength.

Path difference = LN + NM = LN = nλ (n = 1, 2, 3 ….)

Since the triangles OLN and OMN are congruent, hence, LN = NM

So, path difference = 2LN

LN = d Sinθ where d is the distance between two planes

So, path difference = 2d sinθ

For constructive interference 2 d sinθ must be equal to nλ

Or nλ = 2 d sinθ

This relation is called Bragg's equation. Distance between two successive planes d can be calculated from this equation. With X-ray of definite wavelength, reflection at various angles will be observed for a given set of planes separated by a distance 'd'. These reflections correspond to n = 1, 2 , 3 and so on and are spoken of as first order, second order, third order and so on. The angle θ increases as the intensity of the reflected beams weakens.

Example 10: X-rays of wavelength 1.54Å strike a crystal and are observed to be deflected at an angle 22.5°. Assuming that n = 1, calculate the spacing between the planes of atom that are responsible for this reflection.

Solution:

Applying Bragg's equation

$n\lambda = 2d \sin\theta$

Given n = 1, λ = 1.54 Å, θ = 22.5°

Using relation nλ = 2 d sinθ

$$d = \frac{1.54}{2 \sin 22.5^\circ} = \frac{1.54}{2 \times 0.383} = 2.01\text{Å}.$$

Example 11: Calculate the angle at which second order reflection will occur in an X-ray spectrometer. When X-ray of wavelength 1.54Å is diffracted by atoms of a crystal, the interplanar distance is 4.04Å.

Solution:

According to Bragg's equation

$n\lambda = 2 d \sin\theta$

n = 2

λ = 1.54 Å; d = 4.04 Å

$\theta = \text{Sin}^{-1} (2 \times 1.54/2 \times 4.04) = \text{Sin}^{-1} (1.54/4.04)$

$= \text{Sin}^{-1} (0.381)$

= 22° 24'.

Example 12: What will be the wavelength of X-rays, which give a diffraction angle θ equal to 8.4° for a crystal if the inter-nuclear distance is 0.4 nm and only second order diffraction is observed?

Solution:

Applying Bragg's equation

$n\lambda = 2d \sin\theta$

Given n = 2, d = 0.4×10^{-9} m, θ = 8.4°

$$\lambda = \frac{2 \times 0.4 \times 10^{-9} \times \sin 8.4^\circ}{2}$$

$= 0.0584 \times 10^{-9}$ m = 0.584 Å.

MULTIPLE CHOICE QUESTIONS

1. Which of the following molecules will form a linear polymeric structure due to hydrogen bonding ?

(*a*) HC1 (*b*) HF

(*c*) H_2O (*d*) NH_3

2. Which of the following two are isostructural ?

(*a*) XeF_2, IF_2^- (*b*) NH_3, BF_3

(*c*) CO_3^{2-}, $S0_3^{2-}$ (*d*) $PC1_5$, $IC1_5$

3. In which of the following species is the underlined carbon having sp3 hybridization ?

(*a*) CH_3 — COOH .

(*b*) CH_3 — CH_2OH

(*c*) CH_3 — CO — CH_3

(*d*) CH_2 = CH — CH_3

4. In which of the following the bond angle is maximum?

(*a*) NH_3 (*b*) NH_4^+

(*c*) $PC1_5$ (*d*) $SC1_2$

5. Which one of the following statements is not correct for sigma and p-bonds formed between two carbon atoms ?

(*a*) Sigma bond is stronger than pi bond

(*b*) Bond energies of sigma and pi bonds are of the order of 264 $kJmol^{-1}$ and 347 $kJmo1^{-1}$

(*c*) Free rotation of atoms around a sigma bond is allowed but not in case of a pi bond

(*d*) Sigma bond determines the direction between carbon atom but a pi bond has no primary effect in this regard

6. Total number of lone pair of electrons in $XeOF_4$ is ?

(*a*) 0 (*b*) 1

(*c*) 2 (*d*) 3

7. The state of hybridisation of boron and oxygen atoms in boric acid (H_3BO_3) are respectively?

(*a*) sp^3 and sp^2 (*b*) sp^2 and sp^3

(*c*) sp^2 and sp^2 (*d*) sp^1 and sp^3

8. The maximum number of 90° angles between bond pair-bond of electrons is observed in ?

(*a*) dsp^2 hybridization (*b*) sp^3d hybridization

(*c*) dsp^3 hybridization (*d*) sp^3d^2 hybridization

9. H_2O is dipolar where as BeF_2 is not. It is because:

(*a*) H_2O involves 'hydrogen bonding where as BeF_2 is a discrete molecule

(*b*) H_3O is linear 'but BeF_2 is angular

(*c*) H_2O is angular and BeF_2 is linear

(*d*) The electronegativity of F is greater than that of O|

10. Which one of the following has the regular tetrahedral structure ?

(*a*) BF_4^- (*b*) SF_4

(*c*) XeF_4 (*d*) $[Ni(CN)_4]^{2-}$

11. The correct-order of bond angles (smallest first) in H_2S, NH_3, BF_3 and SiH_4 is

(*a*) $H_2S < NH_3 < SiH_4 < BF_3$

(*b*) $NH_3 > H_2S < SiH_4 < BF_3$

(*c*) $H_2S < SiH_4 < NH_3 < BF_3$

(*d*) $H_2S < NH_3 < BF_3 < SIH_4$

12. In an octahedral structure, the pair of d-orbitals involved in d^2sp^3 hybridization is ?

(*a*) $d_{x^2-y^2}$, d_{x^2} (*b*) $d_{zr}, d_a V$

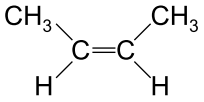
(*c*) d_{xy}, d_{yz} (*d*) $dx^2–y^2\ dz^2$

13. Among the following, the pair in which the two species not isostructural are :

(*a*) IO_3^- and XeO_3 (*b*) BH_4^- and NH^+

(*c*) PF_6^- and SF_6 (*d*) SiF_4 and SF_4

14. Which of the following hydrocarbon has the lowest dipole moment ?

(*a*) 

(*b*) $CH_3 — C \equiv C — CH_3$

(*c*) $CH_3 — CH_2 — C \equiv CH$

(*d*) $CH_2 = CH — C \equiv CH$

The questions given below consist of an Assertion (A) and the Reason (R). Use the following key to choose the appropriate answer

(*a*) If both assertion and reason are correct and reason is the correct explanation of the assertion.

(*b*) If both assertion and reason are correct, but reason is not the correct explanation of the assertion.

(*c*) If assertion is correct but reason is incorrect.

(*d*) If assertion is incorrect but reason is correct.

(*e*) If both assertion and reason are incorrect.

15. The linear structure is not assumed by

(*a*) $SnCI_2$ (*b*) CS_2

(*c*) NO_2^+ (*d*) HCN

16. Which of the following molecule does not have dipole moment greater than zero ?
(*a*) NH_3 (*b*) $CHCI_3$
(*c*) H_2O (*d*) $CC1_4$

17. Which hybrid state cannot be shown by carbon ?
(*a*) sp^3d (*b*) sp^3
(*c*) sp^2 (*d*) *sp*

18. The no. and type of bonds between two carbon atoms in calcium carbide are
(*a*) one σ, one Pi (*b*) one σ, two pi
(*c*) two σ, one pi (*d*) one σ, 1½ pi

19. The formation of adduct between NH_3 and BF_3 involves the formation of
(*a*) ionic bond (*b*) covalent bond
(*c*) coordinate bond (*d*) hydrogen bond

20. The shape of 003 is
(*a*) Tetrahedral (*b*) Pyramidal
(*c*) Trigonal Planar (*d*) Trigonal bipyramidal

21. The C–H bond distance is longest in
(*a*) C_2H_2 (*b*) C_2H_4
(*c*) $C_2H_4Br_2$ (*d*) C_6H_6

22. Which is most ionic?
(*a*) P_2O_5 (*b*) MnO
(*c*) CrO_3 (*d*) Mn_2O_7

23. Among the following species, identify the isostructural pairs
NF_3, $N0_3^-$, BF_3, H_3O^+, NH_3
(*a*) (NF_3, $N0_3^-$] and [BF_3, H_30^+]
(*b*) [NF_3, NH_3] and [NO_3^-, BF_3]
(*c*) [NF_3, H_3O^+] and [NO_3^-, BF_3]
(*d*) [NH_3, BF_3] and [NF_3, H_3O^+]

24. The Geometry and types of hybrid orbitals present about the central atom in BF_3 is
(*a*) Linear, *sp* (*b*) trigonal planar, sp^2
(*c*) tetrahedral, sp^3 (*d*) pyramidal, sp^3

25. Which one of the following has highest dipole moment?
(*a*) NH_3 (*b*) PH_3
(*c*) SbH_3 (*d*) AsH_3

26. Which of the following has zero dipole moment ?
(*a*) CIF (*b*) PCI_3
(*c*) SiF_4 (*d*) $CFCI_3$

27. Which of the following compounds has sp^2 hybridization?
(*a*) CO_2 (*b*) SO_2
(*c*) N_2O (*d*) CO

28. The molecule having highest percentage ionic character is
(*a*) HI (*b*) HBr
(*c*) HCI (*d*) HF

29. The molecule that will have no dipole moment is:
(*a*) 2, 2 - dimethyl propene
(*b*) Trans - 2 - pentene
(*c*) cis - 3 - hexene \
(*d*) 2, 2, 3, 3 tetramethyl butane

30. The geometry of H_2S and its dipole moment are:
(*a*) angular and non-zero
(*b*) angular zero
(*c*) linear and non-zero
(*d*) linear and zero

31. The hybridization of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are
(*a*) sp, sp^3 and sp^2 respectively
(*b*) sp, sp^2 and sp^3 respectively
(*c*) sp^2, sp and sp^3 respectively
(*d*) sp^2, sp^3 and sp respectively.

32. Molecular shapes of SF_4, CF_4 and XeF_4 are
(*a*) the same with 2, 0 and 1 lone pairs of electrons respectively
(*b*) the same with 1, 1 and 1 lone pairs of electrons respectively
(*c*) different with 0, 1 and 2 lone pairs of electrons respectively
(*d*) different with 1, 0 and 2 lone pairs of electrons respectively

33. The correct order of hybridisation of the central atom in the following species : NH_3, $[PtCI_4]^{2-}$, $PC1_5$ and BCI_3 is
(*a*) dsp^2, dsp^3, sp^2 and sp^3
(*b*) sp^3 dsp^2, dsp^3 sp^2
(*c*) dsp^3, sp^2 sp^3 dsp^3
(*d*) dsp^2, sp^3 sp^2 dsp^3

34. Among KO_2, AIO_2^-, BaO_2 and NO_2^+, unpaired electron is present in :
(*a*) NO_2^+ and BaO_2 (*b*) KO_2 and $AI0_2^-$
(*c*) KO_2 only (*d*) BaO_2 only

35. **Assertion (A):** Inonic compound tend to be non-volatile.
Reason (R): The intermolecular forces in these compounds are weak.

36. **Assertion (A):** The dipole moment helps to predict whether a molecule is a polar on non-polar.

Reason (R): The dipole moment helps to predict the geometry of molecule.

37. Assertion (A): BF_3 molecule is planar while NF_3 is pyramidal.

Reason (R): N atom is smaller is size than B atom.

38. Assertion (A): CO_2 is non-polar while H_2O is polar, through both are triatomic.

Reason (R): CO_2 is linear while H_2O is angular.

39. Assertion (A): NO_3^- is planar while NH_3 is pyramidal.

Reason (R): N in $N0_3^-$ has sp^2 and in NH_3 has sp^3 Hybridisation.

40. Assertion (A): Both BF_3 and PF_5 do not obey octet rule.

Reason (R): Both are electron deficient molecules.

41. Assertion (A): Bond angle in H_2O is less than that in H_2S.

Reason (R): Electronegativity of O is more than that of S.

42. Assertion (A): C_2H_2 molecule is planar.

Reason (R): In C_2H_2 carbon atoms remain unhybridised.

43. Assertion (A): cis 1, 2, -dichloro ethene has no dipole moment.

Reason (R): Two C–C1 bonds cancel the bond polarity of each other.

44. Assertion (A): Covalent bonds are rigid and directional.

Reason (R): Covalent compounds undergo molecular reactions which are very slow.

45. Consider the following species:

(1) $[O_2]^{2-}$ (2) CO^+

(3) $[O_2]^+$

Among these species sigma bond alone is present in

(*a*) 1 alone (*b*) 2 and 1

(*c*) 2 alone (*d*) 1, 2 and 3 V

46. The triple bond in N_2 molecule consists of

(*d*) three sigma bonds

(*b*) three pi bonds

(*c*) two sigma bonds and one pi bond

(*d*) one sigma bond and two pi bonds

47. The double bond in O_2 molecule consists of

(*a*) two sigma bonds

(*b*) two p-bonds

(*c*) one sigma bond and one p-bond

(*d*) one c bond and one p-bond

48. Match list I (species) with list II (Hybridisation) and select the correct answer using the codes given below the list:

List-I	***List-II***
A. BCl_3	1. sp^3
B. NH_3	2. $sp^3 d^2$
C. $[Cu(NH_3)_4]^{2+}$	3. sp^2
D. $[Fe(H_2O)_6]^{2+}$	4. $(n-1)^{1-9} ns^2$

Codes:

	A	**B**	**C**	**D**
(*a*)	3	1	4	2
(*b*)	1	3	4	2
(*c*)	1	3	2	4
(*d*)	3	1	2	4

49. Match list I (species) with list II (shape) and select the correct answer using the codes given below the list :

List-I	***List-II***
A. H_2O	1. Angular
B. NH_3	2. Pyramidal
C. CH_4	3. T-shaped
D. CIF_3	4. Tetrahedral

Codes:

	A	**B**	**C**	**D**
(*a*)	3	2	1	2
(*b*)	1	2	4	3
(*c*)	2	1	3	4
(*d*)	4	3	2	1

50. Match list I with II and select the correct answer using the codes given below the list:

List-I	***List-II***
A. CH_4	1. 109°28′
B. NH_3	2. 102°30′
C. NF_3	3. 107°48′
D. H_2O	4. 104°27′

Codes:

	A	**B**	**C**	**D**
(*a*)	1	3	2	4
(*b*)	1	3	4	2
(*c*)	4	1	2	3
(*d*)	4	1	3	2

51. Match List I with List II and select the correct answer using the codes given below the list:

List-I	*List-II*
A. SF_6	1. Tetrahedral
B. NH_3	2. Trigonal bipyramid
C. CH_4	3. Octahedral
D. BF_3	4. Plane triangle

Codes:

	A	B	C	D
(*a*)	3	2	1	4
(*b*)	4	1	2	3
(*c*)	3	1	2	4
(*d*)	2	4	3	1

52. Match List I and List II and select the correct answer using the codes given below the list:

List-I	*List-II*
A. I_3^-	1. T-shaped
B. ClF_3	2. See saw
C. H_2O	3. Angular
D. SF_4	4. Linear

Codes:

	A	B	C	D
(*a*)	4	1	3	2
(*b*)	4	1	2	3
(*c*)	2	3	4	1
(*d*)	3	2	4	1

53. Which of the following species have undistorted octahedral structures ?

1. SF_6 2. PF_6
3. SiF_6^{2-} 4. XeF_6

Codes:

	A	B	C	D
(*a*)	3	1	4	2
(*b*)	1	3	4	2
(*c*)	1	3	2	4
(*d*)	3	1	2	4

54. The bond strength of sign bonds formed by s, p orbitals are such that.

(*a*) $s - s\ \sigma > s - p_x\ \sigma > p_x - p_x\ \sigma$
(*b*) $s - p_x\ \sigma > s - s\ \sigma > p_x - p_x\ \sigma$
(*c*) $p_x - p_x > s - p_x\ \sigma > s - s\ \sigma$
(*d*) $p_x - p_x\ \sigma > s - s\sigma > s - p_x\ \sigma$

55. The molecular geometry of IF_7 as predicated by VSEPR theory is

(*a*) Distorted octahedral
(*b*) Trigonal bipyramidal
(*c*) Trigonal bipyramidal
(*d*) Square Pyramidal

56. Match List I (Hybridisation) with List II (shape) and select the correct answers using the codes given below the list:

List-I	*List-II*
A. dsp^2	1. Spuare planar
B. d^3sp	2. Trigonal prism
C. d^2sp^3	3. Octahedral
D. sp^3d	4. Trigonal bipyramidal

Codes:

	A	B	C	D
(*a*)	1	2	3	4
(*b*)	2	1	3	4
(*c*)	3	4	2	1
(*d*)	4	3	2	1

57. In CO_2 molecule, the bonds between the carbon and oxygen atoms consist of

(*a*) one sigma bond and two pi bonds
(*b*) two sigma bonds and one pi bond
(*c*) two sigma bonds and two pi bonds
(*d*) one sigma bond and one pi bond

58. Match list I (Molecule) with list II (Shape) and select the correct answer using the codes given below the lists:

List-I	*List-II*
A. $(CH_3)_3B$	1. Square planar
B. NH_3Cl	2. Trigonal bipyramid
C. $[ICl_4]^-$	3. Tetrahedral
D. PCl_5	4. Trigonal

Codes:

	A	B	C	D
(*a*)	1	3	4	2
(*b*)	4	3	1	2
(*c*)	4	2	1	3
(*d*)	1	2	4	3

59. Oxygen atom in the water molecule is sp^3 hybridised giving rise to tetrahedral geometry. But the structure of water molecule is V-shaped. This is due to

(*a*) sp^3–*s* bond formation
(*b*) bond pair-bond pair repulsion
(*c*) the high dipole moment of water
(*d*) lone pair-lone pair repulsion

60. Which of the following species have identical bond order ?

(1) CN– (2) O_2^-

(3) NO^+ (4) CN^+

Select the correct answer using the codes given below:

(*a*) 1, 2 and 4 (*b*) 1, 3 and 4

(*c*) 1 and 3 (*d*) 2, 3 and 4

61. Based-on molecular orbital predictions, the net bonds in linear CO_2 molecules are

(*a*) lσ, 3p (*b*) 2σ

(*c*) 2σ, 2p (*d*) 2p

62. The bond order of $[He_2]+$ is

(*a*) 1 (*b*) 0.5

(*c*) 1.5 (*d*) 0.75

63. The magnetic moment of $[Ni(CN)_4]^{2-}$ ion is found to be zero. Then the ion is

(*a*) sp^3 hybridized

(*b*) spd^2 hybridized

(*c*) dsp^2 hybridized

(*d*) dsp^3 hybridized

64. Which of the following compound(s) has/have linear structure ?

(1) $BeCl_2$ (2) H_2O

(3) SO_2

Select the correct answer using the codes given below :

(*a*) 1 and 2 (*b*) 2 and 3

(*c*) 3 alone (*d*) 1 alone

65. Match List 1 (Species) with List II (Bond orders) and select the correct answer:

List-I	***List-II***
A. N_2	1. 1.0
B. O_2	2. 2.0
C. F_2	3. 2.5
D. O_2	4. 3.0

Codes:

	A	**B**	**C**	**D**
(*a*)	4	2	1	3
(*b*)	1	2	3	4
(*c*)	4	3	2	1
(*d*)	2	1	4	3

66. Consider the following statements

The planar shape of $Ni(SiH_3)_3$ is explained by the

1. type of hybrid ordinals of nitrogen
2. additional *d*p–*p*p overlap along the N-Si bond
3. higher electronegative of nitrogen of these statements.

(*a*) 1, 2 and 3 are correct

(*b*) 1 and 2 are correct

(*c*) 2 and 3 are correct

(*d*) 1 and 3 are correct

67. Match List I (Hybrid bond orbitals) with List-II (species) and select the correct answer:

List-I	***List-II***
A. d^2	1. ICl_4^-
B. dsp^2	2. $TeCl_4$
C. sp^3d	3. MnO_4^-
D. $sp^3\ d^2$	4. $[Ni(CN)_4^{2-}]$

Codes:

	A	**B**	**C**	**D**
(*a*)	1	2	3	4
(*b*)	4	3	2	1
(*c*)	3	4	1	2
(*d*)	3	4	2	1

68. The paramagnetism of O_2 molecule is believed to be due to the presence of two electrons with parallel spins in

(*a*) bonding p orbitals

(*b*) antibonding p orbitals

(*c*) bonding σ orbitals

(*d*) anti-bonding σ -orbitals

69. The bond angles in the following compounds are such that

(*a*) $TeH_2 > SeH_2 > SH_2 > OH_2$

(*b*) $TeH_2 > SH_2 > SeH_2 > OH_2$

(*c*) $OH_2 > SH_2 > SeH_2 > TeH_2$

(*d*) $SH_2 > SeH_2 > TeH_2 > OH_2$

70. The MO configuration of N_2 molecule is

(*a*) KK $(\sigma 2s)^2 (\sigma^* 2s)\ (p2p)^4$

(*b*) KK$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (p2p_z)^2\ (\sigma 2p_y)^2$

(*c*) KK$(\sigma 2s)\ (\sigma^* 2s)2\ (p2p)^2\ (p2p)^2\ (p2p_y)^2$

(*d*) KK$(\sigma 2s)\ (\sigma^* 2s)\ (\sigma 2p)^2\ (p2p_z)\ (p^* 2p_y)^2$

71. The hybrid bond orbitals used by chlorine in formed ClF_3 are of the type

(*a*) sp^3 (*b*) sp^2

(*c*) sp^2d (*d*) sp^3d

72. The hybrid bond CH_4 and NH_3 is sp^3 yet CH_4 is tetrahedral and NH_3 is of pyramidal shape become

(*a*) sp^3 (*b*) sp^2

(*c*) sp^2d (*d*) sp^3d

73. Intra-molecular hydrogen bonding is found in

(*a*) Hydrofluoric acid (*b*) Water

(*c*) Methanol (*d*) O-nitrophenol

74. A nodal plane containing the internuclear axis exists m

(*a*) p bonds (*b*) σ bonds

(*c*) d-bond (*d*) antibonding p-orbitals

75. Match List 1 (compound) with List II (shape) and select the correct answer:

List-I **Compound**	***List-II*** **Shape**
A. XeF_5^+	1. Tetrahedral
B. SiF_5^-	2. Square planar
C. AsF_4^+	3. Trigonal bipyramidal
D. ICl_4^-	4. Square pyramidal
	5. Octahedral

Codes:

	A	**B**	**C**	**D**
(*a*)	1	2	5	3
(*b*)	4	3	1	2
(*c*)	1	3	5	2
(*d*)	4	2	1	3

76. The number of octahedral void(s) per atom present in a cubic close-packed structure is

(*a*) 2 (*b*) 4

(*c*) 1 (*d*) 3

77. A metal crystallizes with a face-centered cubic lattice. The edge of the unit cell is 408 pm. The diameter of the metal atom is

(*a*) 144 pm (*b*) 204 pm

(*c*) 288 pm (*d*) 408 pm

78. AB crystallizes in a body centred cubic lattice with edge length 'a' equal to 387 pm. The distance between two oppositively charged ions in the lattice is

(*a*) 300 pm (*b*) 335 pm

(*c*) 250 pm (*d*) 200 pm

79. If 'a' stands for the edge length of the cubic systems: simple cubic, body centred cubic and face centred cubic, then the ratio of the radii of the spheres in these systems will be respectively:

(*a*) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$ (*b*) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$

(*c*) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a$ (*d*) $1a : \sqrt{3}a : \sqrt{2}a$

80. Percentage of free space in a body centred cubic unit cell is

(*a*) 32% (*b*) 34%

(*c*) 28% (*d*) 20%

81. In a metallic crystals

(*a*) The valence electrons constitute a sea of mobile electrons

(*b*) The valence electrons are localized in between the kernels

(*c*) The valence electrons remain within the field of influence of their own kernels

(*d*) Both kernels as well as electrons move rapidly

82. If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentration of cation vacancies will be ($NA = 6.02 \times 10^{23}$ mol^{-1})

(*a*) 6.02×10^{16} mol^{-1} (*b*) 6.02×10^{17} mol^{-1}

(*c*) 6.02×10^{14} mol^{-1} (*d*) 6.02×10^{15} mol^{-1}

83. The appearance of colour in solid alkali metal halides is generally due to

(*a*) Schottky defect (*b*) Frenkel defect

(*c*) Interstitial position (*d*) F-centres

84. In a face-centered cubic lattice, a unit cell is shared equally by how many unit cells?

(*a*) 2 (*b*) 4

(*c*) 6 (*d*) 8

85. A compound formed by elements X and Y crystallizes in a cubic structure in which atoms X are at the corners of the cube and atoms Y are at the face-centers. The formula of the compound is

(*a*) X_3Y (*b*) XY

(*c*) XY_2 (*d*) XY_3

86. The pyknometric density of sodium chloride crystal is 2.165×10^3 kg m^{-3} while its X-ray density is 2.178×10^3 kg m^{-3}. The fraction of the unoccupied sites in sodium chloride crystal is

(*a*) 5.96 (*b*) 5.96×10^{-2}

(*c*) 5.96×10^{-1} (*d*) 5.96×10^{-3}

87. In a compound, atoms of element Y form ccp lattice and those of element X occupy 2/3 rd of tetrahedral voids. The formula of the compound will be

(*a*) X_3Y_4 (*b*) X_4Y_3

(*c*) X_2Y_3 (*d*) X_2Y

88. Total Volume of atoms present in a face centerid cubic unit cell of a metal is (r is atomic radius)

(*a*) $\frac{16}{3}\pi r^3$ (*b*) $\frac{20}{3}\pi r^3$ (*c*) $\frac{24}{3}\pi r^3$ (*d*) $\frac{12}{3}\pi r^3$

89. An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of faces of the cube. The empirical formula of the compound would be

(*a*) A_8B_6 (*b*) A_2B

(*c*) AB_3 (*d*) A_3B

90. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.0 g?

(*a*) 5.14×10^{21} unit cells

(*b*) 1.28×10^{21} unit cells

(*c*) 1.71×10^{21} unit cells

(*d*) 2.57×10^{21} unit cells

91. Which of the following is a molecular crystal?

(*a*) Dry ice (*b*) Quartz

(*c*) Rock salt (*d*) Diamond

92. The edge length of a face centred cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is

(*a*) 288 pm (*b*) 144 pm

(*c*) 618 pm (*b*) 398 pm

93. Sodium chloride, NaCl usually crystallizes in a face centred cubic lattice. How many ions are in contact with any single Na^+ ion?

(*a*) 8 (*b*) 6

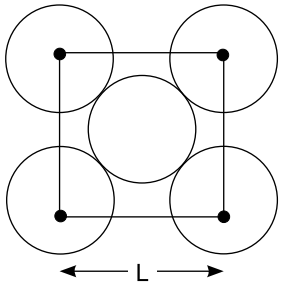
(*c*) 4 (*d*) 1

94. Percentage of free space in cubic close packed structure and in body centred packed structure are respectively

(*a*) 30% and 26% (*b*) 48% and 26%

(*c*) 32% and 48% (*d*) 26% and 32%

95. The packing efficiency of the two dimensional square unit cell shown is



(*a*) 39.27% (*b*) 68.02%

(*c*) 74.05% (*d*) 78.54%

96. AB crystallizes in a body centred cubic lattice with edge length 'a' equal to 387 pm. The distance between two oppositively charged ions in the lattice is

(*a*) 200 pm (*b*) 300 pm

(*c*) 335 pm (*d*) 250 pm

97. A compound contains two types of atoms X and Y. It crystallizes in a cubic lattice with atoms X at the corners of the unit cell and atoms Y at the body centre. The simplest possible formula of this compound is:

(*a*) X_8Y (*b*) X_2Y

(*c*) XY (*d*) XY_8

98. A compound of 'A' and 'B' crystallizes in a cubic lattice in which the 'A' atoms occupy the lattice points at the corners of the cube. The 'B' atoms occupy the centre of each face of the cube. The probable empirical formula of the compound is

(*a*) AB_3 (*b*) AB

(*c*) A_3B (*d*) AB_2

99. Lithium metal crystallises in a body centred cubic crystal. If the length of the side of the unit cell of lithium is 351 pm, the atomic radius of the lithium will be:

(*a*) 300.5 pm (*b*) 75.5 pm

(*c*) 151.8 pm (*d*) 240.8 pm

100. Copper crystallises in a face-centred cubic lattice with a unit cell length of 361 pm. What is the radius of copper atom in pm?

(*a*) 108 (*b*) 181

(*c*) 157 (*d*) 128

101. Copper crystallizes in fcc with a unit cell length of 361 pm. What is the radius of copper atom?

(*a*) 157 pm (*b*) 127 pm

(*c*) 108 pm (*d*) 181 pm

102. A compound is formed by elements A and B. This crystallizes in the cubic structure where A atoms are at the corners of the cube and B atoms are at the body centres. The simplest formula of the compound is

(*a*) AB (*b*) AB_6

(*c*) A_6B (*d*) A_8B_4

103. An ionic compound is expected to have tetrahedral structure if r+/r- lies in the range of

(*a*) 0.414 to 0.732 (*b*) 0.732 to 1

(*c*) 0.155 to 0.225 (*d*) 0.225 to 0.414

104. In which of the following crystals alternate tetrahedral voids are occupied?

(*a*) NaCl (*b*) ZnS

(*c*) CaF_2 (*d*) Na_2O

105. In a solid 'AB' having NaCl structure, 'A' atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is

(*a*) AB_2 (*b*) A_2B

(*c*) A_4B_3 (*d*) A_3B_4

106. A metal has a fcc lattice. The edge length of the unit cell is 404 pm. The density of the metal is 2.72 g $cm^{-3.}$ The molar mass of the metal is

(NA Avogadro's constant = 6.02×10^{23} mol^{-1})

(*a*) 40 g mol^{-1} (*b*) 30 g mol^{-1}

(*c*) 27 g mol^{-1} (*d*) 20 g mol^{-1}

107. A compound formed by elements A and B crystallizes in the cubic structure where A atoms are at the corners of the cube and B atoms are at the face centres. The formula of the compound is

(*a*) AB_3 (*b*) AB

(*c*) A_3B (*d*) A_2B_2

108. A metallic crystal having bcc type staking pattern, what percentage of volume of this lattice is empty space?

(*a*) 68% (*b*) 32%

(*c*) 26% (*d*) 74%

109. A p-type material is electrically

(*a*) positive (*b*) negative

(*c*) neutral

(*d*) depends upon the concentration of p-impurities

110. A solid compound contains X, Y and Z atoms in a cubic lattice with X atoms occupying the corners, Y atoms in the body centred position and Z atoms at the centres of faces of the unit cell. What is the empirical formula of the compound?

(*a*) XY_2Z_3 (*b*) XYZ_3

(*c*) $X_2Y_2Z_3$ (*d*) X_8YZ_6

111. A substance A_xB_y crystallizes in a face centred cubic (fcc) lattice in which atoms 'a' occupy each corner of the cube and atoms 'B' occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y:

(*a*) AB_3 (*b*) A_4B_3

(*c*) A_3B

(*d*) Composition cannot be specified

112. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride?

(*a*) 1.2 g/cm^3 (*b*) 2.16 g/cm^3

(*c*) 3.64 g/cm^3 (*d*) 4.56 g/cm^3

113. AB is an ionic solid. If the ratio of ionic radii of A^+ and B^- is 0.52. What is the coordination number of B^-?

(*a*) 6 (*b*) 3

(*c*) 2 (*d*) 8

114. For a crystal, the angle of diffraction (2) is 90° and the second order line has a d value of 2.28Å. The wavelength (in Å) of X-rays used for Bragg's diffraction is

(*a*) 2.28 (*b*) 2.00

(*c*) 1.613 (*d*) 4.00

115. If AgI crystallizes in zinc blende structure with I- ions at lattice points, what fraction of tetrahedral voids is occupied by Ag^+ ions?

(*a*) 25% (*b*) 50%

(*c*) 100% (*d*) 75%

116. If the distance between Na^+ and Cl^- ions in sodium chloride crystal is X pm, the length of the edge of the unit cell is

(*a*) 4 X pm (*b*) 2 X pm

(*c*) X/2 pm (*d*) X/4 pm

117. If Z is the number of atoms in the unit cell that represents the closest packing sequence ABC ABC _____, the number of tetrahedral voids in the unit cell is equal to

(*a*) Z (*b*) 2Z

(*c*) Z/2 (*d*) Z/4

118. In a face centred cubic (fcc) arrangement, the number of atoms per unit cell is

(*a*) 8 (*b*) 4

(*c*) 2 (*d*) 1

119. In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of B is missing from one of the face centred points, the formula of the compound is

(*a*) A_2B_5 (*b*) A_2B

(*c*) AB_2 (*d*) A_2B_3

120. In a triclinic crystal:

(*a*) $a = b = c, a = b = g \neq 90°$

(*b*) $a \neq b = c, a = b = g = 90°$

(*c*) $a \neq b \neq c, a \neq b \neq g \neq 90°$

(*d*) $a \neq b \neq c, a = g = 90° \neq b$

121. In AgBr, there can occur

(*a*) only Schottky defect (*b*) only Frenkel defect

(*c*) Both (a) and (b) (*d*) Neither (a) nor (b)

122. In an antifluorite structure, cations occupy

(*a*) tetrahedral voids (*b*) centre of cube

(*c*) octahedral voids (*d*) corners of cube

123. In Na_2O having antifluorite structure

(*a*) Oxide ions have a cubic close packed arrangement and Na^+ occupy all the eight tetrahedral voids.

(*b*) Oxide ions have a cubic close packed arrangement and Na^+ occupy all the octahedral voids

(*c*) Na^+ ions have a cubic close arrangement and O^{2-} occupy all the octahedral voids

(*d*) Na^+ ions have a cubic close arrangement and O^{-2} occupy all the tetrahedral voids.

124. In NaCl crystal each Cl^- ion is surrounded by

(*a*) $4Na^+$ ions (*b*) $6Na^+$ ions

(*c*) $1Na^+$ ions (*d*) $2Na^+$ ions

125. Match Column A with B and select the correct option.

Column A	Column B
A. Ionic solid	I. NaCl
B. Metallic solid	II. Fe
C. Covalent solid	III. C (graphite)
D. Molecular solid	IV. Dry ice

(*a*) A - II, B - I, C - IV, D - III

(*b*) A - I, B - II, C - III, D - IV

(*c*) A - III, B - II, C - I, D - IV

(*d*) A - II, B - IV, C - I, D – III

126. Number of atoms per unit cell of bcc is

(*a*) 1 (*b*) 2

(*c*) 4 (*d*) 8

127. Number of unit cells in 4 g of X (atomic mass = 40) which crystallize in bcc pattern is (NA = Avogadro number).

(*a*) 0.1 NA (*b*) 2 × 0.1 NA

(*c*) NA (*d*) 2 × NA

128. R If the pressure on a NaCl structure is increased, then its coordination number will

(*a*) Increase (*b*) Decrease

(*c*) Either (*a*) or (*b*) (*d*) Remain the same

129. Silver (atomic weight = 108 g mol^{-1}) has a density of 10.5 g cm^{-3}. The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as y × 10x. The value of x is

(*a*) 13 (*b*) 9

(*c*) 7 (*d*) 5

130. The coordination number of a metal crystallizing in a hexagonal close packing (hcp) structure is

(*a*) 12 (*b*) 8

(*c*) 6 (*d*) 7

131. The coordination number of Al in the crystalline state of $AlCl_3$ is

(*a*) 4 (*b*) 6

(*c*) 8 (*d*) 10

132. For an ionic crystal of the general formula AX and coordination number 6, the value of radius ratio will be

(*a*) In between 0.732 and 0.414

(*b*) In between 0.414 and 0.225

(*c*) Less than 0.225

(*d*) Greater than 0.732

133. The crystal with metal deficiency defect is

(*a*) NaCl (*b*) FeO

(*c*) KCl (*d*) ZnO

134. The cubic unit cell of a metal (molar mass = 63.55 g mol^{-1}) has an edge length of 362 pm. Its density is 8.92 g.cm^3. The type of unit cell is:

(*a*) Body centred (*b*) Face centred

(*c*) Primitive (*d*) End centred

135. Total number of tetrahedral and octahedral voids in 0.5 mol of a compound forming hcp structure are:

(*a*) 6.022×10^{23} (*b*) 3.011×10^{23}

(*c*) 9.033×10^{23} (*d*) 4.516×10^{23}

136. The number of carbon atoms per unit cell of diamond unit cell is

(*a*) 8 (*b*) 6

(*c*) 4 (*d*) 2

137. The efficiency of packing is 68% in

(*a*) hcp structure (*b*) ccp structure

(*c*) fcc structure (*d*) bcc structure

138. The ionic radii of Rb^+ and I^- are 1.46Å and 2.16Å respectively. The most probable type of structure exhibited by it is

(*a*) NaCl type (*b*) ZnS type

(*c*) CsCl type (*d*) CaF_2 type

139. The number of atoms per unit cell of bcc structure is

(*a*) 1 (*b*) 2

(*c*) 4 (*d*) 6

140. The number of hexagonal faces that are present in truncated octahedron is

(*a*) 14 (*b*) 12

(*c*) 10 (*d*) 8

141. The number of tetrahedral voids in the unit cell of a face centred cubic lattice of similar atoms is

(*a*) 4 (*b*) 6

(*c*) 8 (*d*) 10

142. The radius ratio in CsCl is 0.93. The expected lattice structure is

(*a*) octahedral (*b*) square planar

(*c*) tetrahedral (*d*) body centred cubic

143. The unit cell of a binary alloy composed of A and B metals, has a ccp structure with A atoms occupying the corners and B atoms occupying the centres of each face of the cube. If during the crystallization of this alloy, in the unit cell, two A atoms are missing, the overall composition per unit cell is

(*a*) AB_6 (*b*) AB_4

(*c*) AB_8 (*d*) AB_{24}

144. The white ZnO turns yellow on heating because of

(*a*) Frenkel defect

(*b*) Metal excess defect

(*c*) Metal deficiency defect

(*d*) Schottky defect

145. Three elements A, B and C crystalise into a cubic solid lattice. Atoms A occupy the corners, B occupies the cube centres and C occupies the edges. The formula of the compound is

(*a*) ABC (*b*) ABC_2

(*c*) ABC_3 (*d*) ABC_4

146. To get *n*-type doped semiconductor, the impurity to be added to silicon should have the following number of valence electrons?

(*a*) 1 (*b*) 2

(*c*) 3 (*d*) 5

147. Density of a crystal remains unchanged as a result of

(*a*) Vacancy defect (*b*) Interstitial defect

(*c*) Frankel defect (*d*) Schottky defect

148. What is the coordination number of body centred cube?

(*a*) 4 (*b*) 6

(*c*) 8 (*d*) 12

149. What is the co-ordination number of sodium in Na_2O?

(*a*) 8 (*b*) 6

(*c*) 4 (*d*) 2

150. Which is not the correct statement for ionic solids in which positive and negative ions are held by strong electrostatic attractive forces?

(*a*) The radius ratio increases as coordination number increases

(*b*) As the difference in size of ions increases coordination number increases

(*c*) When coordination number is eight, the radius ratio lies between 0.225 to 0.414

(*d*) In ionic solid of the type AX (ZnS, Wurtzite) the coordination number of Zn^{2+} and S^{2-} respectively are 4 and 4

151. Which of the following statements about amorphous solids is incorrect?

(*a*) They melt over a range of temperature.

(*b*) They are rigid and incompressible.

(*c*) There is no orderly arrangement of particles.

(*d*) They are anisotropic.

152. Which one of the following compound exhibits both Schottky and Frenkel defects?

(*a*) NaCl (*b*) AgCl

(*c*) AgBr (*d*) AgI

153. Which one of the following defects in the crystals lowers its density?

(*a*) F-centres (*b*) Schottky defect

(*c*) Frenkel defect (*d*) Interstitial defect

154. Which one of the following is a covalent crystal?

(*a*) Dry ice (*b*) Rock salt

(*c*) Ice (*d*) Quartz

155. The ability of a given substance to assume two or more crystalline structure is called

(*a*) polymorphism (*b*) isomorphism

(*c*) amorphous (*d*) isomerism

156. Lithium has a bcc structure. Its density is 530 kg m^{-3} and its atomic mass is 6.94 g mol^{-1}. Calculate the edge length of a unit cell of Lithium metal (NA = 6.02×10^{23} mol^{-1})

(*a*) 527 pm (*b*) 264 pm

(*c*) 154 pm (*d*) 352 pm

157. The ionic radii of A^+ and B^- ions are 0.98×10^{-10} m and 1.81×10^{-10} m. The coordination number of each ion in AB is

(*a*) 8 (*b*) 2

(*c*) 6 (*d*) 4

158. Which among the following solids crystalises as a face centred cube?

(*a*) Iron (*b*) Rubidium

(*c*) Uranium (*d*) Platinum

159. Volume occupied by single CsCl ion pair in a crystal is 7.014×10^{-23} cm^3. The smallest Cs – Cs internuclear distance is equal to length of the side of the cube corresponding to volume of one CsCl ion pair. The smallest Cs to Cs internuclear distance is nearly

(*a*) 4.4 Å (*b*) 4.3 Å

(*c*) 4 Å (*d*) 4.5 Å

160. A crystalline solid XY_3 has ccp arrangement for its element Y. X occupies

(*a*) 66% of tetrahedral voids
(*b*) 33% of tetrahedral voids
(*c*) 66% of octahedral voids
(*d*) 33% of octahedral voids

161. Following statement is incorrect regarding MO theory .
(a) Molecule has orbitals of varying energy levels in the same way as an isolated atom has.
(b) Each molecular orbital can accommodate maximum two electrons with opposite spins.
(c) Paul's exclusion principle, Hund's rule maximum multiplicity and Aufbau's principal hold true for molecule.
(d) Only half filled atomic orbitals overlaps to give molecular orbitals.

162. Choose the wrong statement.
(a) $E^+ < E^-$
(b) Total number of MO's < Total number of AO's combined to form the molecule.
(c) MO's are formed by the linear combination of atomic orbitals.
(d) MO theory was put forth by F. Hund and R.S. Mulliken in 1930.

163. Which of the following combination will not give sigma (σ) bond.
(a) s-s (b) s-p
(c) p-p lateral overlap (d) p-p side ways overlap

164. Bond order of H_2^+ ion is
(a) 0.5 (b) 1
(c) 2 (d) 1.5

165. Number of unpaired electrons in O_2 molecule.
(a) 2 (b) 1
(c) 3 (d) 4

166. Which molecule/species has the highest bond order?
(a) O_2 (b) O_2^+
(c) O_2^- (d) O_2^{--}

167. Of the following species, which has the shortest bond length.
(a) NO (b) NO^+
(c) NO^{2+} (d) NO^-

168. sp^2 hybridization is found in
(a) BeF_2 (b) C_2H_2
(c) CO_2 (d) C_2H_4

169. Choose the correct statement.
(a) sp^3d hybridization imparts trigonal bipyramidal geometry to the molecule.
(b) sp^2 hybridization imparts tetrahedral geometry to the molecule.
(c) Bond angle in sp^3 hybridization is 106.5°
(d) Central carbon atom in CO_3^{--} ion has sp^3 hybridisation.

170. Which of the following molecule has heighest bond angle.
(a) H_2O (b) H_2S
(c) H_2Se (d) H_2Te

171. Which of the following molecule has least solubility in water?
(a) HF (b) CH_3OH
(c) CH_3OCH_3 (d) C_2H_5OH

172. The free electron model of metallic bond failed in explaining.
(a) High electrical and thermal conductivity
(b) Malleability and ductility
(c) High tensile strength
(d) Comparative softness and hardness of sodium and osmium metals.

173. Choose the wrong statement.
(a) Tertiary structure between protein is largely affected by hydrogen bonding.
(b) Water expands between 0°C to 4°C.
(c) Two coins of DNA molecule are held together by H-bonding at specific places.
(d) Density of ice is less than that of liquid water.

174. Bond order of a molecule is calculated by the following formula.
(a) BO = [Number of electrons in BMO's – Number of electrons in ABMO's]
(b) BO = ½[Number of electrons in ABMO's – Number of electrons in BMO's]
(c) BO = ½[Number of electrons in BMO's – Number of electrons in ABMO's]
(d) BO = ¼[Number of electrons in BMO's – Number of electrons in ABMO's]

175. Number of unpaired electrons in CN^- species is/are
(a) 2 (b) 1
(c) 0 (d) 3

176. Which of the following does not show hydrogen bonding?
(a) Liquid NH_3 (b) Liquid HCl
(c) Liquid H_2O (d) Liquid HF

177. Which of the following geometry correspond to dsp^2 hybridization?
(a) Square planar (b) Octahedral
(c) Tetrahedral (d) Trigonal bipyramidal

178. Hydrogen bonding would not affect the boiling point of
(a) HI (b) NH_2
(c) CH_3OH (d) H_2O

179. MO theory was proposed by
(a) Warner (b) Kossel
(c) Mosley (d) Mulliken

180. The ion which does not show paramagnetism is
(a) O_2 (b) O_2^+
(c) O_2^{2-} (d) H_2^+

181. Which of the following has maximum bond order?
(a) H_2 (b) N_2
(c) F_2 (d) O_2

182. The bond order of H_2^+ ion is
(a) 0.5 (b) 1.0
(c) 2.0 (d) 1.5

183. Which of the following bonds is most stable?
(a) s-s (b) p-p
(c) s-p (d) p-d

184. VSEPR theory was proposed by
(a) Nyhom and Gillipsie (b) Nyhom
(c) Gillipsie (d) Kossel

185. Which one is semiconductor?
(a) Na (b) Ge
(c) C (d) He

186. Hydrogen bond is absent in
(a) H_2O (b) NH_3
(c) C_2H_5OH (d) $C_2H_5OC_2H_5$

187. The boiling point of a compound is raised by
(a) Ionic bonding
(b) Covalent bonding
(c) Intermolecular hydrogen bonding
(d) Intramolecular hydrogen bonding

188. The number of unpaired electrons in an O_2^+ molecule is
(a) 0 (b) 1
(c) 2 (d) 3

189. The total number of electrons in one molecule of CO_2 is
(a) 22 (b) 44
(c) 66 (d) 88

190. Which is the weakest band among the following?
(a) Ionic (b) Covalent
(c) Metallic (d) Hydrogen bond

191. Acetylene molecule contains
(a) 5σ-bond
(b) 4σ-bonds and 1π-bond
(c) 3σ-bonds and 2π-bonds
(d) 2σ-bonds and 3π-bonds

192. An sp^3 hybrid orbital contains
(a) ½ s character (b) ½ s character
(c) ⅔ s character (d) ¾ s character

193. A molecule that contains unpaired electrons is
(a) CO_2 (b) H_2
(c) O_2 (d) H_2O_2

194. Lattice energy of a solid increases if
(a) Ions are large (b) Ions are small
(c) Ions are of equal size (d) None of these

195. What is the maximum number of hydrogen bonds in which a water molecule can participate?
(a) 4 (b) 3
(c) 2 (d) 1

196. If the tetrahedral sites in a CC array of negative ions (B) were half-filled with captions (A), the empirical formula of the compound would be
(a) AB (b) AB_2
(c) A_2B_3 (d) A_2B

197. The number of atoms per unit cell in a simple cubic, FCC and CC BCC arrangement are, respectively
(a) 3, 14, 9 (b) 1, 4, 2
(c) 1, 2, 4 (d) 4, 1, 2

198. The weakest bond among the following is
(a) Hydrogen (b) Covalent
(c) Ionic (d) Metallic

199. The space occupied by spheres in a BCC arrangement is
(a) 46.4% (b) 52.4%
(c) 68% (d) 74%

200. The co-ordination number of each sphere in the HCP arrangement is
(a) 4 (b) 6
(c) 8 (d) 12

201. The hydrogen bond is the strongest in
(a) F—H—F (b) F—H—O
(c) S—H—O (d) O—H—S

202. The ionic radii of Rb^+ and I^- are 1.47Å and 2.16 Å respectively. The most probable type of geometry shown by RBI in the basis of radius ratio rule is
(a) CsCl type (b) NaCl type
(c) ZnS type (d) Boron oxide type

203. A covalent bond is formed as a result of
(a) Transfer of electrons from one atom to another
(b) Electrostatic attraction between two atoms
(c) Sharing of electrons contributed by both atoms
(d) Sharing of electrons contributed by only one atom

204. Which is distilled first
(a) liquid H_2 (b) liquid CO_2
(c) liquid O_2 (d) liquid N_2

205. $\frac{1}{2}$ is isoelectric with
(a) K^+ (b) F^-
(c) Cl^- (d) None of these

206. Which statement is incorrect
(a) A pi (π) bond is weaker than sigma (σ) bond
(b) A sigma bond is weaker than pi bond
(c) A double bond is stronger than single bond
(d) A covalent bond is stronger than H-bond

207. Which among the following halide has the highest melting point
(a) NaCl (b) NaBr
(c) NaI (d) NaF

208. Which of the following is paramagnetic
(a) O_2^- (b) CN^-
(c) CO (d) NO^+

209. Which of the following have a giant covalent structure
(a) Diamond (b) SiO_2
(c) $SiCl_4$ (d) CO_2

210. Bond energy varies as
(a) $- > = > \equiv$ (b) $\equiv > = >$
(c) $= > - > \equiv$ (d) $- > \equiv > =$

211. Which of the following is not diamagnetic
(a) O_2^+ (b) O_2
(c) O_2^- (d) O_2^{2-}

212. Which of the following has lowest bond order
(a) O_2^+ (b) O_2
(c) O_2^- (d) O_2^{2-}

213. Which of the following has highest bond order
(a) O_2^+ (b) O_2
(c) O_2^- (d) O_2^{2-}

214. Which of the following species is paramagnetic
(a) O_2^- (b) CN^-
(c) CO (d) NO^+

215. The shape of the molecule in which the hybridization of the central atom is sp^3 is
(a) Angular (b) Tetrahedral
(c) Octahedral (d) Linear

216. Which of the following has minimum bond length
(a) O_2 (b) O_2^+
(c) O_2^- (d) O_2^{2-}

217. Which of the following has unpaired electrons in antibonding molecular orbitals
(a) O_2 (b) N_2
(c) C_2 (d) B_2

218. Which of the following has unpaired electrons in antibonding molecular orbital
(a) O (b) N_2
(c) F_2 (d) H_2^+

219. The bond order in is the same as in
(a) N_2+ (b) CN^-
(c) NO^+ (d) CO

220. The bond order for
(a) 2 (b) $\frac{1}{2}$
(c) 3
(d) None of these

221. The valence bond theory
(a) Under estimates the importance of covalent structures
(b) Under estimates the importance of ionic structures
(c) Puts equal emphasis on both ionic and covalent structures
(d) None of the above

222. The bond order of molecule is given by
(a) Total number of electrons in bonding and antibonding orbital
(b) Half the difference between the number of electrons in bonding and antibonding orbital
(c) The difference between the number of electrons in bonding and antibonding orbital
(d) Twice the difference between the number of electrons in bonding and antibonding orbital

223. The number of atoms in a face-centered cubic unit cell is
(a) 4 (b) 5
(c) 6 (d) 2

224. Close packing is maximum in the crystal lattice of
(a) Simple cubic (b) Face centered
(c) Body centered (d) None of these

225. Lattice energy of a solid increases if
(a) Ions are large (b) Ions are small
(c) Ions are of equal size (d) None of these

226. The co-ordination number (CN) for an atom in a primitive cubic unit cell is
(a) 8 (b) 6
(c) 1 (d) None of these

227. Crystals which are good conductors of electricity and heat are
(a) Ionic (b) Covalent
(c) Metallic (d) Molecular

228. Missing of one caption and one anion from the crystal lattice is called
(a) Ionic defect (b) Crystal defect
(c) Schottky defect (d) Frenkel defect

229. In a body-centered cubic cell, an atom at the centre of body is shared by
(a) 1 unit cell (b) 4 unit cells
(c) 3 unit cells (d) 2 unit cells

230. The crystal lattice of electrovalent compound is composed of
(a) Atoms
(b) Molecules
(c) Oppositely charged ions
(d) Both molecules and ions

231. Sodium chloride crystal consists of
(a) NaCl molecules (b) Na and Cl atoms
(c) Na^+ and Cl^- ions (d) Na^- and ions

232. In graphite, carbon is
(a) Sp-hybridized (b) Hybridized
(c) Hybridized (d) None of these

233. Which of the following does not have hydrogen bonding
(a) Phenol (b) Liquid NH_3
(c) Water (d) Liquid HCl

234. The electrons used in the bonding atoms
(a) Belong to outermost shell
(b) Belong to penultimate shell
(c) Belong to outermost shell and sometimes to penultimate shell
(d) Belong to penultimate shell and sometimes to outermost shell

235. Which of the following molecules possesses the smallest bond length
(a) F_2 (b) Cl_2
(c) Br_2 (d) I_2

236. Which of the following results in strongest bonding
(a) Electrovalent (b) Co-ordinate
(c) Covalent (d) H-bond

237. Which of the following possesses lowest energy
(a) NO (b) O_2
(c) N_2 (d) CO

238. Blue phases are not characterized by
(a) Exhibit continuous Bragg's reflections in visible range of electromagnetic radiation
(b) Appear in temperature range between a chiral nematic phase and isotropic liquid phase
(c) Have a regular 3-dimensional cubic structure
(d) They exist in very narrow temperature range

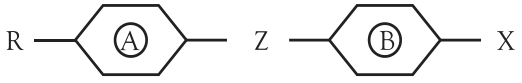
239. In thermotropic liquid crystals following is incorrect
(a) At very high temperature changes into conventional isotrpic liquid phase
(b) At too low temperature it form a conventional an isotropic crystal
(c) Soap is a thermotropic liquid crystal
(d) Exhibit a variety of phases as a function of temperature

240. Choose the incorrect statement regarding liquid crystals
(a) These changes are not reversed on cooling
(b) When heated it undergoes two sharp changes one after the other
(c) Translucent liquid phase show anisotropy
(d) Soap is a lyotropic liquid crystal

241. Cholesteric liquid phase are not characterized by
(a) Like nematic phase, there is long range order in cholesteric phase
(b) Showing strong colour effect in polarised light
(c) They are twisted around on axis
(d) They are optically active

242. In smectic liquid crystals following is incorrect
(a) Molecules in mesomorphic phase align in layers
(b) They retain short range order
(c) When allowed to flow, layers slide over one another like soap retaining their parallelism
(d) The inter layer attractions in these phases are weak as compared to lateral forces of attraction between molecules

243. Following is incorrect chemical constitution requirement for liquid crystalline behaviour



(a) Terminal group 'X' contributes to dielectric anisotropy
(b) R-side chain should be alkyl/alkoxy group
(c) Aromatic rings 'A' and 'B' should be necessarily same
(d) Substitution over the rings A and B by polar groups change the dielectric properties of liquid crystals

244. In nematic liquid crystal phase following is wrong
(a) Have extreme usefulness in LCDs
(b) These have thread like topological defects
(c) Have fluidity similar to that of ordinary liquids
(d) Have less fluidity than smectic phase

245. Bragg's equation is given by
(a) $n\theta = 2\theta \sin\lambda$ (b) $n\theta = 2d\theta \sin\lambda$
(c) $2n\theta = 2d \sin\alpha$ (d) None of these

246. The number of atoms in a face-centered cubic cell is
(a) 4 (b) 6
(c) 8 (d) 12

247. The number of atoms in a simple cubic unit cell is
(a) 4 (b) 3
(c) 2 (d) 1

248. In the graphite crystal, carbon is
(a) Sp-hybridised (b) Sp^2-hybridized
(c) Sp^3-hybridised (d) None of these

249. In a simple cubic cell, each point group in a comer is shoned by
(a) 2 unit cells (b) 1 unit cell
(c) 8 unit cells (d) 4 unit cells

250. In a face-centered cubic cell, an atom at the face-centered is shared by
(a) 4 unit cells (b) 2 unit cells
(c) 1 unit cells (d) 6 unit cells

251. Which one shows colour effect ?
(a) Nematic liquid crystal
(b) Smectic liquid crystal
(c) Cholestery liquid crystal
(d) None of these

252. When atoms are present at the centre of any two parallel faces of a unit cell, it is known as
(a) Face-centered (b) Body-centred
(c) End-cnetered (d) None of these

253. The total number of elements of symmetry in a cubic crystal is
(a) 20 (b) 22
(c) 23 (d) 13

254. Which one is not the allotropy of carbon?
(a) Fullerene (b) Diamond
(c) Graphite (d) Dakelite

255. Crystalline solids are
(a) Super cooled liquid (b) Isotropic
(c) Anisotropic (d) None of these

256. Which one of the following is an amorphus solid?
(a) Diamond (b) Graphite
(c) Glass (d) Common salt

257. In the Bragg's equation for diffraction 'n' represents.
(a) The number of moles
(b) The quantum number
(c) The Avogadro's number
(d) The order of reflection

258. How many crystal systems are known?
(a) 7 (b) 8
(c) 6 (d) 4

259. Which of the following system has not been correctly characterized?
(a) Cubic, $a = b = c, \beta = \gamma = \neq = 90°$
(b) Cubic, $a\ \alpha\ b = c, \beta = \gamma = \neq = 90°$
(c) Tetragonal, $a\ \alpha\ b = c, \beta = \gamma = \neq = 90°$
(d) Monoclinic, $a \neq b\ \alpha\ c, \gamma = \beta = 90°, \neq \frac{a}{2}\ 90°$

260. The edge of a bcc crystal of an element is 'q' an M is the atoms Mass and N is the Avogadro's number. The density of the crystal is
(a) $4M/a^3N$ (b) $2M/a^3N$
(c) $2M/Ma^3$ (d) M/a^32N

261. A Fcc element (atomic mass = (∞) has an edge length of 400 pm. Its density is
(a) 6.23 g/cm^3 (b) 6.43 g/cm^3
(c) 6.53 g/cm^3 (d) 7.23 g/cm^3

262. An element (atomic mass = 100) having bcc structure, has a unit cell of edge length 400 pm. The density of the element is
(a) 5.19 g/cm^3 (b) 10.38 g/cm^3
(c) 7.29 g/cm^3 (d) 7.23 g/cm^3

263. In a face-centered cubic lattice, a unit cell is shared equally by how many unit cells ?
(a) 2 (b) 4
(c) 6 (d) 8

264. The number of atoms per unit cell in a simple cubic, fcc and bcc arrangement are
(a) 1, 2, 3 (b) 1, 4, 2
(c) 1, 2, 4 (d) 4, 1, 2

265. Which of the following is weaker secondary force of attraction
(a) Ionic bonds (b) Hydrogen bonds
(c) Covalent bonds (d) Metallic bonds

266. Solids are not characterized by their
(a) High compressibility
(b) Ordered arrangement of their constituent particles
(c) Specific geometric shape and size
(d) Rigidity

267. Crystalline solids are not characterized by
(a) Anisotropy
(b) Sharp melting point
(c) Characteristic geometry
(d) Refractive index remain same along all directions

268. Total number of elements of symmetries for a cubic crystal are
(a) 23 (b) 22
(c) 24 (d) 20

269. For a hexagonal crystal the elements of symmetry are
(a) 15 (b) 16
(c) 14 (d) 17

270. If a lattice plane intersects the X, Y, Z axes at distances (1, 1, 2). What will be Miller indices?
(a) (221) (b) (012)
(c) (122) (d) (212)

271. Number of atoms per unit cell of face-centered cubic crystals are
(a) 4 (b) 3
(c) 1 (d) 5

272. Total number of atomic arrangements in three-dimensional space (*i.e.,* Bravis lattices) are
(a) 15 (b) 16
(c) 14 (d) 17

273. Atomic radius of atom in face centred cubic cells is
(a) $\frac{a}{2}$ (b) $\frac{a\sqrt{2}}{4}$
(c) $\frac{a\sqrt{3}}{4}$ (d) a

274. Atomic packing fraction (Afp) for body-centered cubic crystal will be
(a) 0.52 (b) 0.43
(c) 0.68 (d) 0.73

275. Co-ordination number related with simple cubic cell is
(a) 6 (b) 7
(c) 8 (d) 3

276. Value of radius ratio for planar triangle geometry is
(a) below 0.155 (b) 0.155 to 0.255
(c) 0.255 to 0.414 (d) 0.732 to 0.999

277. Ac-cording to Bragg's law
(a) $n\lambda = d \sin\theta$ (b) $n\lambda = 2\, d \sin\theta$
(c) $n\lambda = 2\, d \cos\theta$ (d) $n\lambda = \frac{Z \times M}{Z_0 \times V} \sin\theta$

278. At what glancing angle would the first order diffraction from (110) plane of KCl can be observed by using X-ray of 150 pm. The unit cell dimension is 305 pm.
(a) 20.347° (b) 25.83°
(c) 18.46° (d) 15.71°

279. Which of the following is not a cause of defect or imperfections in crystal
(a) Faster crystallization of a solid from its solution
(b) Applying local pressure on crystalline solids
(c) Vacancies left in crystal at the time of improper crystallization.
(d) Slow coding of not metals.

280. Following is not an effect of defect on properties of crystal.
(a) Increase melting point
(b) Charged refractive index
(c) Change magnetic strength
(d) Density decreases

281. Following is a non-stoichiometric defect
(a) Frenkel (b) Edge dislocations
(c) Frenkel (d) F-centres.

282. Choose the incorrect statement
(a) Graphite contain mobile electrons
(b) Carbon atoms are in sp^2-hybridized state in graphite
(c) Carbon atoms are arranged in hexagonal network sheets
(d) Graphite is bad conductor of electricity

283. Choose in correct statement related to fullerenes
(a) It is an isotrope of carbon
(b) It is an allotrope of carbon
(c) C_{60} is stable, spherical and also called as bueky ball
(d) Crystal structure of fullerene is face-centered cubic

FILL IN THE BLANKS

1. The molecules of a gas, liquid or solid are held together by …….. forces.
2. Liquids have …… volume but their shape is …….
3. When the vapour pressure of a liquid becomes ……. to the external pressure, the corresponding ……. is known as its boiling point.
4. Vapour pressure of a liquid …….. with increase in temperature.
5. Viscosity of a liquid ……. with rise in temperature.
6. Surface tension …….. with rise in temperature.
7. Viscosity of glycerin is ……. than water under similar conditions.
8. A liquid state is regarded as a …….. gas or a …….. solid.
9. The boiling point of a liquid changes with change of ……. pressure.
10. Poise is the unit of ……
11. Liquid rises in capillary tubes due to ……
12. Solids have …….. shape and ……. volume.
13. Amorphous solids ……. have …….. melting points.
14. A crystal is defined as a solid figure which has a definite geometrical shape with …… faces and …… edges.
15. Solids are of two types ……. and ……..
16. In NaCl ionic crystal, each ion is surrounded by …… ions and each ion is surrounded by ……ions.
17. In cubic crystals, there are…… elements of symmetry.
18. Crystals can be classified into…….. systems.
19. The smallest portion of a crystal which has the structural characteristics of the space lattice is called the……..
20. An atom at the corner of the unit cell makes ……. contribution to a particular unit cell.
21. In cubic, tetragonal and rhombic systems of crystal structure, the angle between the edges is ……
22. In face-centered cubic structure the empty space is ……. %.
23. In a crystal lattice, the number of nearest neighbours to each atom is called …….
24. The unit cell of sodium chloride has ……. ions ……. and ions.
25. KCl crystal is a……. conductor of electricity.
26. Diamond and graphite are examples of …… crystals.
27. The existence of different chemical compounds in same crystalline form is called ……..
28. The bond energy of N_2 is……. than that of O_2.
29. Two atoms of similar electronegativity are expected to form…… compounds.
30. A bond is……. than a bond.
31. With increase in bond order, bond length …… and bond strength increases.
32. The nature of the bond between hydrogen and chlorine in the HCl molecule in the vapour phase is ……
33. Hydrogen bond is a…….. than a covalent bond.
34. The strongest hydrogen bond is formed between…….. and hydrogen.
35. Bond formation is an energy……. process.
36. In water, oxygen is tetrahedrally hybridized, the angle in H—O—H is……
37. Multiple bond exist in a molecule of……
38. Conversion of sodium atom into sodium ion is an…….. process.
39. Conversion of chlorine atom into chloride ion is an……. Process.
40. N_2 molecule contains……. and……. bonds.
41. The H-bond energy is around…….. kJ.
42. ……. value of lattice energy of a crystal favours the formation of an electrovalent bond.
43. The shape of NH_3 is……
44. Proton takes part in…… bonding.
45. Bragg's equation is……..
46. Nematic liquid crystals gave..... fluidity than smectic phase.
47. Liquid crystal when heated undergoes..... sharp changes.
48. Blue phase exit in very..... temperature range.
49. Soap is a..... liquid crystal.
50. Cholesteric liquid phase are optically.....

ANSWERS

1. (*b*)	**2.** (*a*)	**3.** (*b*)	**4.** (*b*)	**5.** (*d*)	**6.** (*b*)	**7.** (*b*)	**8.** (*d*)	**9.** (*c*)	**10.** (*a*)
11. (*a*)	**12.** (*d*)	**13.** (*d*)	**14.** (*b*)	**15.** (*a*)	**16.** (*d*)	**17.** (*a*)	**18.** (*b*)	**19.** (*c*)	**20.** (*b*)
21. (*c*)	**22.** (*b*)	**23.** (*c*)	**24.** (*b*)	**25.** (*a*)	**26.** (*c*)	**27.** (*b*)	**28.** (*d*)	**29.** (*c*)	**30.** (*a*)
31. (*b*)	**32.** (*d*)	**33.** (*b*)	**34.** (*c*)	**35.** (*c*)	**36.** (*a*)	**37.** (*b*)	**38.** (*a*)	**39.** (*a*)	**40.** (*c*)
41. (*b*)	**42.** (*c*)	**43.** (*c*)	**44.** (*b*)	**45.** (*a*)	**46.** (*d*)	**47.** (*c*)	**48.** (*a*)	**49.** (*b*)	**50.** (*a*)
51. (*c*)	**52.** (*a*)	**53.** (*d*)	**54.** (*c*)	**55.** (*c*)	**56.** (*a*)	**57.** (*c*)	**58.** (*b*)	**59.** (*d*)	**60.** (*c*)
61. (*c*)	**62.** (*b*)	**63.** (*c*)	**64.** (*d*)	**65.** (*a*)	**66.** (*d*)	**67.** (*d*)	**68.** (*c*)	**69.** (*c*)	**70.** (*b*)
71. (*d*)	**72.** (*b*)	**73.** (*d*)	**74.** (*a*)	**75.** (*b*)	**76.** (*c*)	**77.** (*c*)	**78.** (*b*)	**79.** (*a*)	**80.** (*a*)
81. (*d*)	**82.** (*b*)	**83.** (*d*)	**84.** (*c*)	**85.** (*d*)	**86.** (*d*)	**87.** (*b*)	**88.** (*a*)	**89.** (*c*)	**90.** (*d*)
91. (*d*)	**92.** (*b*)	**93.** (*b*)	**94.** (*d*)	**95.** (*d*)	**96.** (*c*)	**97.** (*c*)	**98.** (*a*)	**99.** (*c*)	**100.** (*d*)
101. (*b*)	**102.** (*a*)	**103.** (*d*)	**104.** (*b*)	**105.** (*d*)	**106.** (*c*)	**107.** (*a*)	**108.** (*b*)	**109.** (*c*)	**110.** (*a*)
111. (*a*)	**112.** (*b*)	**113.** (*a*)	**114.** (*c*)	**115.** (*b*)	**116.** (*b*)	**117.** (*b*)	**118.** (*b*)	**119.** (*a*)	**120.** (*c*)
121. (*c*)	**122.** (*a*)	**123.** (*a*)	**124.** (*b*)	**125.** (*b*)	**126.** (*b*)	**127.** (*c*)	**128.** (*c*)	**129.** (*c*)	**130.** (*a*)
131. (*b*)	**132.** (*b*)	**133.** (*b*)	**134.** (*b*)	**135.** (*c*)	**136.** (*a*)	**137.** (*d*)	**138.** (*c*)	**139.** (*b*)	**140.** (*c*)
141. (*c*)	**142.** (*d*)	**143.** (*b*)	**144.** (*b*)	**145.** (*c*)	**146.** (*d*)	**147.** (*c*)	**148.** (*c*)	**149.** (*c*)	**150.** (*c*)
151. (*d*)	**152.** (*c*)	**153.** (*b*)	**154.** (*d*)	**155.** (*c*)	**156.** (*d*)	**157.** (*c*)	**158.** (*d*)	**159.** (*c*)	**160.** (*d*)
161. (*d*)	**162.** (*b*)	**163.** (*d*)	**164.** (*a*)	**165.** **(a)**	**166.** (*b*)	**167.** (*b*)	**168.** (*d*)	**169.** (*a*)	**170.** (*a*)
171. (*c*)	**172.** (*d*)	**173.** (*b*)	**174.** (*c*)	**175.** **(c)**	**176.** (*b*)	**177.** (*a*)	**178.** (*a*)	**179.** (*d*)	**180.** (*c*)
181. (*b*)	**182.** (*a*)	**183.** (*a*)	**184.** (*a*)	**185.** **(b)**	**186.** (*d*)	**187.** (*c*)	**188.** (*c*)	**189.** (*a*)	**190.** (*d*)
191. (*c*)	**192.** (*d*)	**193.** (*a*)	**194.** (*b*)	**195.** **(a)**	**196.** (*a*)	**197.** **(b)**	**198.** (*a*)	**199.** (*d*)	**200.** (*d*)
201. (*a*)	**202.** (*b*)	**203.** (*c*)	**204.** (*a*)	**205.** **(b)**	**206.** (*b*)	**207.** (*a*)	**208.** (*a*)	**209.** (*a*)	**210.** (*b*)
211. (*a*)	**212.** (*d*)	**213.** (*a*)	**214.** (*a*)	**215.** **(b)**	**216.** (*b*)	**217.** (*a*)	**218.** (*d*)	**219.** (*a*)	**220.** (*b*)
221. (*b*)	**222.** (*b*)	**223.** (*a*)	**224.** (*b*)	**225.** **(c)**	**226.** (*b*)	**227.** (*a*)	**228.** (*a*)	**229.** (*a*)	**230.** (*c*)
231. (*c*)	**232.** (*b*)	**233.** (*d*)	**234.** (*a*)	**235.** **(a)**	**236.** (*a*)	**237.** (*c*)	**238.** (*a*)	**239.** (*c*)	**240.** (*a*)
241. (*a*)	**242.** (*b*)	**243.** (*c*)	**244.** (*d*)	**245.** **(b)**	**246.** (*a*)	**247.** (*d*)	**248.** (*d*)	**249.** (*c*)	**250.** (*b*)
251. (*c*)	**252.** (*c*)	**253** (*c*)	**254.** (*d*)	**255.** **(c)**	**256.** (*c*)	**257.** (*d*)	**258.** (*a*)	**259.** (*b*)	**260.** (*b*)
261. (*a*)	**262.** (*a*)	**263.** (*c*)	**264.** (*b*)	**265.** **(b)**	**266.** (*a*)	**267.** (*d*)	**268.** (*a*)	**269.** (*a*)	**270.** (*a*)
271. (*a*)	**272.** (*a*)	**273.** (*b*)	**274.** (*c*)	**275.** **(a)**	**276.** (*b*)	**277.** (*b*)	**278.** (*a*)	**279.** (*d*)	**280.** (*a*)
281. (*d*)	**282.** (*d*)	**283.** (*a*)							

ANSWERS – FILL IN THE BLANKS

1. intermolecular,
2. fixed, not definite,
3. equal, temperature,
4. increases,
5. decreases,
6. decreases
7. higher,
8. condensed, molten,
9. external
10. viscosity,
11. surface tension,
12. definite, fixed,
13. donot, sharp,
14. flat, sharp,
15. amorphous, crystalline
16. six, six
17. 23
18. seven
19. unit cell
20. 1/8
21. 90°
22. 26
23. co-ordination number
24. 4, 4
25. bad
26. covalent
27. isomorphism
28. less
29. non-polar
30. stronger
31. decreases
32. polar covalent
33. weaker bond
34. fluorine
35. evolution
36. 104°
37. N_2
38. endothermic
39. exothermic
40. 1, 2
41. 8.4 to 42
42. High
43. pyramidal
44. co-ordinate
45. $\lambda=2d\sin\theta$
46. higher
47. two
48. narrow
49. lyotropic
50. active