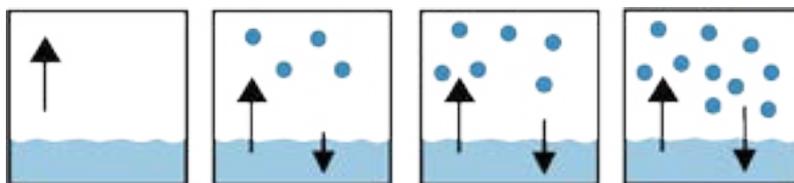CHAPTER

4

LIQUIDS AND SOLIDS

SOLID

Animation 4.1: Solid, Liquid, Gas
Source & Credit: everythingscientific

INTRODUCTION

The existence of matter in our surrounding in the form of gases, liquids and solids is due to difference of interacting forces among the constituent particles.

4.1 INTERMOLECULAR FORCES

To understand the properties of liquids and solids, we need to know the kinds of intermolecular forces present in them and their relative strength. It is important to realize that the attraction between the molecules is much weaker than the attraction between atoms within a molecule. In a molecule of HCl, there is a covalent bond between H and Cl which is due to the mutual sharing of electrons. Both atoms satisfy their outermost shells and it is their firm need to remain together, hence this linkage is very strong.

HCl molecules in the neighbourhood attract each other, but the forces of attraction are weak. These forces are believed to exist between all kinds of atoms and molecules when they are sufficiently close to each other. Such intermolecular forces are called van der Waals forces and they have nothing to do with the valence electrons.

These intermolecular forces bring the molecules close together and give particular physical properties to the substances in gaseous, liquid and solid states. Four types of such forces are mentioned here.

1. Dipole-dipole forces
2. Ion-dipole forces
3. Dipole-induced dipole forces
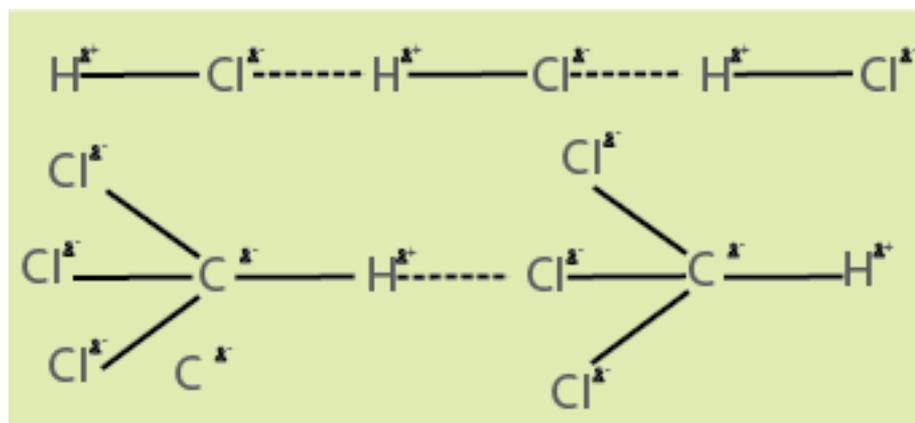4. Instantaneous dipole-induced dipole forces or London dispersion forces

Animation 4.2 : Intermolecular forces
Source & Credit: intermolecularforcess
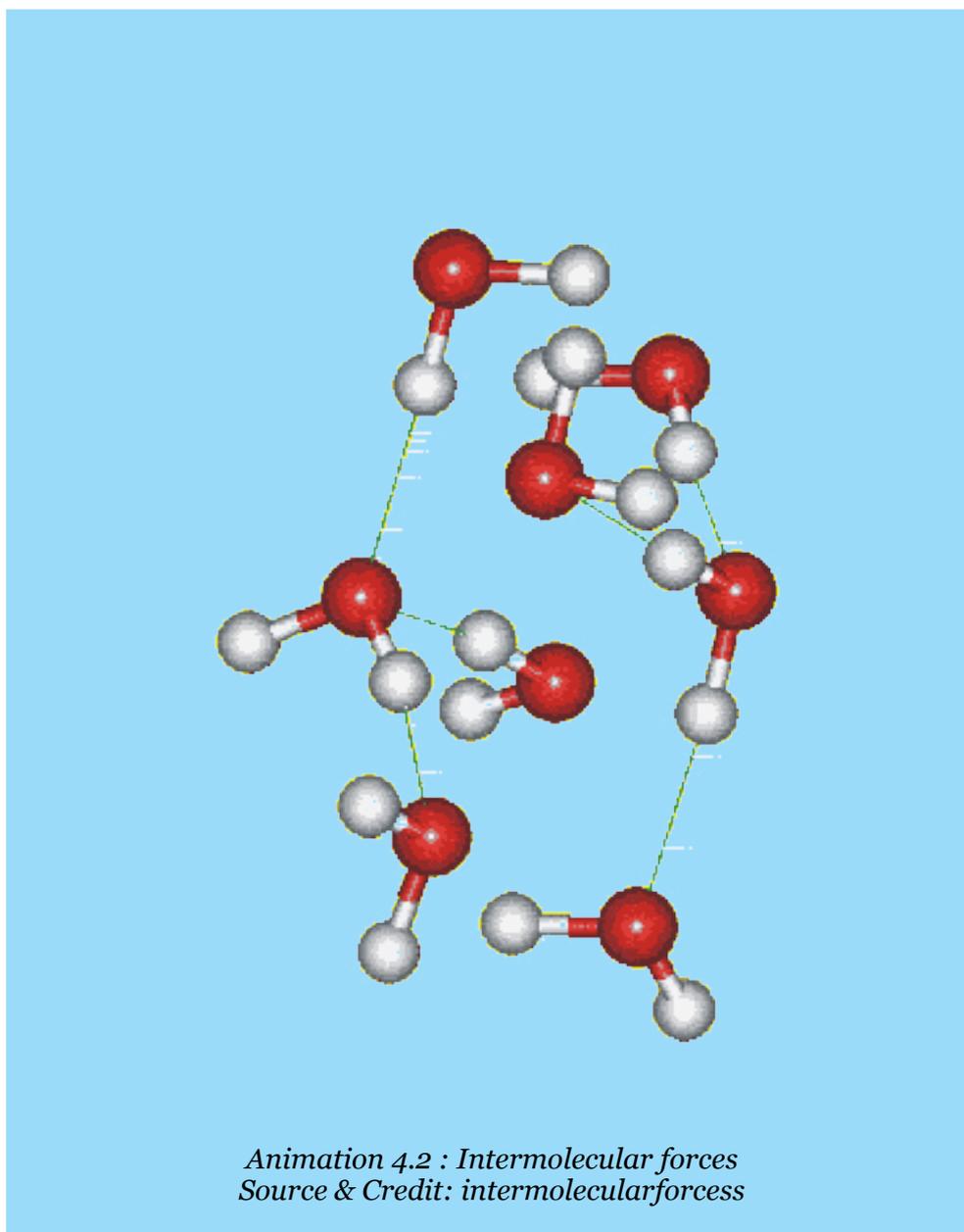
4.1.1 Dipole-dipole Forces

In case of HCl molecule both atoms differ in electronegativity. Chlorine being more electronegative, develops the partial negative charge and hydrogen develops the partial positive charge. So, whenever the molecules are close to each other, they tend to line up. The positive end of one molecule attracts the negative end of the other molecule and these electrostatic forces of attraction are called dipole-dipole forces. However, thermal energy causes the molecules not to have a perfect alignment.

Anyhow, there is a net attraction between the polar molecules. These forces are called as dipole-dipole forces and they are approximately one percent as effective as a covalent bond. The strength of these forces depends upon the electronegativity difference between the bonded atoms and the distance between the molecules. The distances between molecules in the gaseous phase are greater so these forces are very weak in this phase. In liquids these forces are reasonably strong. The examples of the molecules which show dipole-dipole attractions are numerous. Two of these are given below i.e., for HCl and $CHCl_3$ (chloroform) Fig (4.1).

Greater the strength of these dipole-dipole forces, greater are the values of thermodynamic parameters like melting points, boiling points, heats of vapourization and heats of sublimation.

Show Fig. (4.1) Dipole - dipole forces present in HCl molecules and chloroform ($CHCl_3$) molecules.

4.1.2 Dipole-induced Dipole Forces

Sometimes, we have a mixture of substances containing polar and non-polar molecules. The positive end of the polar molecule attracts the mobile electrons of the nearby non-polar molecule. In this way polarity is induced in non-polar molecule, and both molecules become dipoles. These forces are called dipole-induced dipole forces or as Debye forces. The following figure makes the idea clear Fig (4.2).

Permanent Polar Molecule   Non-Polar Molecule   Permanent Dipole   Induced Dipole
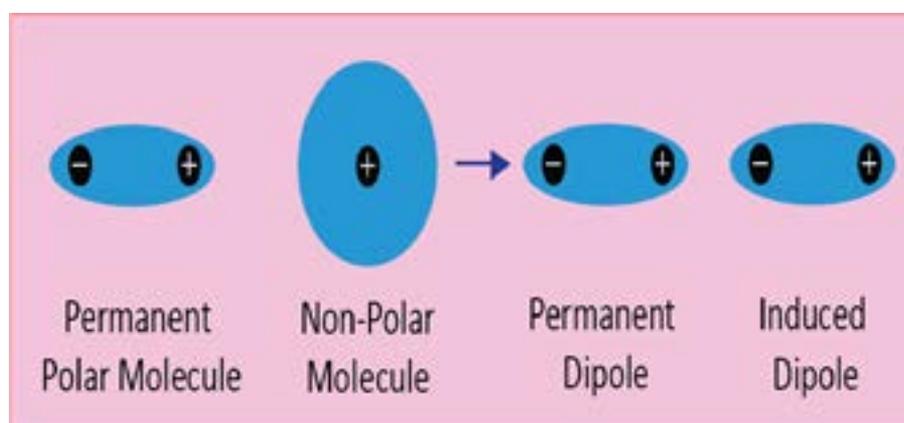
Fig (4.2) Dipole-induced dipole interactions

4.1.3 Instantaneous Dipole-induced Dipole Forces or London Dispersion Forces

Intermolecular forces among the polar molecules, as discussed in section 4.1.1 are very easy to understand. But the forces of attraction present among the non-polar molecules like helium, neon, argon, chlorine and methane need special attention because under normal conditions such molecules don't have dipoles. We know that helium gas can be liquefied under appropriate conditions. In other words forces of attraction operate among the atoms of helium which cause them to cling together in the liquid state.

A German physicist Fritz London in 1930 offered a simple explanation for these weak attractive forces between non-polar molecules.

In helium gas, the electrons of one atom influence the moving electrons of the other atom. Electrons repel each other and they tend to stay as far apart -as possible. When the electrons of one atom come close to the electron of other atom, they are pushed away from each other. In this way,a temporary dipole is created in the atom as shown in the Fig (4.3). The result is that, at any moment, the electron density of the atom is no more symmetrical. It has more negative charge on one side than on the other. At that particular instant, the helium atom becomes a dipole. This is called instantaneous dipole.
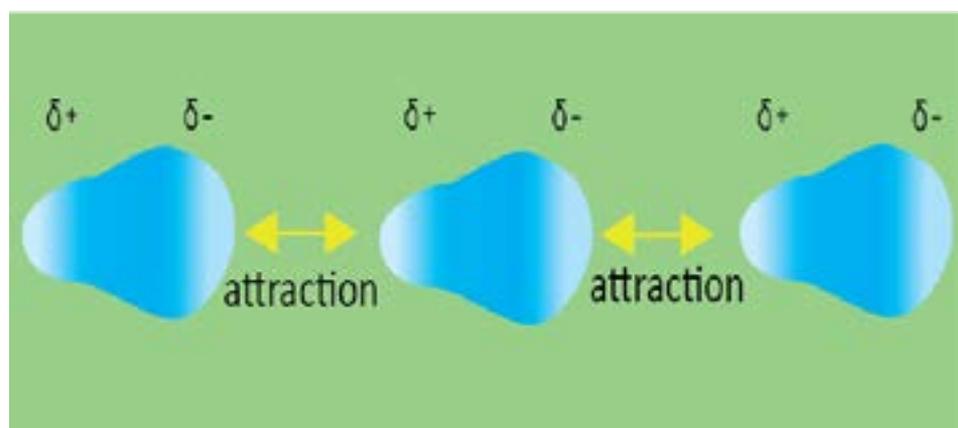

Fig. (4.3) Instantaneous dipole-induced
dipole attractions between helium atoms.

This instantaneous dipole then disturbs the electronic cloud of the other nearby atom. So,a dipole is induced in the second atom. This is called induced dipole. The momentary force of attraction created between instantaneous dipole and the induced dipole is called instantaneous dipole-induced dipole interaction or London force.

It is a very short-lived attraction because the electrons keep moving. This movement of electrons cause the dipoles to vanish as quickly as they are formed. Anyhow, a moment later, the dipoles will appear in different orientation and again weak attractions are developed.

London forces are present in all types of molecules whether polar or non-polar, but they are very' significant for non-polar molecules like Cl_2, H_2 and noble gases (helium, neon,etc.)
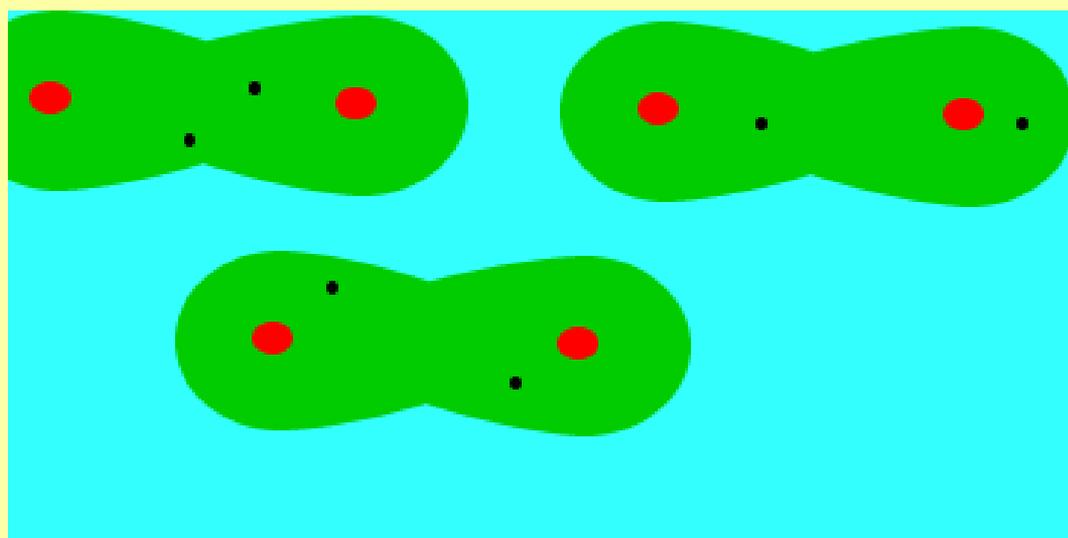
Animation 4.3 : London Dispersion Forces
Source & Credit: dynamicscience

4.1.4 Factors Affecting the London Forces

London forces are weaker than dipole- dipole interactions. The strength of these forces depend upor the size of the electronic cloud of the atom or molecules. When the size of the atom or molecule is large then the dispersion becomes easy and these forces become more prominent. The elements of the zero group in the periodic table are all mono-atomic gases. They don't make covalent bonds with other atoms because their outermost shells are complete. Their boiling points increase down the group from helium to radon. Boiling points of noble gases are given in Table (4.1)
The atomic number increases down the group and the outermost electrons move away from the nuclei. The dispersion of the electronic clouds becomes more and more easy. So the polarizability of these atoms go on increasing.

Polarizability is the quantitative measurement of the extent to which the electronic cloud can be polarized or distorted. When we say that a species (atom, molecule or ion) is polarized, it means that temporary poles are created. This is possible if electronic cloud can be disturbed or distorted. This increased distortion of electronic cloud creates stronger London forces and hence the boiling points are increased down the group.

Similarly, the boiling points of halogens in group VII-A also increase from fluorine to iodine Table (4.1). All the halogens are non-polar diatomic molecules, but there is a big difference in their physical states at room temperature. Fluorine is a gas and boils at -188.1 °C, while iodine is a solid at room temperature which boils at +184.4 °C. The polarizability of iodine molecule is much greater than that of fluorine.

Table(4.1) Boiling points of halogens and noble gases

Another important factor that affects the strength of London forces is the number of atoms in a non-polar molecule. Greater the number of atoms in a molecule, greater is its polarizability. Let us discuss the boiling points of saturated hydrocarbons. These hydrocarbons have chain of carbon atoms linked with hydrogen atoms. Compare the length of the chain for C_2H_6 and C_6H_{14}.

They have the boiling points - 88.6 °C and 68.7 C,respectively. This means that the molecule with a large chain length experiences stronger attractive forces. The reason is that longer molecules have more places along its length where they can be attracted to other molecules. It is very interesting to know that with the increasing molecular mass of these hydrocarbons, they change from gaseous to liquid and then finally become solids. The Table (4.2) gives the boiling points and the physical states of some hydrocarbons.

Table (4.2) Boiling points and physical states of some hydrocarbons

Name	B.P °C (1 atm)	Physical state at S.T.P	Name	B.P °C (1 atm)	Physical state at S.T.P
Mathane	-164	Gas	Pentane	36.1	Liquid
Ethane	-88.6	Gas	Hexane	68.7	Liquid
Propane	-42.1	Gas	Decane	174.1	Liquid
Butane	0.5	Gas	Isodecane	327	Solid

4.1.5 Hydrogen Bonding

To understand hydrogen bonding, let us consider the molecule of water. Oxygen is more electronegative element as compared to hydrogen, so water is a polar molecule. Hence there will be dipole-dipole interactions between partial positively charged hydrogen atoms and partial negatively charged oxygen atoms. Actually, hydrogen bonding is something more than simple dipole-dipole interaction. Firstly, oxygen atom has two lone pairs. Secondly hydrogen has sufficient partial positive charge. Both the hydrogen atoms of water molecule create strong electrical field due to their small sizes.

The oxygen atom of the other molecule links to form a coordinate covalent bond with hydrogen using one of its lone pairs of electrons. Fig (4.4).

Fig (4.4) Hydrogen bonding in water.

Thus loose bond formed is definitely stronger than simple dipole-dipole interaction. Because of the small size of the hydrogen atom, it can take part in this type of bonding. This bonding acts as a bridge between two electronegative oxygen atoms. Hence hydrogen bonding is the electrostatic force of a atraction between a highly electronegative atom and partial positively charged hydorgen atom.
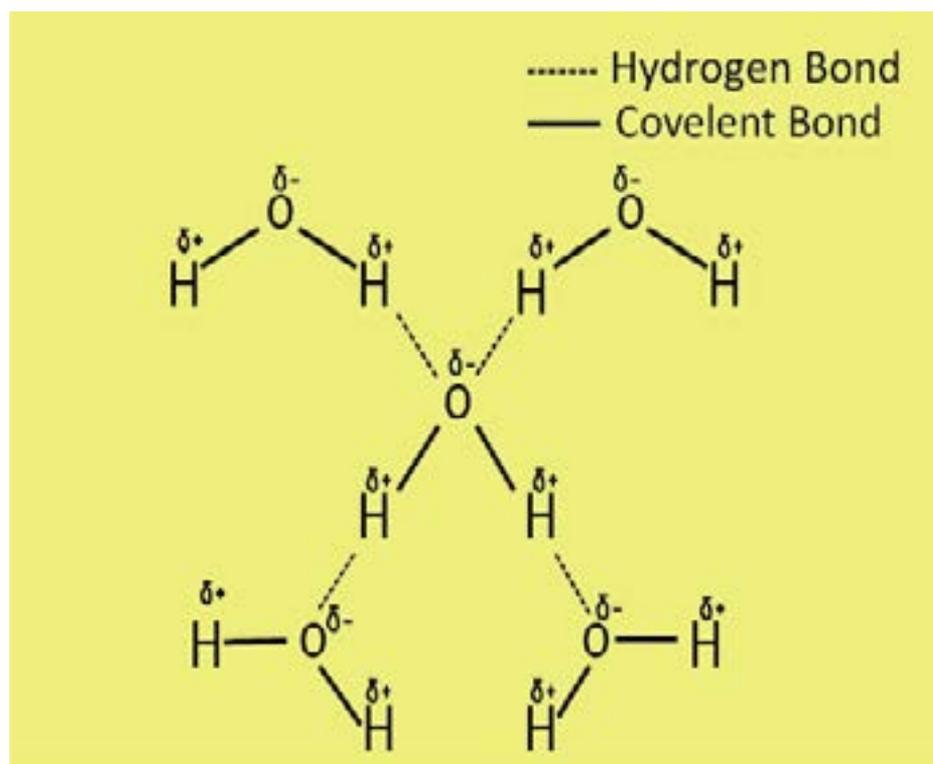
The electronegative atoms responsible for creating hydrogen bonding are fluorine, oxygen, nitrogen and rarely chlorine. The strength of hydrogen bond is generally twenty times less than that of a covalent bond.

Animation 4.4 : hydrogen bonding
Source & Credit: stream1
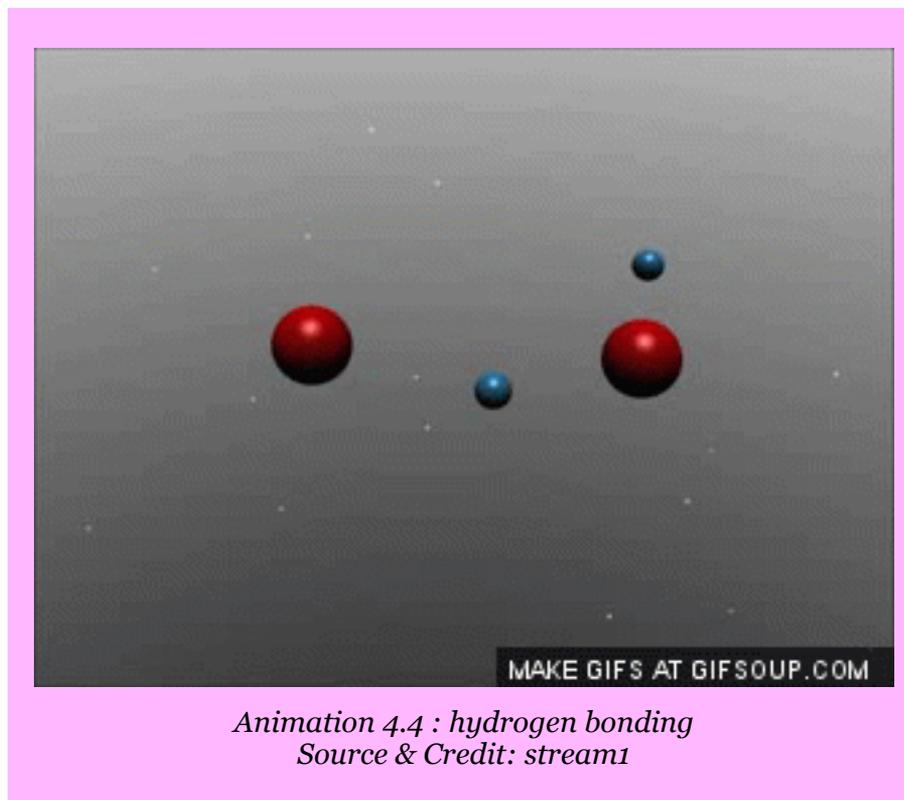
It is not advisable to limit the hydrogen bonding to the above-m entioned electronegative atoms. The three chlorine atoms in chloroform are responsible for H- bonding with other molecules. These atoms deprive the carbon atom of its electrons and the partial positively charged hydrogen can form a strong hydrogen bond with oxygen atom of acetone Fig (4.5).

Fig (4.5) Hydrogen bonding between chloroform and acetone

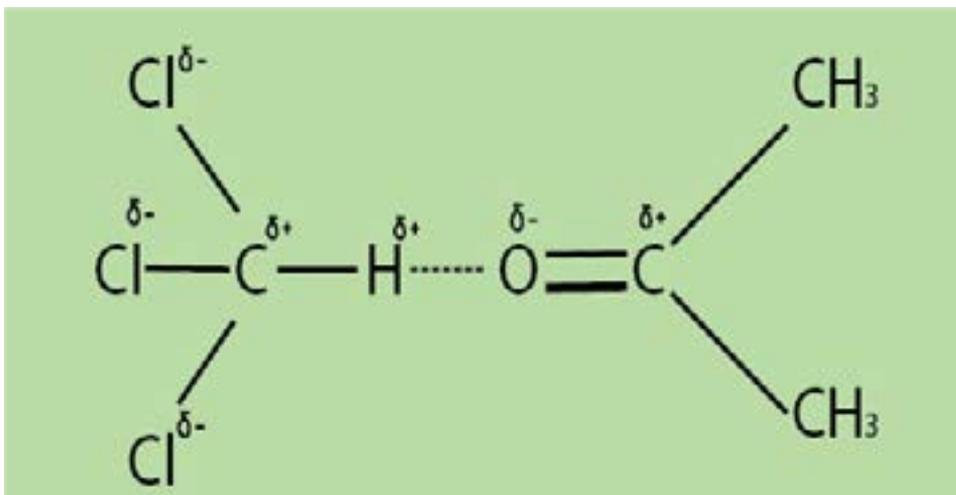The hydrogen bonding present in the molecules of ammonia and those of hydroflouric acid can be depicted as follows Fig (4.6).The molecules of HF join with each other in a zig- zag manner.

The exceptional, low acidic strength of HF molecule as compared to HCl, HBr and HI is due to this strong hydrogen bonding, because the partial positively charged hydrogen is entrapped between two highly electronegative atoms.
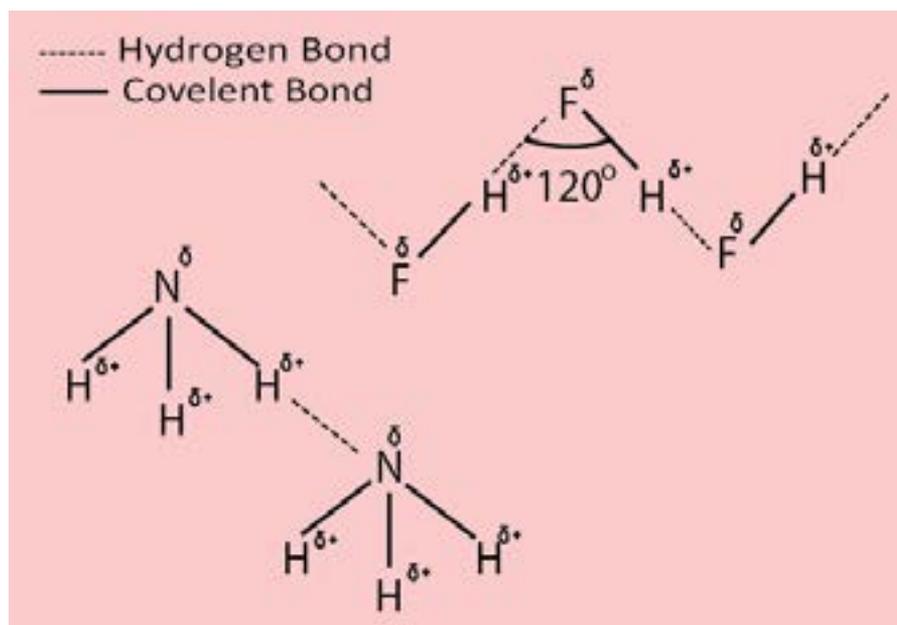
Fig (4.6) Hydrogen bonding in NH_3 and HF molecules.

4.1.6 Properties and Application of Compounds Containing Hydrogen Bonding

1.   Thermodynamic Properties of Covalent Hydrides

Our discussion shows that hydrogen bonding exists in compounds having partial positively charged hydrogen and highly electronegative atoms bearing partial negative charge. Obviously such intermolecular attractions will influence the physical properties like melting and boiling points. Let us compare the physical properties of hydrides of group IV-A, V-A, VI-A and VII-A. The graphs are plotted between the period number of the periodic table on x-axis and boiling points in kelvin on y-axis Fig (4.7).

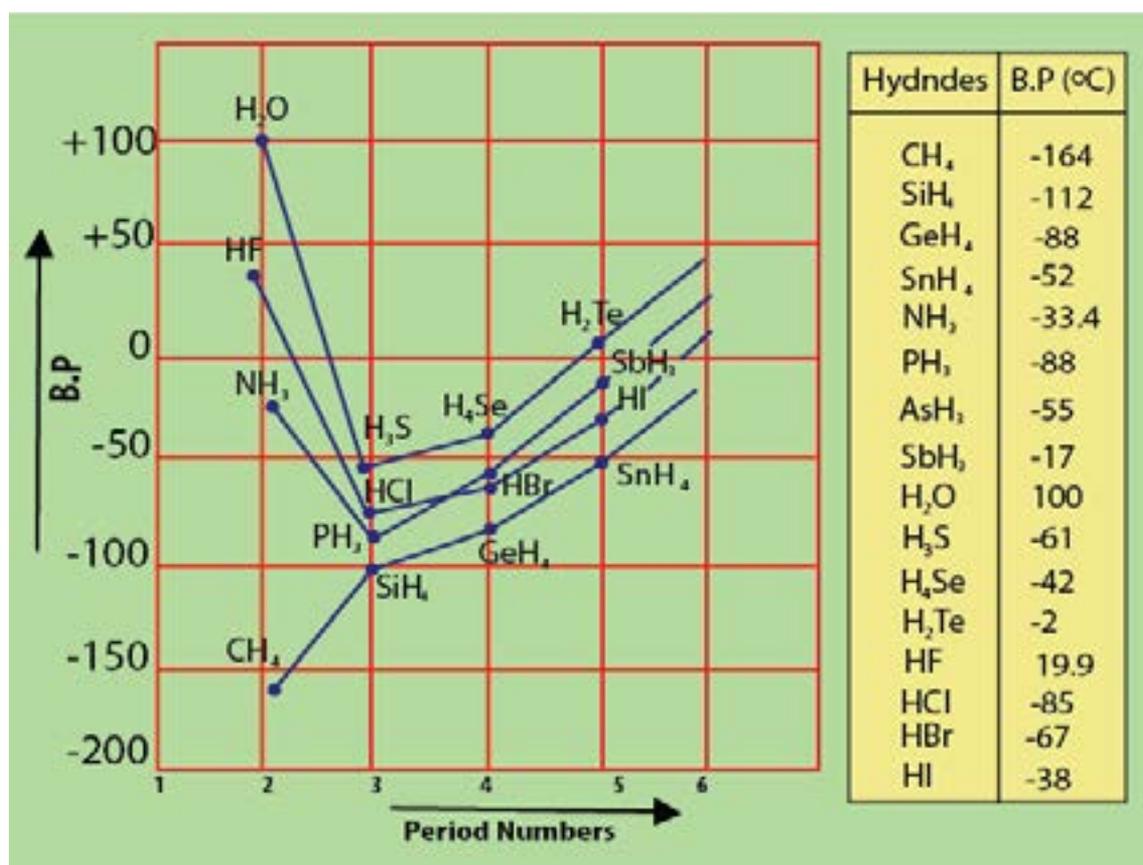| Hydndes	B.P ($^{\circ}$C)
CH_4	-164
SiH_4	-112
GeH_4	-88
SnH_4	-52
NH_3	-33.4
PH_3	-88
AsH_3	-55
SbH_3	-17
H_2O	100
H_2S	-61
H_4Se	-42
H_2Te	-2
HF	19.9
HCl	-85
HBr	-67
HI	-38

Fig (4.7) A Graph between period number and the boiling points of hydrides of IV-A, V-A, VI-A and VII-A group elements.

A look at the boiling points of hydrides of group IV-A convinces us, that they have low boiling points as compared to those of group V-A, VI-A, VII-A. The reason is that these elements are least electronegative. CH_4 has the lowest boiling point because it is a very small molecule and its polarizability is the least.

When we consider the hydrides of group V-A, VI-A, VII-A then NH_3, H_2O and HF show maximum boiling points in the respective series. The reason is, the enhancec electronegative character of N, 0 and F. That is why, water is liquid at room temperature, but H_2S and H_2Se are gases.

It is interesting to know that the boiling point of water seems to be more affected by hydrogen bonding than that of HF Fluorine is more electronegative than oxygen. So, we should expect H-bonding in HF to be stronger than that in water and as a result the boiling point of HF should be higher than that of H_2O. However, it is lower and the reason is that the fluorine atom can make only one hydrogen bond with electropositive hydrogen of a neighboring molecule. Water can form two hydrogen bonds per molecule, as it has two hydrogen atoms and two lone pairs on oxygen atom. Ammonia can form only one hydrogen bond per molecule as it has only one lone pair.

The   boiling point of HBris slightly higher than that of HCl. It means that chlorine is electronegative enough to form a hydrogen bond. Sometimes it is thought that HCl has a strong dipole-dipole interaction but in reality, it is a border line case. The hydrides of fourth period GeH_4, AsH_3, H_2Se, HBr show greater boiling points than those of third period due to greater size and enhanced poiarizabilities.

2.   Solubility of Hydrogen- Bonded Molecules

Water is the best example of H-bonded system. Similarly ethyl alcohol (C_2H_5OH) also has the tendency to form hydrogen bonds. So, ethyl alcohol can dissolve in water because both can form hydrogen bonds with each other. Similarly carboxylic acids are also soluble in water, if their sizes are small. Hydrocarbons are not soluble in water at all, because they are non-polar compounds and there are no chances of hydrogen bonding between water and hydrocarbon molecules.

3.   Structure of Ice

The molecules of water have tetrahedral structure. Two lone pairs of electrons on oxygen atom occupy two corners of the tetrahedron. In the liquid state, water molecules are extensively associated with each other and these associations break and are reformed because the molecules of water are mobile. When the temperature of water is decreased and ice is formed then the molecules become more regular and this regularity extends throughout the whole structure. Empty spaces are created in the structure as shown in the following Fig (4.8b). That is why when water freezes it occupies 9% more space and its density decreases. The result is that ice floats on water. The structure of ice is just like that of a diamond because each atom of carbon in diamond is at the center of tetrahedron just like the oxygen of water molecule in ice, Fig (4.8 b).
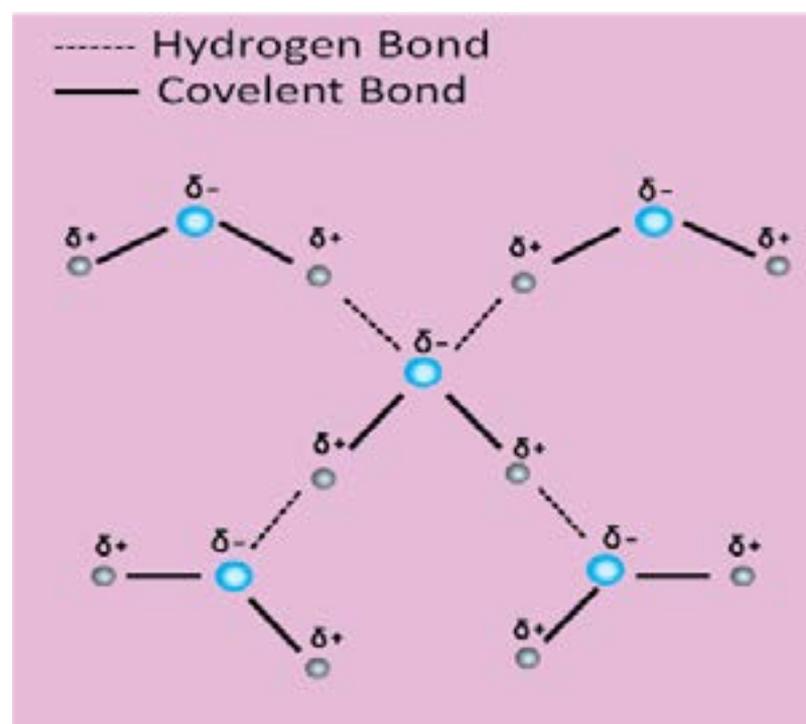

Fig (4.8 a) Structure of liquid water

The lower density of ice than liquid water at 0 °C causes water in ponds and lakes to freeze from surface to the downward direction. Water attains the temperature of 4°C by the fall of temperature in the surrounding. As the outer atmosphere becomes further cold, the water at the surface becomes less dense. This less dense water below 4 °C stays on the top of slightly warm water underneath. A stage reaches when it freezes. This layer of ice insulates the water underneath for further heat loss. Fish and plants survive under this blanket of ice for months.

Fig (4.8 b) Structure of ice

Keeping the whole discussion in view we are forced to believe that the pattern of life for the plants and animals would have been totally different in the absence of hydrogen bonding in water.
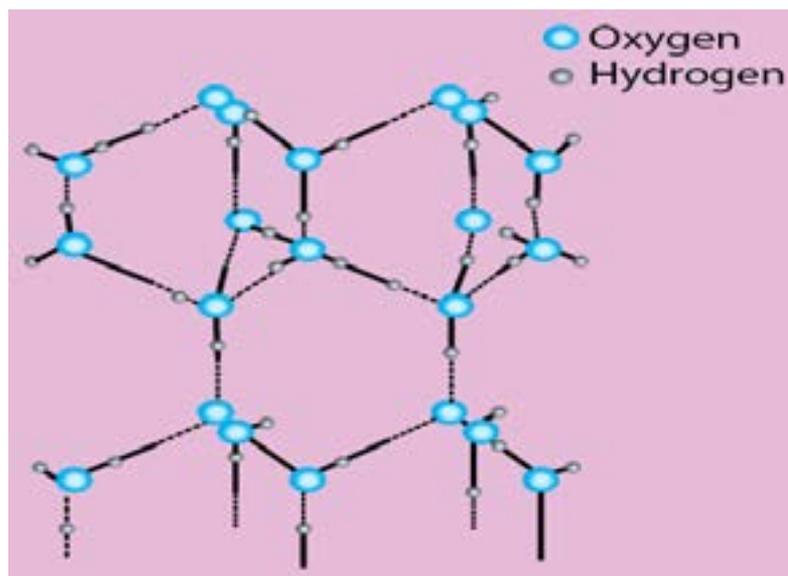
4.   Cleansing Action of Soaps and Detergents

Soaps and detergents perform the cleansing action because the polar part of their molecules are water soluble due to hydrogen-bonding and the non-polar parts remain outside water, because they are alkyl or benzyl portions and are insoluble in water.

5.   Hydrogen Bonding in Biological Compounds and Food Materials

Hydrogen bonding exists in the molecules of living system. Proteins are the important part of living organisms. Fibres like those found in the hair, silk and muscles consist of long chains of amino acids. These long chains are coiled about one another into a spiral. This spiral is called a helix. Such a helix may either be right handed or left handed. In the case of right handed helix the groups like >N H and > C = 0 are vertically adjacent to one another and they are linked together by hydrogen bonds. These H-bonds link one spiral to the other. X-ray analysis has shown that on the average there are 27 amino acid units for each turn of the helix, Fig (4.9 a).

Deoxyribonucleic acid (DNA) has two spiral chains. These are coiled about each other on a common axis. In this way, they give a double helix. This is 18-20 Å in diameter. They are linked together by H-bonding between their sub units, Fig (4.9 b).
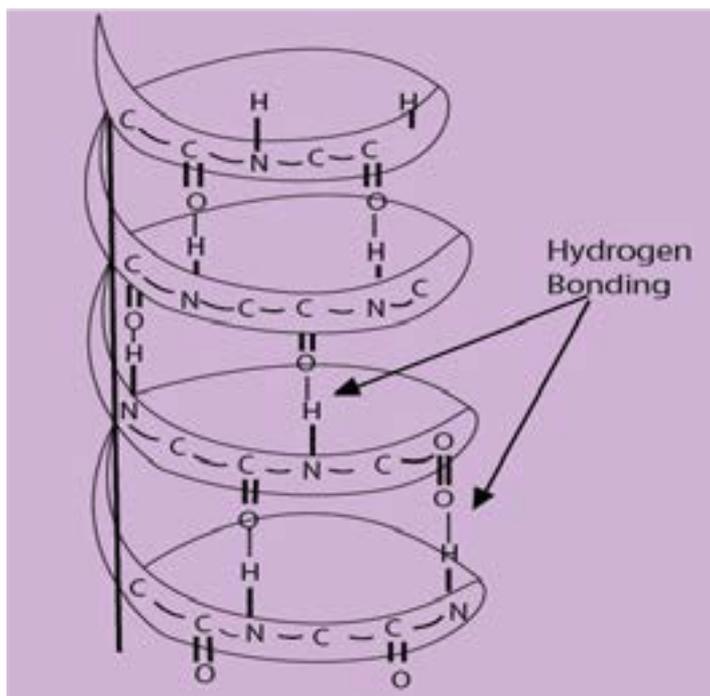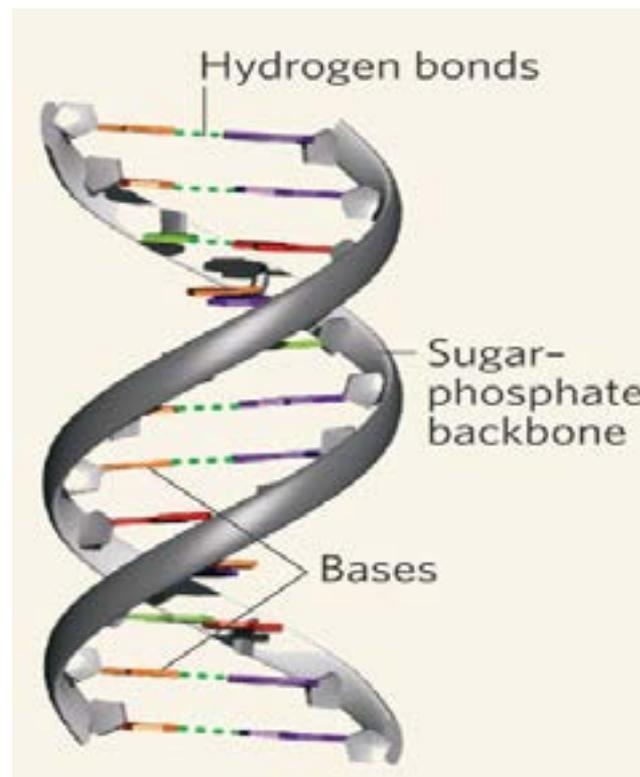
Fig (4.9 a) Hydrogen bonding

Fig (4.9 b) Hydrogen bonding in
DNA double helix

The food materials like carbohydrates include glucose, fructose and sucrose. They all have -OH groups in them which are responsible for hydrogen bonding in them.

6. Hydrogen Bonding in Paints, Dyes and Textile Materials

One of the most important properties of paints and dyes is their adhesive action. This property is developed due to hydrogen bonding. Similar type of hydrogen bonding makes glue and honey as sticky substances.

We use cotton, silk or synthetic fibres for clothing. Hydrogen bonding is of vital importance in these thread making materials. This hydrogen bonding is responsible for their rigidity and the tensile strength.

4.2.0   EVAPORATION

In order to understand evaporation, we have to examine the movement of molecules in liquids. The molecules of a liquid are not motionless. The energy of molecules is not equally distributed. The molecules which have low kinetic energy move slowly, while others with high kinetic energy move faster. If one of the high speed molecules reaches the surface, it may escape the attractions of its neighbouring molecules and leaves the bulk of the liquid. **This spontaneous change of a liquid into its vapours is called evaporation and it continues at all temperatures.** Evaporation causes cooling. The reason is that when high energy molecules leave the liquid and low energy molecules are left behind, the temperature of the liquid falls and heat moves from the surrounding to the liquid and then the temperature of the surrounding also falls.

Animation 4.5 : Evaporation
Source & Credit: stem
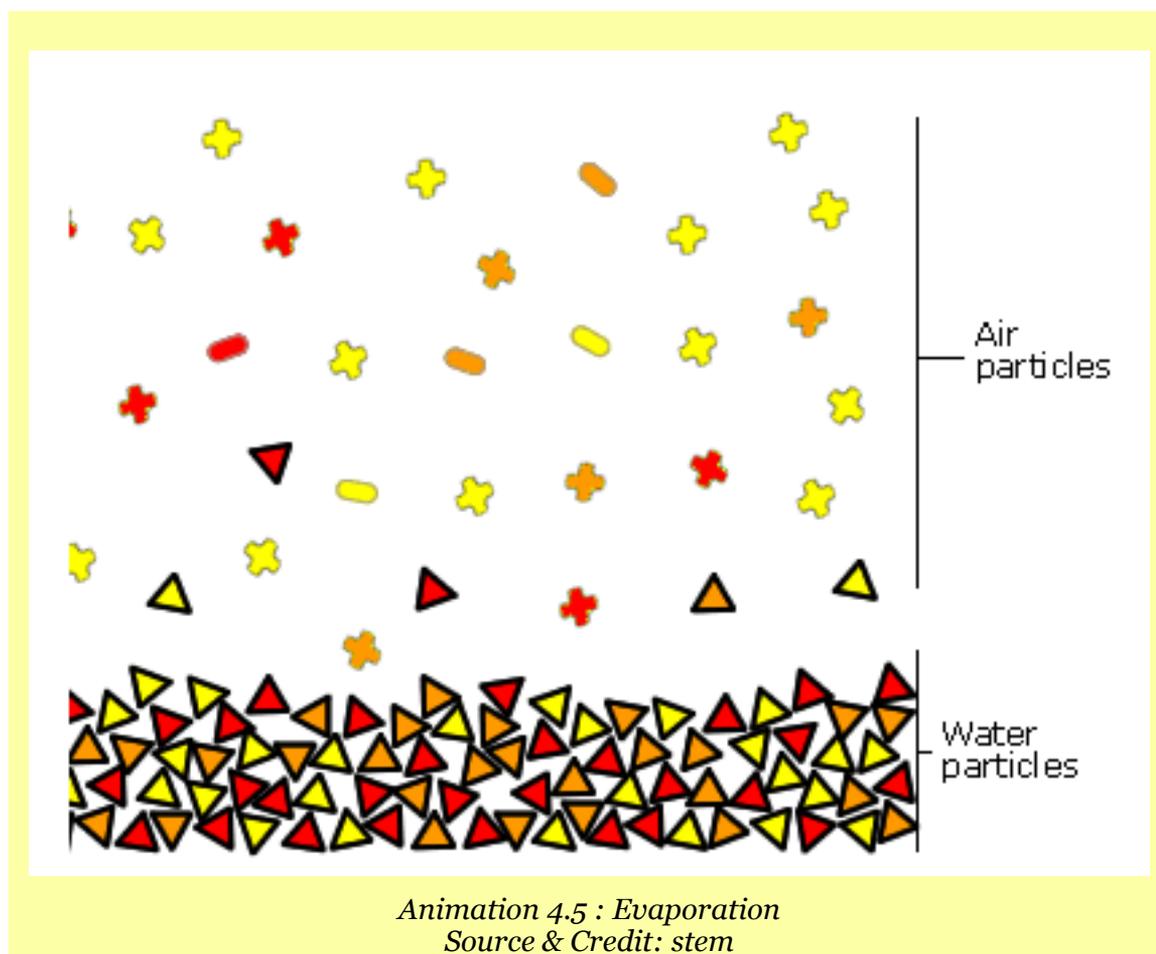
There are many factors which control the rate of evaporation of a liquid. Since evaporation occurs from liquid surface, so if surface area is increased then more molecules are able to escape and liquid evaporates more quickly. For liquids having same surface area, the rate of evaporation is controlled by the temperature and the strength of intermolecular forces.

At high temperature, the molecules having greater energy increase and so rate of evaporation increases. Similarly, if intermolecular forces are weak, the rate of evaporation is faster. For example, gasoline, whose molecules experience weaker London forces of attraction, evaporate much faster than water.

4.2.1 Vapour Pressure

When the molecules of a liquid leave the open surface, they are mixed up with air above the liquid. If the vessel is open these molecules go on leaving the surface. But if we close the system the molecules of liquid start gathering above the surface. These molecules not only collide with the walls of the container, but also with the surface of the liquid as well.

There are chances that these molecules are recaptured by the surface of liquid. This process is called condensation. The two-processes i.e., evaporation and condensation continue till a stage reaches when the rate of evaporation becomes equal to the rate of condensation. This is called the state of dynamic equilibrium Fig (4.10). So the vapour pressure of a liquid is a pressure exerted by the vapours of the liquid in equilibrium with the liquid at a given temperature.
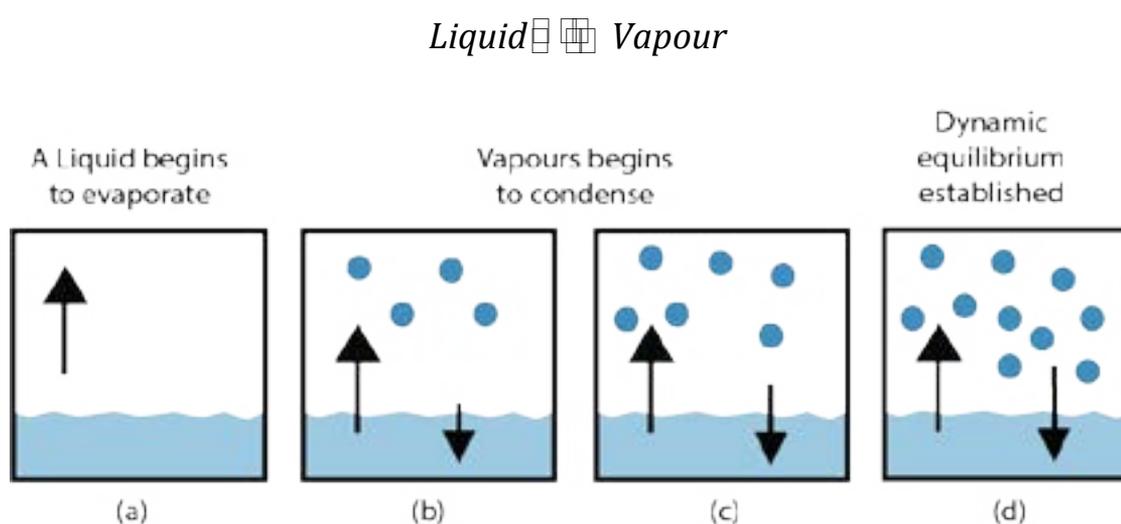
$$Liquid \rightleftharpoons Vapour$$

Fig (4.10) Evaporation of a liquid and establishment
of dynamic equilibrium between liquid and its vapours.

The number of molecules leaving the surface is just equal to the number of molecules coming back into it at a constant temperature. The molecules which are in the liquid state at any moment may be in vapour state in the next moment.

The magnitude of vapour pressure does not depend upon the amount of liquid in the container or the volume of container. It also does not depend on surface area of a liquid. The larger surface area also presents a larger target for returning the molecules, so the rate of condensation also increases.

Animation 4.6 : Vapour Pressure
Source & Credit: mecaflux

Vapour Pressure Increases with Temperature

The values of vapour pressures of various liquids depend fairly upon the nature of liquids i.e. on the sizes of molecules and intermolecular forces, but the most important parameter which controls the vapour pressure of a liquid is its temperature. At an elevated temperature, the kinetic energy of molecules is enhanced and capability to leave the surface increases. It causes the increase of vapour pressure. Table(4.3) shows change in vapour pressure of water at different temperatures. The Table (4.3) shows that increases of vapour pressure goes on increasing for the same difference of temperature from 0°C to 100°C for water. There is increase of vapour pressure from 4.579 torr to 9.209 torr for change of temperature from 0°C to 10°C. But the increase is from 527.8 torr to 760 torr when temperature changes from 90°C to 100°C. The difference in the strength of intermolecular forces in different liquids is directly related to their vapour pressures at a particular temperature. The stronger the intermolecular forces the lower the vapour pressure. The following Table (4.4) shows that at 20 °C isopentane has the highest vapour pressure, while glycerol has the lowest.

Tablc (4.3) Vapour pressures of water (torr) at various temperatures

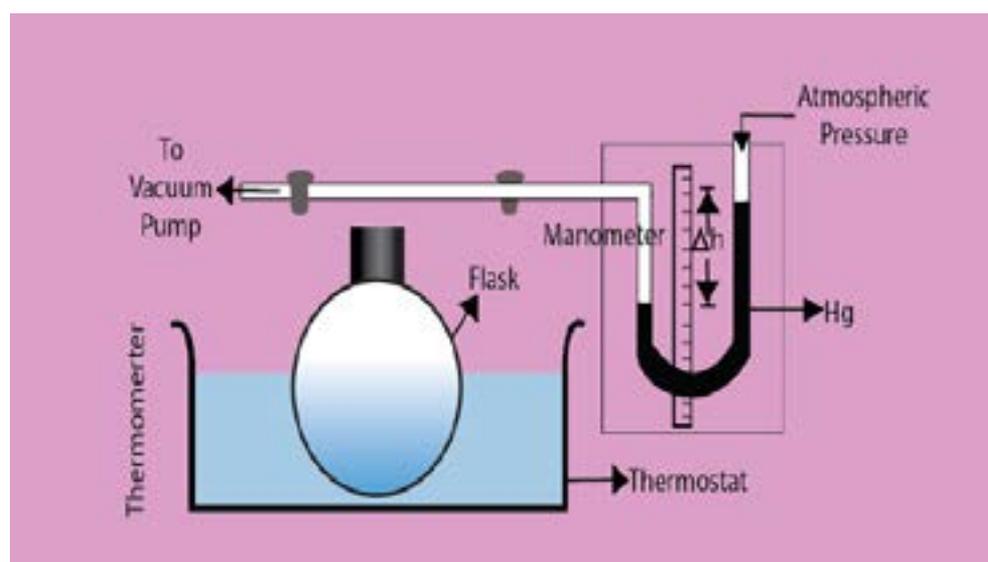| Temperature (⁰C)	Vapour Pressure (Torr)
0	4.579
10	9.209
20	17.54
30	31.82
37	47.07
40	55.32
50	92.51
60	149.4
70	233.7
80	355.1
90	527.8
100	760.0

4.2.2 Measuremerr of Vapour Pressure

There are many methods for the measurement of vapour pressure of a liquid. One of the important methods is described in the following paragraph.

Table (4.4) Vapour pressure of some important liquids at 20°C

Name of compound	Vapour pressure at 20 ^{0}C (torr)
Isopentane	580
Ethyl ether	442.2
Chloroform	170
CarbonTetrachloride	87
Ethanol	43.9
Mercury	0.012
Glycerol	0.00016

Manometric Method

Manometric method is comparatively an accurate method. The liquid whose vapour pressure is to be determined is taken in a flask placed in a thermostat, as shown in the Fig(4.11). One end of the tube from the flask is connected to a manometer and the other end is connected to a vacuum pump. The liquid is frozen with the help of a freezing mixture and the space above the liquid is evacuated. In this way, the air is removed from the surface of the liquid alongwith the vapours of that liquid. The frozen liquid is then melted to release any entrapped air. Liquid is again frozen and realeased air To is evacuated. This process is repeated many times till almost all the air is removed.

Fig. (4.11) Measurement of vapour pressure of a in the heights of the columns of-Hg in liquid by manometric method

Now the liquid is warmed in the thermostat to that temperature at which its vapour pressure in the flask is to be determined. Difference in the heights of the columns of-Hg in liquid by manometric method the two limbs of the manometer determines the vapour pressure of the liquid.

The column of mercury in the manometer facing the vapours of the liquid is depressed. The other column, which faces the atmospheric pressure, rises. Actually, the pressure on the surface of the liquid in the flask is equal to the sum of the atmospheric pressure and the vapour pressure of liquid. For this reason, the column of manometer facing the liquid is more depressed than facing the atmosphere, and it is given by the following equation.

$$P = P_a + \Delta h$$

Where

P = Vapour pressure of the liquid at one atm pressure.

P= Atmospheric pressure.

Δh = Difference in the heights of the mercury levels in the two limbs of the manometer, giving us the vapour pressure of liquid.

4.2.3 Boiling Point

When a liquid is heated, the vapour pressure goes on increasing. A stage reaches when the vapour pressure of the liquid becomes equal to the external atmospheric pressure. This temperature is called the boiling point of the liquid. The reason for this is that the bubbles of vapours which are formed in the interior of the liquid have greater internal pressure than atmospheric pressure on the surface of liquid. This thing makes the bubble to come out of the liquid and burst upon the surface. Thus a constant stream of bubbles comes out at the boiling point.

When a liquid is heated, the kinetic energy of its molecules increases and hence the temperature also increases. At the boiling point, the kinetic energy of the molecules becomes maximum and any further heating at this stage will not increase the temperature.

Animation 4.7 : Boiling Point
Source & Credit: chem
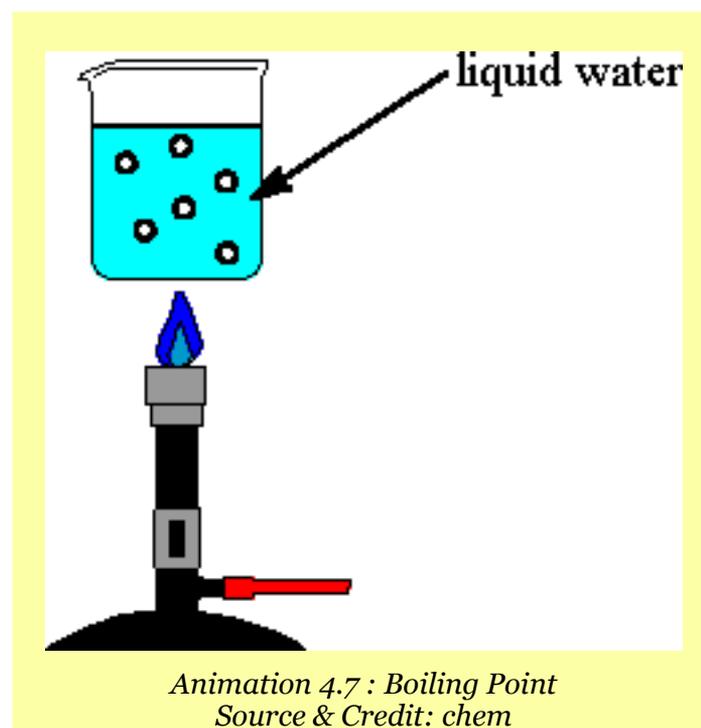
This heat will only be utilized to break the intermolecular forces and convert the liquid into its vapours. **The amount of heat required to vapourize one mole of a liquid at its boiling point is called its molar heat of vapourization.** The molar heat of vapourization of water is 40.6 kjmol^{-1}. The boiling points of some commonly available liquids at one atmospheric pressure are shown in the Table (4.5).

Table (4.5) Boiling points of some common liquids at 760 torr.

Liquid	B.P (^{0}C)	Liquids	B.P (^{0}C)
Acetic Acid	118.50	Carbontetrachloride	76.50
Acetone	56.00	Ethanol	78.26
Aniline	184.4	Naphthalene	218.00
Benzene	80.15	Phenol	181.80
Carbon disulphide	46.30	Water	100.00

The Fig. (4.12) shows the variation of vapour pressure of water, ethyl alcohol, ethylene glycol and diethylether with temperature. It shows that the liquids reach upto their boiling points when their vapour pressures are equal to 760 torr at sea level. The way these curves start at 0 ^{0}C is interesting. Water takes start at 4.8 torr while diethyl ether at around 200 torr. This is due to difference in the strengths of their intermolecular forces. The curve for water goes alongwith temperature axis to a greater extent at the beginning as compared to ether. It means that water can hardly overcome its intermolecular forces at low temperatures. It is clear from the curves that the vapour pressure increases very rapidly when the liquids are closer to their boiling points.
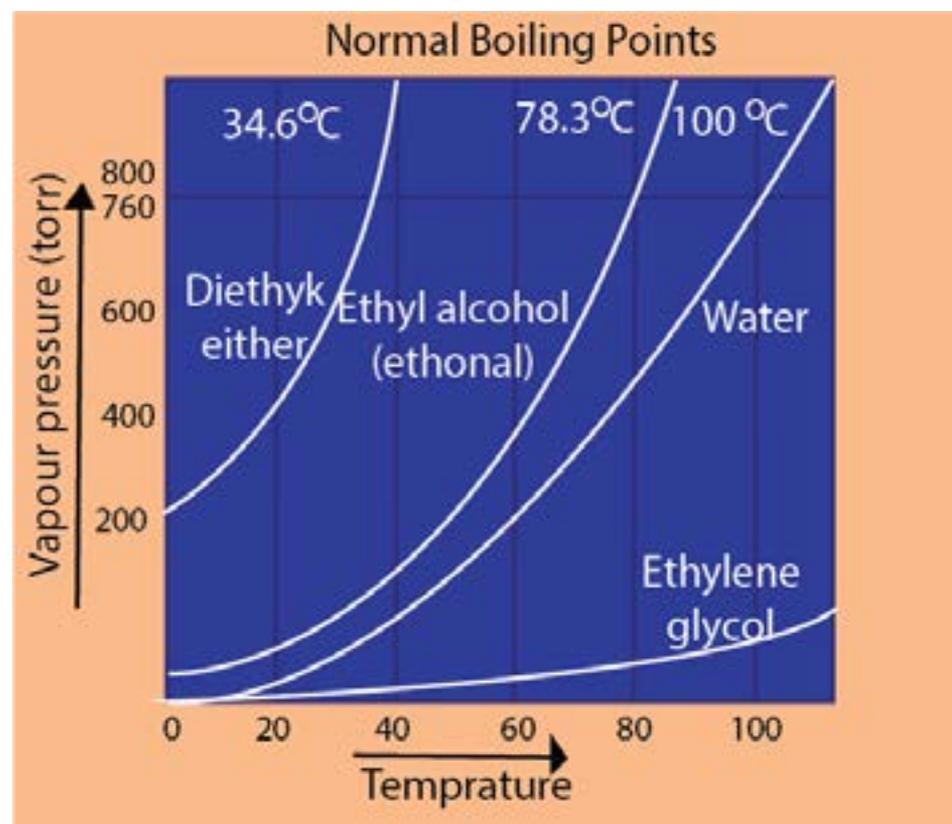

Fig (4.12) Vapour pressures(torr) of four common liquids shown as a function of temperature(°C).

4.2.4 Boiling Point and External Pressure

We have already explained that when vapour pressure of a liquid becomes equal to the external pressure then the liquid boils, so when external pressure is changed, its boiling point will also be changed. A liquid can be made to boil at any temperature by changing the external pressure. When the external pressure is high the liquid requires greater amount of heat to equalize its vapour pressure to external pressure. In this way boiling point is raised. Similarly, at a lower external pressure a liquid absorbs less amount of heat and it boils at a lower temperature.

For example, water shows B.P of 120 °C at 1489 torr pressure and boils at 25 °C at 23.7 torr. Water boils at 98 °C at Murree hills due to external pressure of 700 torr while at the top of Mount Everest water boils at only 69 ^{0}C 323 torr.

We can increase the external pressure artificially on the surface of boiling water by using a pressure cooker. Pressure cooker is a closed container. The vapours of water formed are not allowed to escape. In this way, they develop more pressure in the cooker and the boiling temperature increases. As more heat is absorbed in water, so food is cooked quickly under increased pressure.

Liquids can be made to boil at low temperatures, where they can be distilled easily. This process is called vacuum distillation. Vacuum distillation has many advantages. It decreases the time for the distillation process and is economical because less fuel is required. The decomposition of many compounds can be avoided e.g. glycerin boils at 290 °C at 760 torr pressure but decomposes at this temperature. Hence, glycerin cannot be distilled at 290 °C. Under vacuum, the boiling temperature of glycerin decreases to210 ^{0}C at 50 torr. It is distilled at this temperature without decomposition and hence can be purified easily.

4.2.5 Energetics of Phase Changes

Whenever, matter undergoes a physical change, it is always accompanied by an energy change. This change in energy is the quantitative measurement of the difference in the strength of intermolecular forces.

The change in energy is mostly in the form of heat. **If a physical or a chemical change takes place at a constant pressure, then the heat change during this process is also called enthalpy change.** This is denoted by ΔH. These enthalpy changes are usually expressed per mole of the substances. Three types of enthalpy changes are associated with usual physical changes.

(i) Molar Heat of Fusion (ΔH_f)

It is the amount of heat absorbed by one mole of a solid when it melts into liquid form at its melting point. The pressure, during the change is kept one atmosphere.

(ii) Molar Heat of Vapourization (ΔH_v)

It is the amount of heat absorbed when one mole of a liquid is changed into vapours at its boiling point. The pressure, during the change is kept one atmosphere.

(iii) Molar Heat of Sublimation (ΔH_s)

It is the amount of heat absorbed when one mole of a solid sublimes to give one mole of vapours at a particular temperature and one atmospheric pressure.

All these enthalpy changes are positive, because they are endothermic processes.

4.2.6 Energy Changes and Intermolecular Attractions

When a solid substance melts then atoms, molecules or ions undergo relatively small changes in intermolecular distances and the potential energy also undergoes a small change. But when a liquid evaporates, then larger changes in intermolecular distances and in potential energy takes place. So ΔH of vapourization of a substance is greater than ΔH of fusion. The values of ΔH_s are even larger than ΔH_v because attractive forces in solids are stronger than those in liquids.

The values of ΔH_v and ΔH_s tell us directly the energy needed to separate molecules from each other. So from these values, we can compare the strengths of intermolecular forces in different compounds.

From the following Table (4.6), we are convinced that ΔH_v for H_2O, NH_3 and SO_2 are reasonably high due to polar nature of molecules. ΔHV for iodine is the highest amongst its family members due to its greater polarizability. Similarly, hexane (C_6H_{14}) has the highest ΔH_v value amongst the hydrocarbons due to larger size of its molecules. Actually, the London dispersion forces in I_2 and C_6H_{14} are sufficiently strong and these are responsible for such a behaviour.

Table (4.6) Heats of Vaporization of some substances

Substance	ΔH_v (kJ/mol)
H_2O	+40.6
NH_3	+21.7
HCl	+15.6
SO_2	+24.3
F_2	+5.9
Cl_2	+10.00
Br_2	+15.00
I_2	+22.00
CH_4	+8.60
C_2H_6	+15.1
C_3H_8	+16.9
C_6H_{14}	30.1

4.2.7 Change of State and Dynamic Equilibrium

Whenever, a change of state occurs the system moves towards the condition of dynamic equilibrium. Dynamic equilibrium is a situation when two opposing changes occur at equal rates. Being a chemist, we should know that the concept of dynamic equilibrium is the fate or the ultimate goal of all the reversible chemical reactions and all the physical changes.

At 0°C, solid water (ice) exists in dynamic equilibrium with liquid water.

$$ice \underset{}{\overset{0^o C}{\rightleftharpoons}} water$$

4.3 Liquid Crystals

Whenever we study the properties of crystalline solids, we come to know that the pure solids melt sharply. The temperature remains constant at the melting point until all the solid melts.

In 1888, Frederick Reinitzer, an Austrian botanist discovered a universal property. He was studying an organic compound cholesteryl benzoate. This compound turns milky liquid at 145°C and becomes a clear liquid at 179°C. When the substance is cooled, the reverse process occurs. This turbid liquid phase was called liquid crystal.

Uptil now, it has been reported that, there are many crystalline solids which melt to a turbid liquid phase, before finally melting to a clear liquid. These turbid liquid phases can flow as liquids. They have the properties like liquids as surface tension, viscosity, etc. But it is very interesting to know that the molecules of such turbid liquids possess some degree of order as well. It means that these turbid liquids resemble crystals in certain properties and the most important properties are optical ones. These turbid liquids are hence called liquid crystals. So, **a liquid crystalline state exists between two temperatures i.e. melting temperature and clearing temperature.** A crystalline solid may be isotropic or anisotropic, but liquid crystals are always anistropic.

$$Crystal \rightleftharpoons Liquid crystal \rightleftharpoons Liquid$$

From 1888 to until about 30 years ago, liquid crystals were largely a laboratory curiosity. But now they have found a large number of applications.

Those substances which make the liquid crystals are often composed of long rod like molecules. In the normal liquid phase, these molecules are oriented in random directions. In liquid crystalline phase, they develop some ordering of molecules. Depending upon the nature of ordering, liquid crystals can be divided into nematic, smectic and cholesteric.

The properties of liquid crystals are intermediate between those of crystals and isotropic liquids. They have the fluidity of the liquids and the optical properties of the crystals.

Uses of Liquid Crystals

Due to the remarkable optical and electrical properties, liquid crystals find many practical applications. Many organic compounds and biological tissues behave as liquid crystals. The unique properties of liquid crystals have intrigued the scientists since their discovery, nearly hundred years ago. Some of their important uses are as follows.

(i) Like solid crystals, liquid crystals can diffract light. When one of the wavelengths of white light is reflected, from a liquid crystal it appears coloured. As the temperature changes, the distances between the layers of the molecules of liquid crystals change. Therefore, the colour of the reflected light changes accordingly. Thus liquid crystals can he used as temperature sensors.

(ii) Liquid crystals are used to find the point of potential failure in electrical circuits. Room thermometers also contain liquid crystals with a suitable temperature range. As the temperature changes, figures show up in different colours.

(iii) Liquid crystalline substances are used to locate the veins, arteries, infections and tumors. The reason is that these parts of the body are warmer than the surrounding tissues. Specialists can use the techniques of skin thermography to detect blockages in veins and arteries. When a layer of liquid crystal is painted on the surface of the breast, a tumor shows up as a hot area which is coloured blue. This technique has been successful in the early diagnosis of breast cancer.

(iv) Liquid crystals are used in the display of electrical devices such as digital watches, calculators and laptop computers. These devices operate due to the fact that temperature, pressure and electro-magnetic fields easily affect the weak bonds, which hold molecules together in liquid crystals.

(v) In chromatographic separations, liquid crystals are used as solvents.

(vi) Oscillographic and TV displays also use liquid crystal screens.

SOLIDS

4 .4 INTRODUCTION

Solids are those substances which are rigid, hard, have definite shape and definite volume. The atoms, ions and molecules that make up a solid are closely packed. They are held together by strong cohesive forces. The constituent atoms, ions or molecules of solids cannot move at random. There exists a well ordered arrangement in solids.

4.4.1 Types of Solids

Solids can be classified on the basis of the regular arrangements of constituent atoms, ions or molecules. There are two types of solids in this respect.

(i)   Crystalline Solids

Those solids in which atoms, ions or molecules are arranged in a definite three dimensional pattern are called crystalline solids This recurring regular geometrical pattern of structure extends three dimensionally.

(ii)   Amorphous Solids

All solids are not crystalline .The word amorphous means shapeless. **Amorphous substances are those whose constituent atoms, ions, or molecules do not possess a regular orderly arrangement.** The best examples are glass, plastics, rubber, glue, etc. These substances have solid state properties and virtually complete maintenance of shape and volume. But they do not have an ordered crystalline state.

Many crystalline solids can be changed into amorphous solids by melting them and then cooling the molten mass rapidly. In this way the constituent particles do not find time to arrange them selves.

A long range regularity does not exist in amorphous solids but they can possess small regions of orderly arrangements. These crystalline parts of otherwise amorphous solids are known as crystallites. Amorphous solids don't have sharp melting points that is why particles of glass soften over a temperature range and can be moulded and blown into various shapes. They do not possess definite heats of fusion.

4.4.2 Properties of Crystalline Solids

1.   Geometrical Shape

All the crystalline solids have a definite, distinctive geometrical shape due to definite and orderly arrangement of atoms, ions or molecules in three-dimensional space. For a given crystal, the interfacial angles, at which the surfaces intersect, are always the same no matter in which shape they are grown. The faces and angles remain characteristic even when the material is ground to a fine powder.

2.   Melting Points

Crystalline solids have sharp melting points and can be identified from their definite melting points.

3.   Cleavage Planes

Whenever the crystalline solids are broken they do so along definite planes. These planes are called the cleavage planes and they are inclined to one another at a particular angle for a given crystalline solid. The value of this angle varies from one solid to another solid.

4.   Anisotropy

Some of the crystals show variation in physical properties depending upon the direction. Such properties are called anisotropic properties and the phenomenon is referred to as anisotropy. The physical properties of crystalline solids like refractive index, coefficient of thermal expansion, electrical and thermal conductivities are sometimes anisotropic in nature for some crystals.

The variation in these properties with direction is due to fact that the orderly arrangement of the particles in crystalline solids is different in different directions. For example, electrical conductivity of graphite is greater in one direction than in another. Actually electrons in graphite are mobile for electrical conduction parallel to the layers only. Therefore, its conductivity in this direction is far better than perpendicular to the other direction. Similarly, cleavage itself is an anisotropic behaviour.

5.   Symmetry

The repetition of faces, angles or edges when a crystal is rotated by 360° along its axis is called symmetry. This an important property of the crystal and there are various types of symmetry elements found in crystals like, center of symmetry, plane of symmetry and axis of symmetry, etc.

6.   Habit of a Crystal

The shape of a crystal in which it usually grows is called habit of a crystal. Crystals are usually obtained by cooling the saturated solution or by slow cooling of the liquid substance. These are formed by growing in various directions. If the conditions for growing a crystal are maintained, then the shape of the crystal always remains the same. If the conditions are changed the shape of the crystal may change. For example, a cubic crystal of NaCl becomes needle like when 10% urea is present in its solution as an impurity.

7.   Isomorphism

Isomorphism is the phenomenon in which two different substances exist in the same crystalline form. These different substances are called isomorphs of each other.

A crystalline form is independent of the chemical nature of the atoms and depends only on the number of atoms and their way of combinations.

Mostly the ratio of atoms in various compounds are such that isomophism is possible. Their physical and chemical properties are quite different from each other. Anyway, isomorphic substances crystallize together in all proportions in homogeneous mixtures. Following examples tell us the nature of the compound, their crystalline forms and the ratio of their atoms.

Isomorphs	Crystalline form	Atomic ratio
$NaNO_3$, KNO_3	rhombohedral	1:1:3
K_2SO_4, K_2CrO_4	orthorhombic	2:1:4
$ZnSO_4$, $NiSO_4$	-do-	1:1:4
NaF, MgO	cubic	1:1
Cu, Ag	cubic	1:1
Zn, Cd	hexagonal	1:1

The structures of the negatively charged ions like NO_3^{-1} and CO_3^{2-}, are the same. Similarly shapes of SO_4^{2-} and CrO_4^{2-} are also alike. CO_3^{2-} and NO_3^{1-} are triangular planar units, while SO_4^{2-} and CrO_4^{2-} are both tetrahedral.

8.   Polymorphism

Polymorphism is a phenomenon in which a compound exists in more than one crystalline forms. That compound which exists in more than one crystalline forms is tailed a polymorphic, and these forms are called polymorphs, and these forms are called polymorphs of each other.

Polymorphs have same chemical properties, but they differ in the physical properties. The difference in physical properties is due to different structural arrangement of their particles.

The following compounds are important polymorphs.

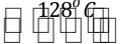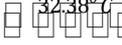| Substance	crystalline forms
$AgNO_3$	Rhombohedral, Othorhombic
$CaCO_3$	Trigonal and orthorhombic

9.   Allotropy

The existence of an element in more than one crystalline forms is known as allotropy and these forms of the element are called allotropes or allotropic forms. Sulphur, phosphorus, carbon and tin are some important examples of elements which show allotropy.

Element	Crystalline forms
Sulphur, S	Rhombic, monoclinic
Carbon, C	cubic (diamond), hexagonal (graphite)
Tin, Sn	grey tin (cubic), white tin (tetragonal)

10.   Transition Temperature

It is that temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other. At this temperature, one crystalline form of a substance changes to another.
Above and below this temperature, only one form exists. A few examples for those substances which show allotropy and possess a transition temperature are given below

(i) Grey Tin (cubic) $\xrightarrow{13.2^{o}C}$ White tin (Tetragonal)

(ii) Sulphur S_8 (rhombic) $\xrightarrow{95.5^{o}C}$ Sulphur S_8(monoclinic)

(iii) KNO_3 (orthorhombic) $\xrightarrow{128^{o}C}$ KNO_3(rhombohedral)

(iv) Na_2SO_4-10H_2O (hydrated form) $\xrightarrow{32.38^{o}C}$ N a$_2SO_4$(anhydrous from) + 10 H_2O

(v) Na_2CO_3- 10 H_2O (higher hydrated form) $\xrightarrow{32.38^{o}C}$ Na_2CO_3-7H_2O(lowerhydratedform)+3H_2O

It has been noticed that the transition temperature of the allotropic forms of an element is always less than its melting point.

4.5 CRYSTAL LATTICE

A crystal is made up of atoms, ions or molecules. In crystalline solids, these atoms, ions or molecules are located at definite positions in space. These positions are represented by points in a crystal. These points are called as lattice points or lattice sites. This arrangement of points in a crystal is called crystal lattice or space lattice.
So a crystal lattice is an array of points representing atoms, ions or molecules of a crystal, arranged at different sites in three dimensional space. Fig. (4.13) shows a crystal lattice with a cubic structure.
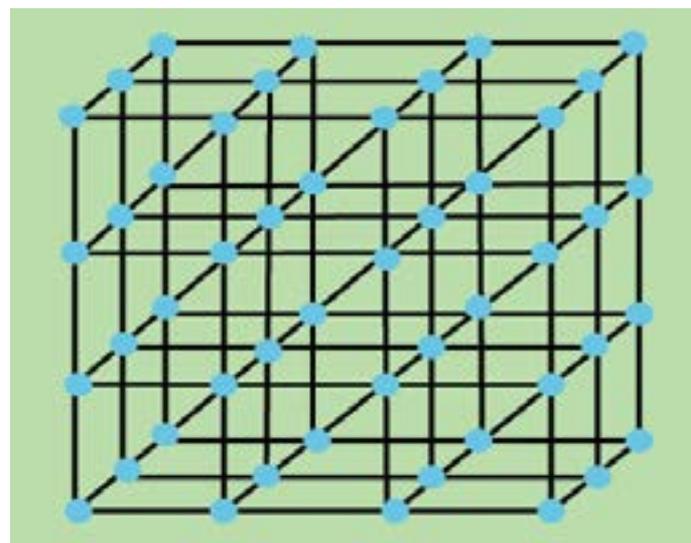

Fig (4.13) Cubic crystal lattice

4.5.1 Unit Cell

When we look at the cubic crystal lattice in Fig (4.14), we see that it is actually composed of many small parts. **The smallest part of the crystal lattice has all the characteristic features of the entire crystal and is called a unit cell.**

It means that a unit cell of a crystal lattice is the smallest block or geometrical figure, from which the entire crystal can be built up by repeating it in three dimensions. It shows the structural properties of a given crystal. The complete information about the crystalline structure is present within a unit cell which repeats itself in three dimensions to form a crystal.

If we know the exact arrangement of atoms in a unit cell, we in fact know their arrangement in the whole crystal.

The quantitative aspects of a crystal lattice are deduced from the size and shape of the unit cell. There are three unit cell lengths a, b, c and three unit cell angles α , β and γ. These six parameters are shown in Fig (4.14)

The angle 'α' is between the lengths 'b' and 'c', the angle 'β' is between the sides 'a' and 'c' and angle' γ' is between sides 'a' and 'b'. The unit cell lengths a, b, c, may be assigned along x, y and z axis, respectivly but angles α , β and γ have to be decided accordingly. The choice of x, y, z may be along any of the three axis. These six parameters of the unit cell are called unit cell dimensions or crystallographic elements.

Keeping in view the structure of the unit cell we can understand the crystal system.
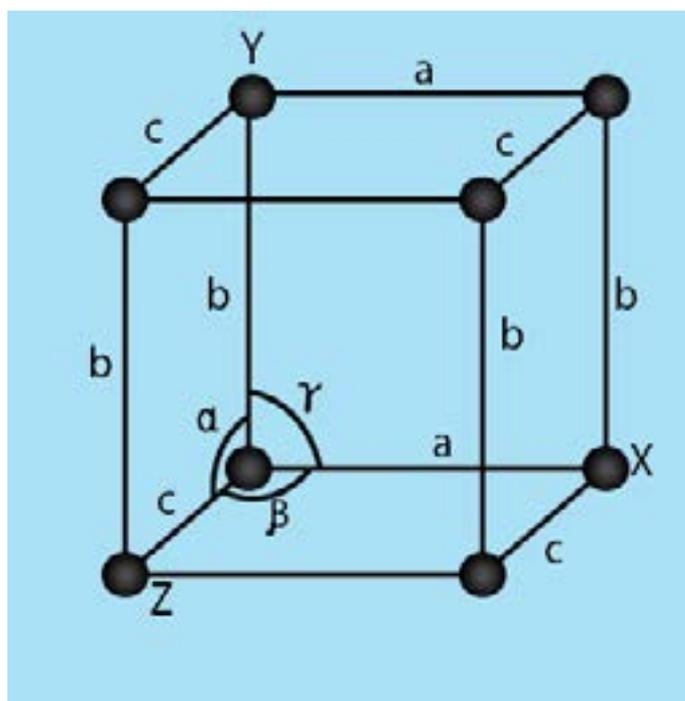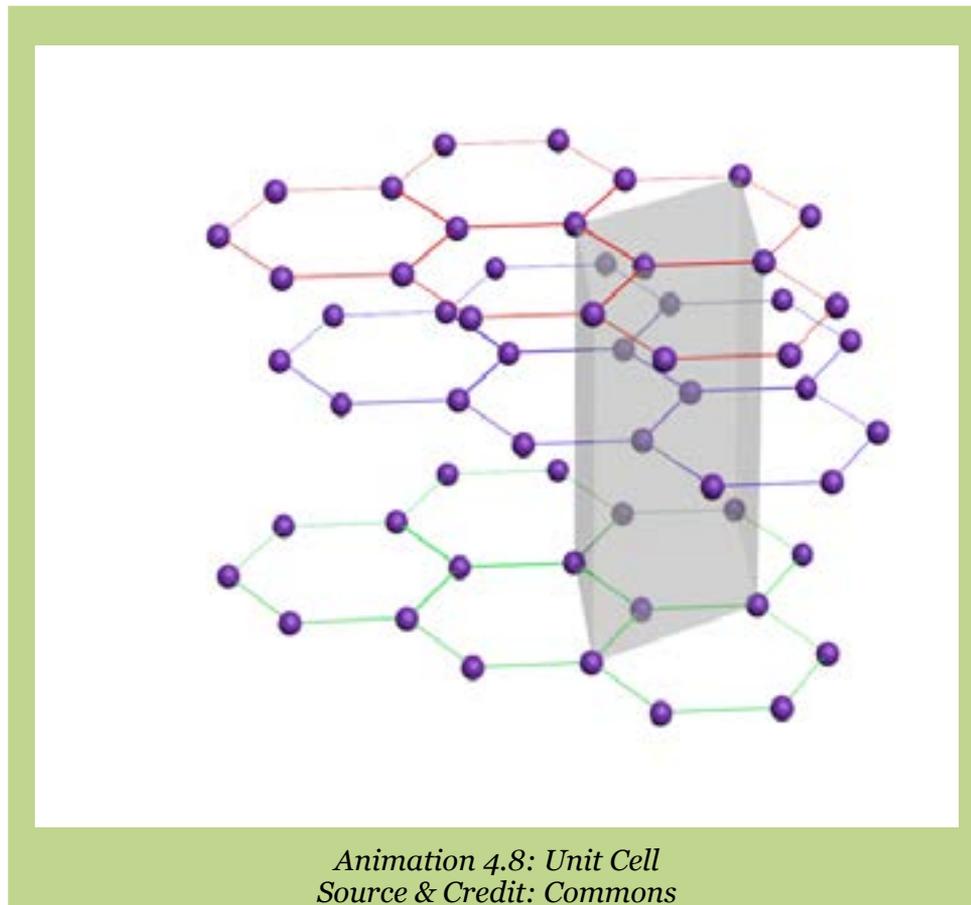

Fig (4.14) Six crystallographic elements specify the size and
shape of a unit cell

Animation 4.8: Unit Cell
Source & Credit: Commons

4.6 CRYSTALS AND THEIR CLASSIFICATION

A crystal system may be identified by the dimensions of its unit cell along its three edges or axes, a, b, c and three angles between the axes α , β , γ.

There are seven crystal systems. These seven crystal systems are described as follows Fig (4.15).

1.   Cubic system

In this system all the three axes are of equal length and all are at right angles to one another.

Animation 4.9: Classification of Crystals
Source & Credit: wikipedia
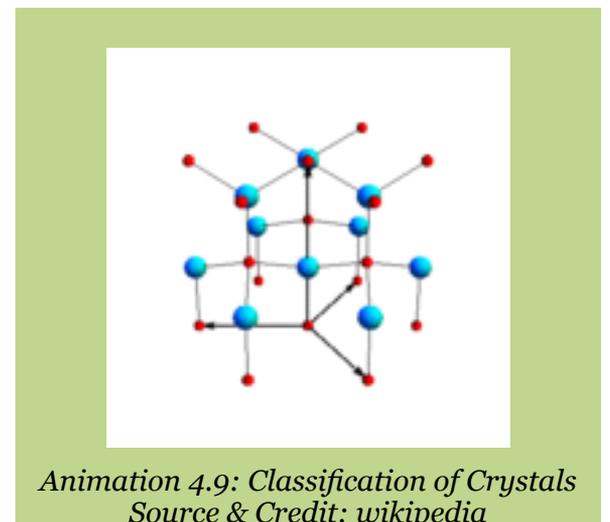
2.   Tetragonal system

In this system two axes are of equal length and the third axis is either shorter or larger than the other two. All angles are 90°.

3.   Orthorhombic Or Rhombic System

All the three axes are of unequal length and all are at right angle to each other.

4.   Monoclinic System

All the three axes are of unequal length; two of these axes are at right angle to each other while the third angle is greater then 90°.

5.   Hexagonal System

In this system two axes are of equal length and are in one plane making an angle of 120° with each other. The third axis which is different in length than the other two is at right angle to these two axes.

6.   Rhombohedral System Or Trigonal System

All the three axes are of an equal length like cubic system but the three angles are not equal and lie between 90° and 120°.

Fig (4.15) Seven crystal systems

7.   Triclinic System

All the three axes and the three angles are unequal and none of the angles is 90°.

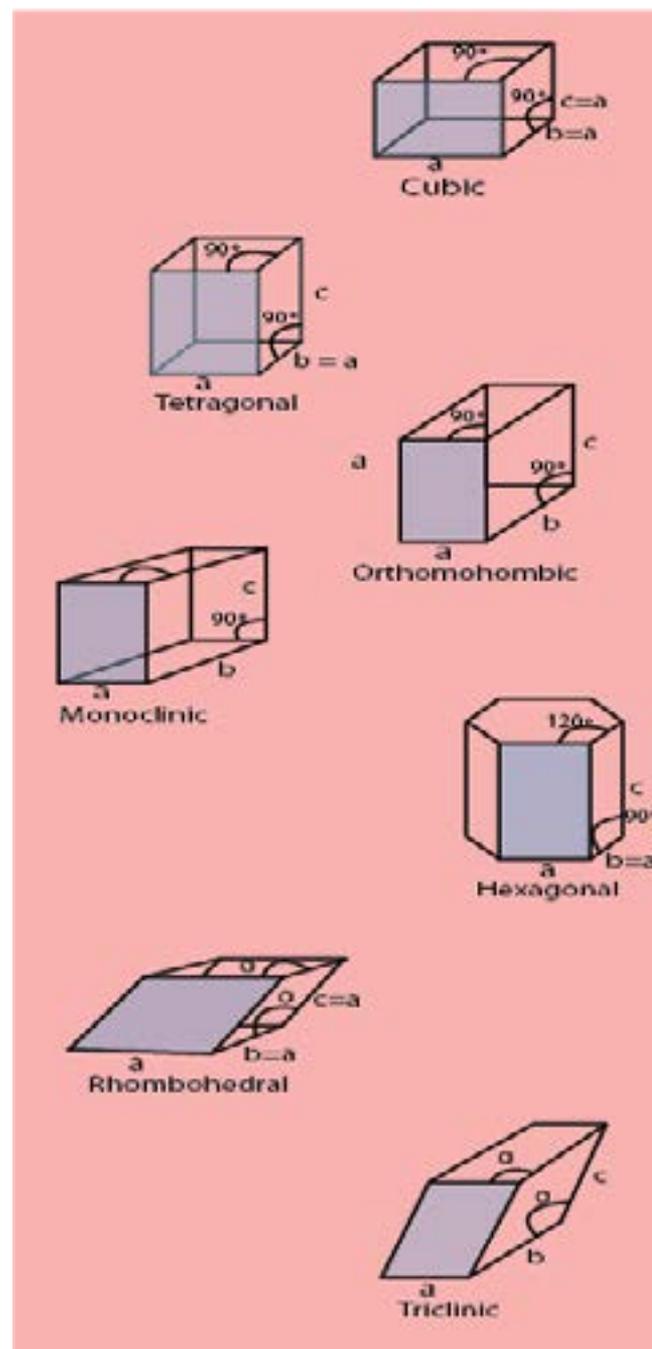Table (4.7) shows the unit cell dimensions of the seven crystal systems alongwith their examples

Table (4.7) Seven Crystal Systems

Sr. No	Crystal system	Axes	Angles	Examples
1.	cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^o$	Fe, Cu, Ag, Au, NaCl, NaBr, Dimond
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^o$	Sn, SnO_2, MnO_2, NH_4Br
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$	Idoine, Rhombic, Sulphur, $BaSO_4$, K_2SO_4
4.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^o, \beta \neq 90^o$	Sugar, Sulphur, Borax, $NaSO.10H_2O$
5.	Hexagonal	$a = b \neq c$	á=â=90° , ã=120°	Graphite, ZnO, CdS, Ice, Zn, Cd
6.	Rhombohedral or Trignol	$a = b = c$	$\alpha = \beta = \gamma > 90^o$ and $< 120^o$	Bi, Al_2O_3, $NaNO_3$, KNO_3
7.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^o$	H_3BO_3, $K_2Cr_2O_7$, $CuSO_4.5H_2O$

4.7 CLASSIFICATION OF SOLIDS

In the preceding section, we noted that the crystals are classified into seven systems depending upon the dimensions of the unit cells. A unit cell contains a definite number of atoms, ions, or molecules. These atoms, ions or molecules are held together by different types of cohesive forces. These forces may be chemical bonds or some type of interactions. There are four types of crystalline solids depending upon the type of bonds present in them.

(i)   Ionic solids
(ii)   Covalent solids
(iii)   Metallic solids
(iv)   Molecular solids

4.7.1 Ionic Solids

Crystalline solids in which the particles forming the crystal are positively and negatively charged ions are called ionic solids. These ions are held together by strong electrostatic forces of attraction. These attractive forces are also called ionic bonds. The crystals of NaCl, KBr, etc are ionic solids.

Properties of Ionic Solids

The cations and anions are arranged in a well defined geometrical pattern, so they are crystalline solids at room temperature. Under ordinary conditions of temperature and pressure they never exist in the form of liquids or gases.

Ionic crystals are very stable compounds. Very high energy is required to separate the cations and anions from each other against the forces of attraction. That is why ionic crystals are very hard, have low volatility and high melting and boiling points.

Ionic solids do not exist as individual neutral independent molecules. Their cations and anions attract each other and these forces are non-directional. The close packing of the ions enables them to occupy minimum space. A crystal lattice is developed when the ions arrange themselves systematically in an alternate manner.

The structure of the ionic crystals depends upon the radius ratio of cations and anions. For example.NaCl and CsF have the same geometry because the radius ratio in both the cases is the same.

In the case of ionic crystals we always talk about the formula mass of these substances and not the molecular mass, because they do not exist in the form of molecules.
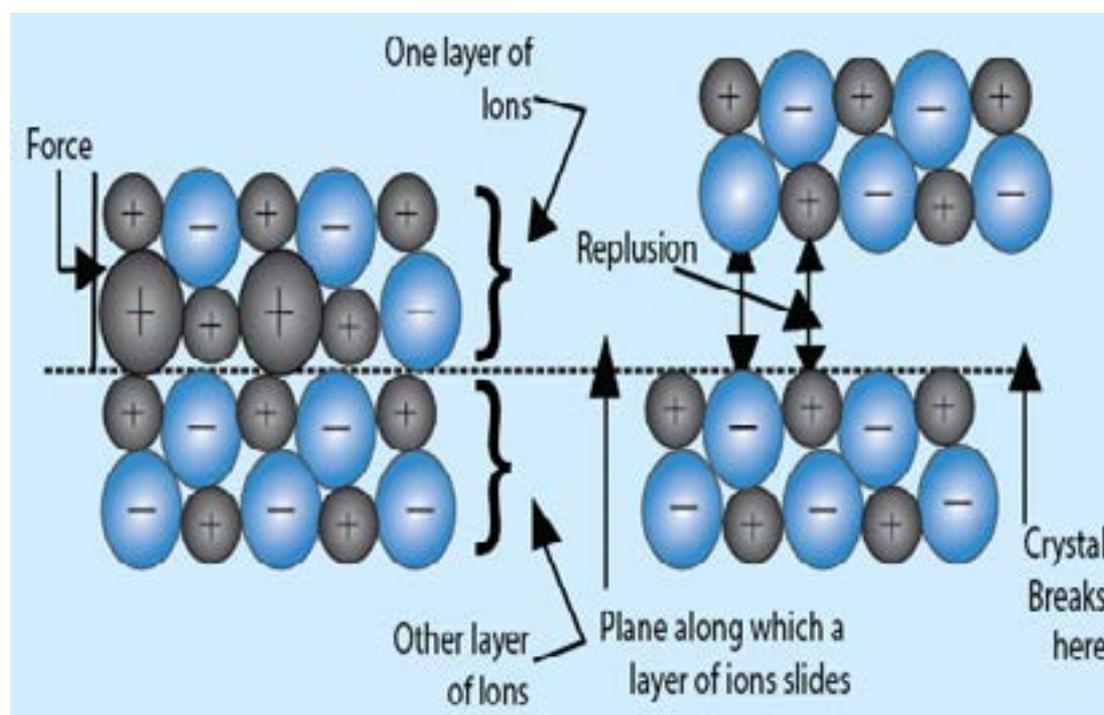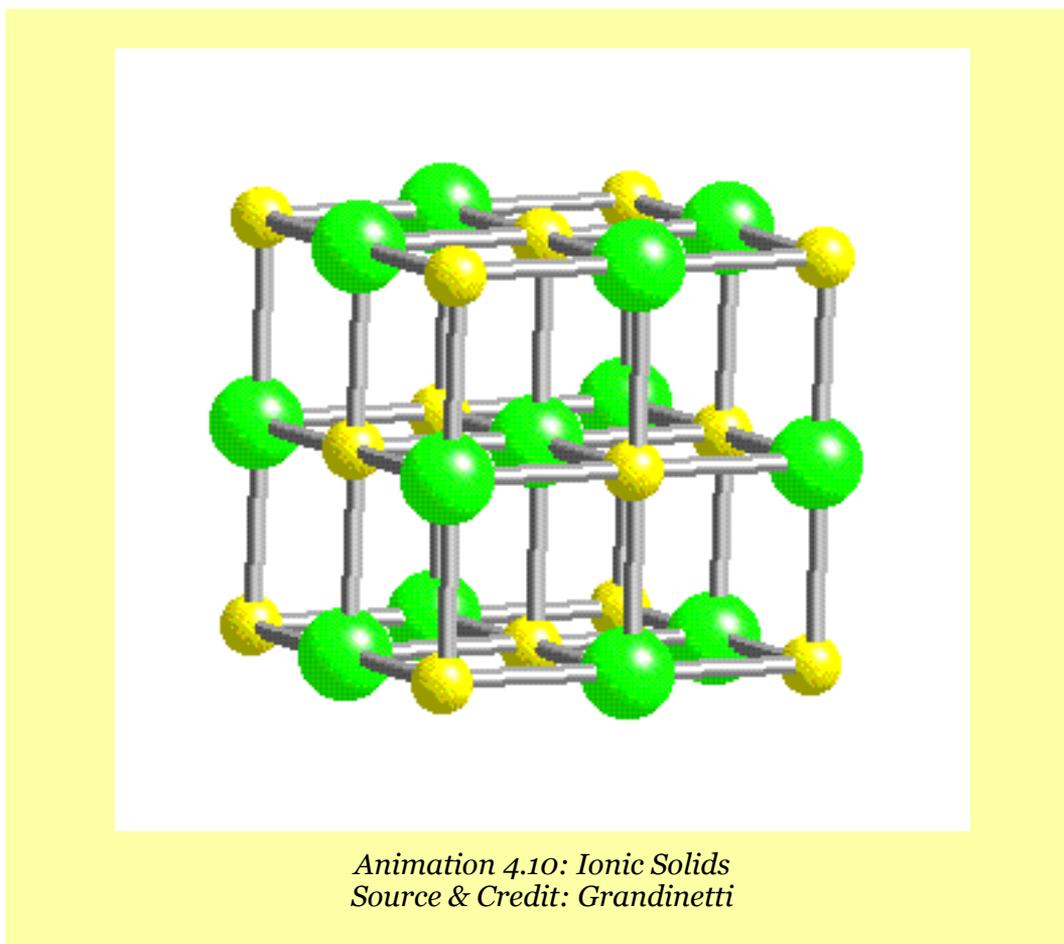

Fig (4.16) Explanation of brittleness of ionic crystals

Animation 4.10: Ionic Solids
*Source & Credit: Grandinetti*

Ionic crystals do not conduct electricity in the solid state, because on account of electrostatic force existing between them the cations and anions remain tightly held together and hence occupy fixed positions. Ionic crystals conduct electricity when they are in solution or in the molten state. In both cases ions become free.

Ionic crystals are highly brittle because ionic solids are composed of parallel layers which contain cations and anions in alternate positions, so that the opposite ions in the various parallel layers lie over each other.

When an external force is applied, one layer of the ions slides a bit over the other layer along a plane. In this way the like ions come in front of each other and hence begin to repel. So, the application of a little external force develops repulsion between two layers causing brittleness Fig (4.16).

Ionic solids are mostly of high density due to close packing of ions. Such compounds having the ionic crystals give ionic reactions in polar solvents and these are very fast reactions.

The properties like isomorphism and polymorphism are also associated with the ionic crystals. In order to understand the structure of ionic crystals, let us explain the structure of sodium chloride crystals.

Animation 4.11: classification of solids
Source & Credit: Askiitians
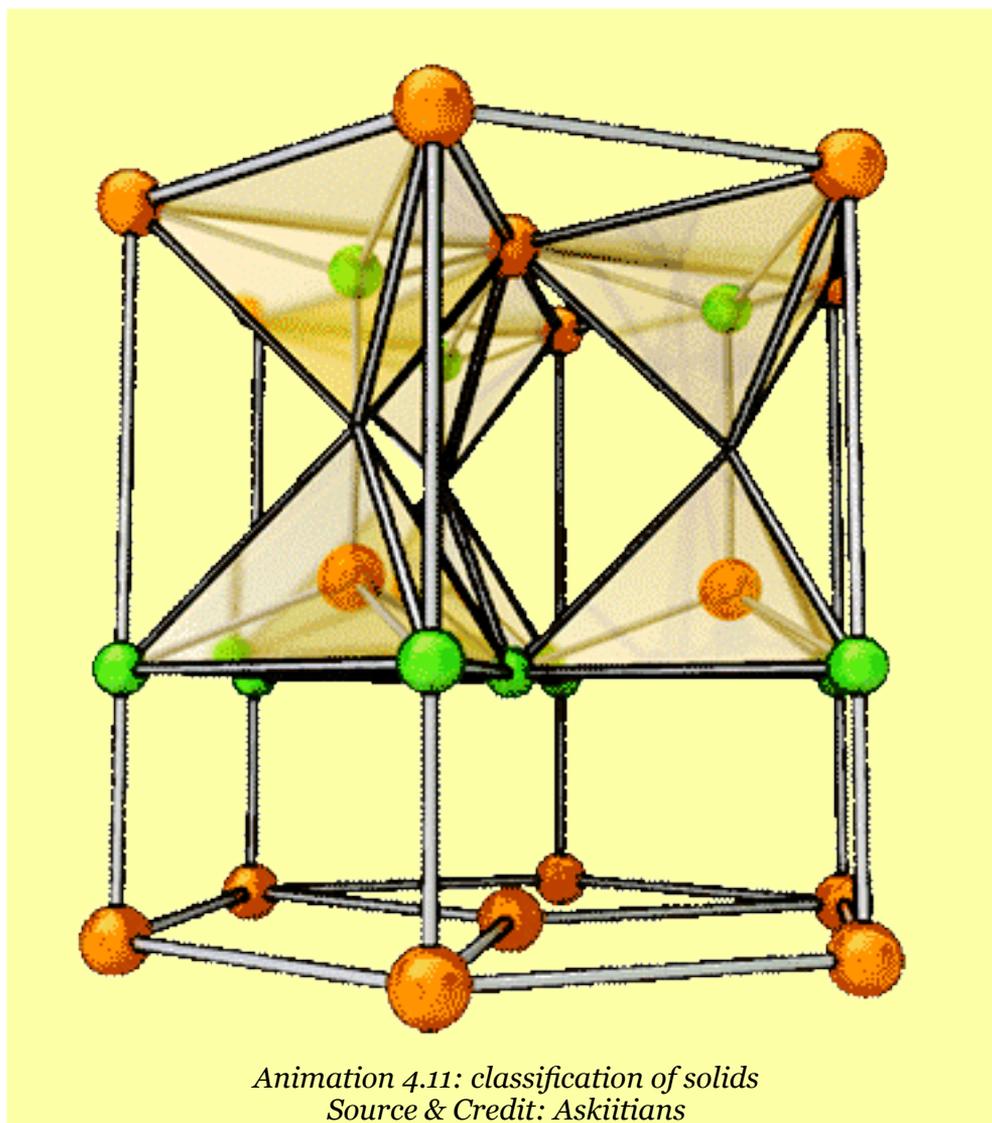
Structure of Sodium Chloride

The structure of ionic crystals depends upon the structure and the size of their ions. Each ion is surrounded by a certain number of ions of opposite charge. In the structure of NaCl each Na^+ ion is surrounded by six chloride ions. Fig (4.17) shows how these ions are arranged in the crystal lattice. It is clear that Na^+ has ten electrons while Cl^- has total 18 electrons. The size of the Cl^- is bigger than that of Na^+

The distance between two nearest ions of the same kind i.e., Cl^- ions is 5.63 $\overset{o}{A}$. So the distance between two adjacent ions of different kind is 5.63/2 = 2.815 $\overset{o}{A}$.
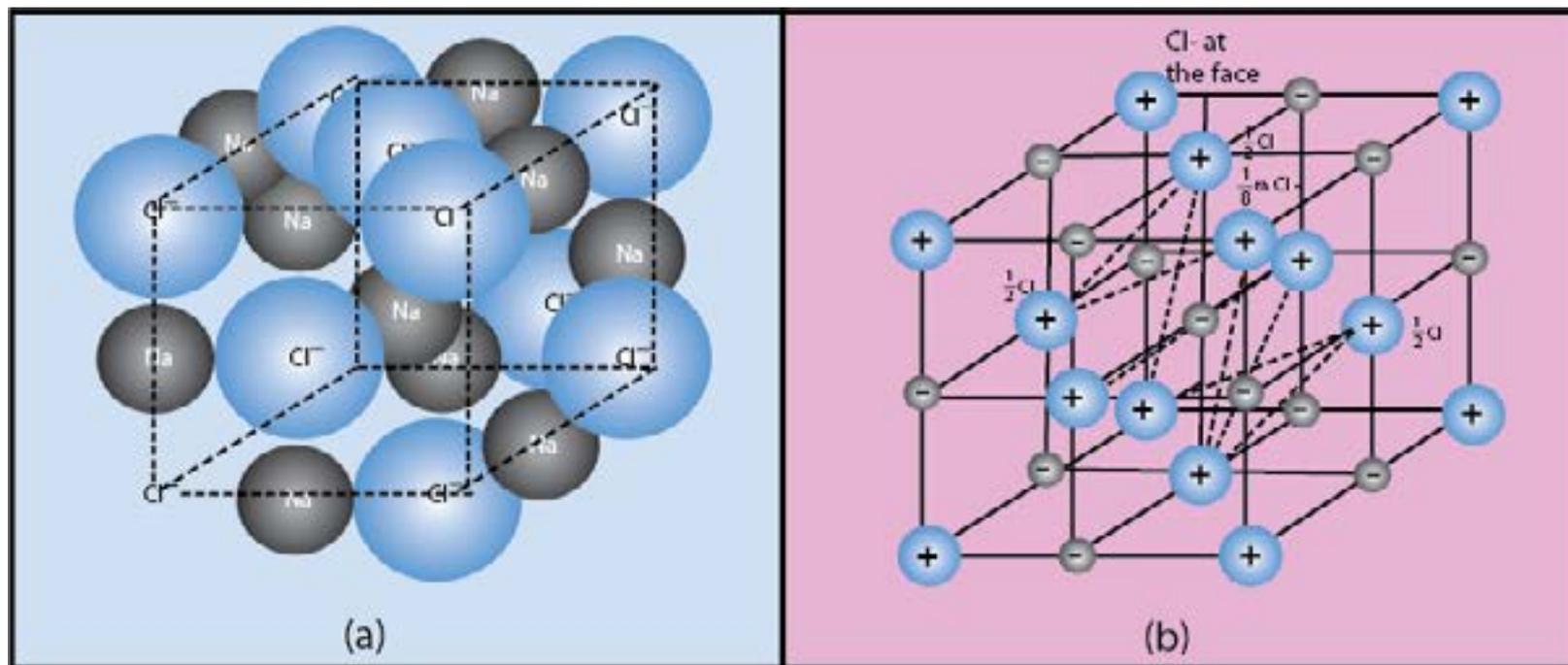
Figs (4.17 a, b) The unit cell of sodium chloride showing that four NaCl formula units are present in a unit cell.

The location of Na^+ and Cl^- is such that each Na^+ is surrounded by six Cl^- placed at the corners of a regular octahedron Fig. (4.17 a). So the coordination number of each Na^+ is six. Similarly, each Cl^- is also surrounded by six Na^+. Na^+ and $C1^-$ are not connected to one another by pairs because all six Cl^- ions are at the same distance away from one Na^+. It has been observed that independent molecules of NaCl do exist in the vapour phase. Anyhow, in solid NaCl there are no independent molecules of NaCl. That is why NaCl is said to have formula unit of NaCl.

While looking at the Fig.(4.17 b), we see that there are eight Cl^- at the comers of the cube, and each is being shared amongst eight cubes. l/8th part of each Cl^- ion is considered for this unit cell. So, one complete Cl^- is contributed by eight corners. Similarly,six chloride ions are present at the face centres and each is being shared between t wo cells. Thus.per unit cell there are 8/8 + 6/2 = 4 Cl^- ions. You can justify the presence of 4 Na^+ , if you take a unit cell having $8Na^+$ at eight corners and $6Na^+$ at faces. So, there are equal number of Na^+ ions, and therefore 4 NaCl units are present per unit cell. Fig (4.17b)

Lattice Energy

Solids are composed of atoms, ions or molecules. However, many solids of daily importance are ionic in nature. As mentioned earlier these ions exist in a three dimensional array which is called as lattice.

When the oppositely charged ions are brought, close to each other energy is released. **So the lattice energy is the energy released when one mole of the ionic crystal is formed from the gaseous ions. It is also defined as the energy required to break one mole of solid into isolated ions in the gas phase.** It is expressed in kj mole^{-1}.

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad\qquad \Delta H = -787\,\text{kJmole}^{-1}$$

Tables (4.8) Lattice energies of ionic compounds

Ionic compound	Lattice energy (kJ/mol^{-1})
LiCl	-833
NaF	-895
NaCl	-787
KCl	-690
NaBr	-728
KBr	-665
NaI	-690

Table (4.8) shows the lattice energies of many ionic compounds. It is clear from the table that lattice energy decreases with the increase in the size of the cation keeping the anion same. It also decreases with the increase in the size of anion. The reason in both cases is the same. With the increase in the size of either cation or anion, the packing of oppositely charged ions becomes less and less tight. The calculations related to the measurement of lattice energy will be discussed in chapter seven.

4.7.2. Covalent Solids

Covalent solids are also called atomic solids, because they are composed of neutral atoms of the same or of different elements. These atoms are held together by covalent bonds.

Covalent solids are of two types.

(i)   Whenthecovalentbondsjointoformgiantmoleculeslikediamond,siliconcarbideoraluminiumnitride.

(ii)   When atoms join to form the covalent bonds and separate layers are produced like that of graphite, cadmium iodide and boron nitride.

Properties of Covalent Crystals

The bonding in covalent crystals extend in three dimensions. They contain a network of atoms. The valencies of atoms are directed in definite directions, so the packing of atoms in these crystals is looser than those of ionic and metallic crystals. Thus covalent crystals have open structure.

These crystals are very hard and considerable amount of energy is required to break them. They have high melting points and their volatility is very low.

Due to the absence of free electrons and ions they are bad conductors of electricity. However, graphite has a layered structure and the electrons are available in between the layers. These electrons are delocalised and conductivity becomes possible. Graphite is not a conductor perpendicular to the layers.

Mostly covalent crystalline solids are insoluble in polar solvents like water but they are readily soluble in non-polar solvents like benzene and carbon tetrachloride. The covalent crystals having giant molecules like diamond and silicon carbide are insoluble in all the solvents. Because of their big size, they do not interact with the solvent molecules. The chemical reactions of such crystalline solids are very slow.

Let us try to understand the structure of diamond, which is a well known covalent solid.

Structure of Diamond

Diamond is one of the allotropic modifications of carbon. It is best understood by taking into consideration the number of electrons in the outermost shell of carbon, which are four. The four atomic orbitals (one 2s and three 2p) undergo sp^3 hybridization to give four sp^3 hybridized orbitals. They are directed in space along the four corners of a tetrahedron Fig. (4.18 a).

This is the unit cell of diamond and a large number of such unit cells undergo sp^3-sp^3 overlapping to form a huge structure. Each carbon atom is linked with four other carbon atoms. The bonds between carbon atoms are covalent which run through the crystal in three-dimensions. All the bond angles are 109.5° and the bond lengths are 154 pm.
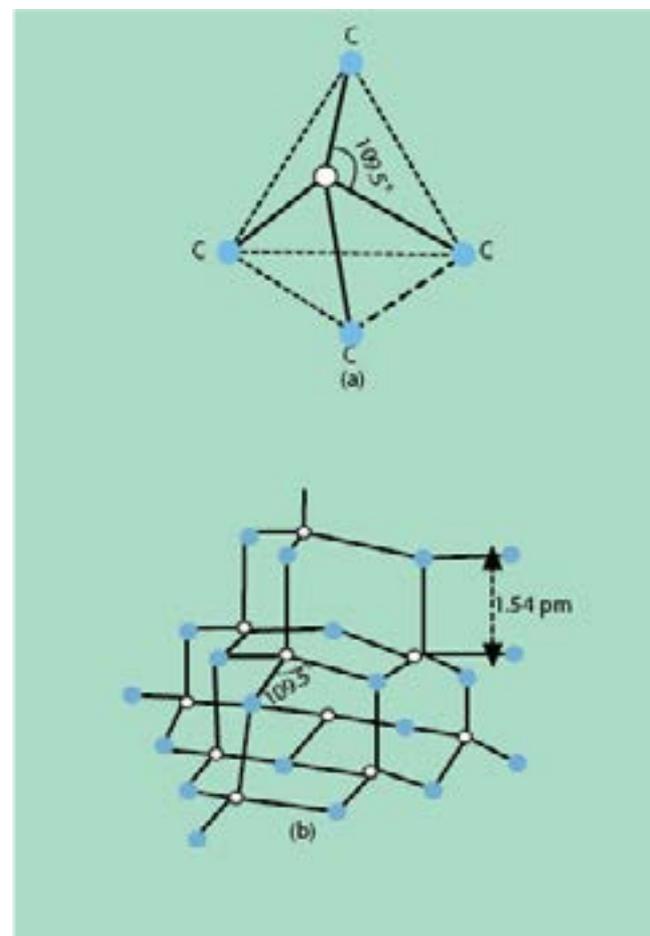
The whole lattice is, therefore, continuous and because of the continuity of C-C covalent bonding, the entire diamond crystal behaves as a huge or giant three-dimensional carbon molecule. This is also called a macro-molecule.

Fig.(4.18b), The overall structure of diamond looks face centred-cubic Fig. (4.18 c)
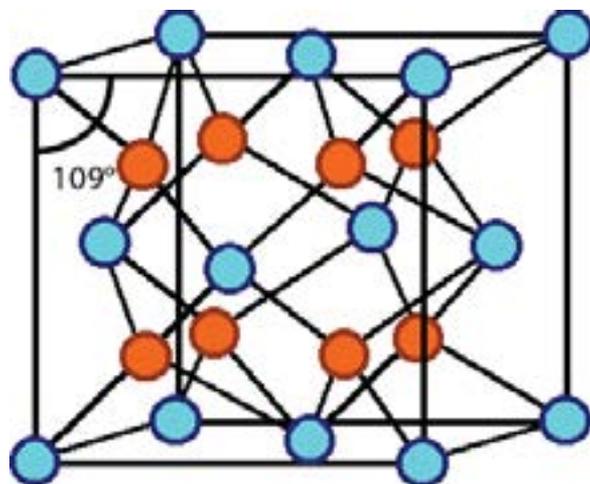
Fig(4.18 c) face-centered cubic structure
of diamond

4.7.3. Molecular Solids

Those solid substances in which the particles forming the crystals are polar or non-polar molecules or atoms, of a substance are called molecular solids. For instance, in solidified noble gases, there are non-polar atoms. Two types of of diamond intermolecular forces hold them together.

(i)   Dipole-dipole interactions.

(ii)   van der Waals forces.

These intermolecular forces are much weaker than the forces of attraction between the cations and the anions in ionic crystals, and between the atoms in the covalent crystals.

Ice and sugar are the best examples of crystals having polar molecules whereas iodine, sulphur, phosphorus and carbon dioxide form the molecular crystals containing nonpolar molecules. Polar molecular solids have usually higher melting and boiling points as compared to non-polar molecular solids.

Properties of the Molecular Solids

X-ray analysis has shown the regular arrangements of atoms in constituent molecules of these solids, and we get the exact positions of all the atoms.

The forces, which hold the molecules together in molecular crystals, are very weak so they are soft and easily compressible.

They are mostly volatile and have low melting and boiling points. They are bad conductors of electricity, have low densities and sometimes transparent to light. Polar molecular crystals are mostly soluble in polar solvents, while non-polar molecular crystals are usually soluble in non-polar solvents.

Iodine is one of the best examples of a molecular solid. Let us discuss the structure of iodine molecule.

Structure of Solid Iodine

In the solid state the molecules of iodihe align in the form of layer lattice. This is shown in Fig (4.19). I -I bond distance is 271.5 pm and it is appreciably longer than in gaseous iodine (266.6 pm). As expected from its structure, iodine is a poor conductor of electricity.
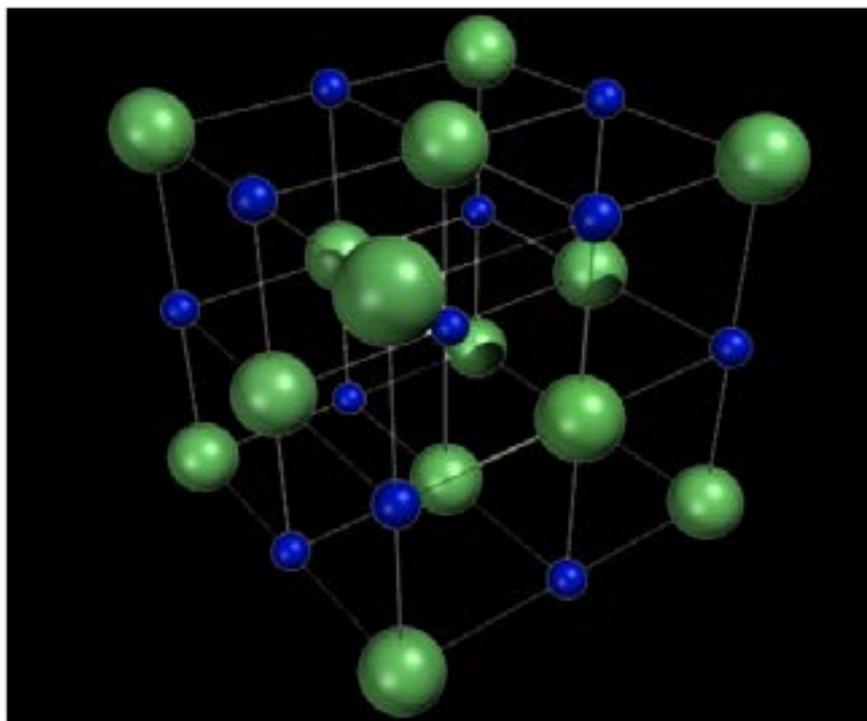

Fig (4.19) Face centered cubic structure of iodine

4.7.4. Metallic Solids

In order to explain properties of metallic solids various theories have been proposed. A few of them are mentioned here.

The first theory of metallic bonding is called electron pool or electron gas theory. This theory was proposed by Drude and extended by Loren (1923). According to this theory, each atom in a metal crystal loses all of its valence electrons. These valence electrons form a pool or a gas. The positively charged metal ions are believed to be held together by electron pool or gas. These positively charged ions occupy definite positions at measurable distances from each other in the crystal
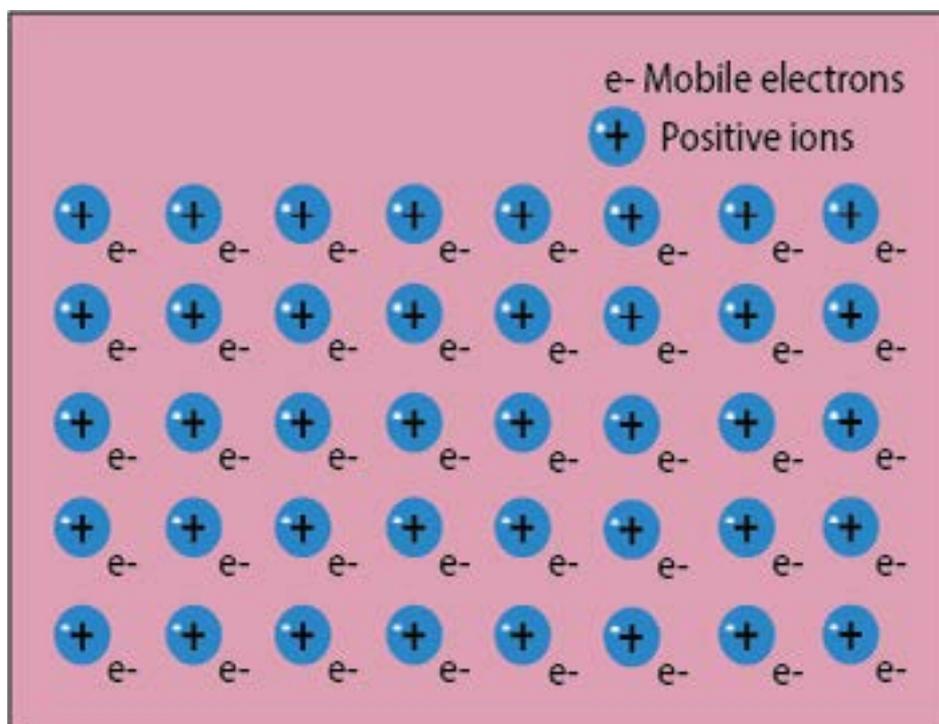

Fig (4.20) Positive ions surrounded by mobile electrons

lattice. Valence elect rons are not attached to any individual ion or a pair of ions rather belong to t he crystal as a whole. These electrons are free to move about from one part of the crystal to the other. The force, which binds a metal cation to a number of electrons within its sphere of- influence, is known as metallic bond. The following Fig. (4.20) gives an idea of electron gas model.

L. Pauling has tried to explain the metallic bond according to valence bond theory. According to this theory, the metallic bond is treated essentially as covalent in character. However, it is assumed that the covalent bonds are not localized but are highly delocalized in metal structure.

Recently, molecular orbital theory was applied to explain the characteristics of metallic solids. According to this theory, it is assumed that the electrons in the completely filled orbitals are essentially localized, while atomic orbitals containing the valence electrons interact or overlap to form a set of delocalized orbitals. These delocalized orbitals are the molecular orbitals which extend over the entire crystal lattice. Such a combination of atomic orbitals produce as a large number of closely spaced states. These states of energy are also known as bands of energy. That is why it is also called a band theory. The energy gap between two bands determines the properties of the metallic solids.

Properties of Metallic crystals

Metals are good conductor of electricity. When electric field is applied between two ends of a metal then the mobile electrons begin to move towards the positive pole and the new electrons from the negative pole take their place Fig. (4.21a) Sometimes, the electrical conductivity of metals decrease with the increase in temperature. The reason is that with the increase in temperature the positive metal ions also begin to oscillate and the motion hinders the free movement of mobile electrons between the positive ions. This hindrance decreases the electrical conductivity.
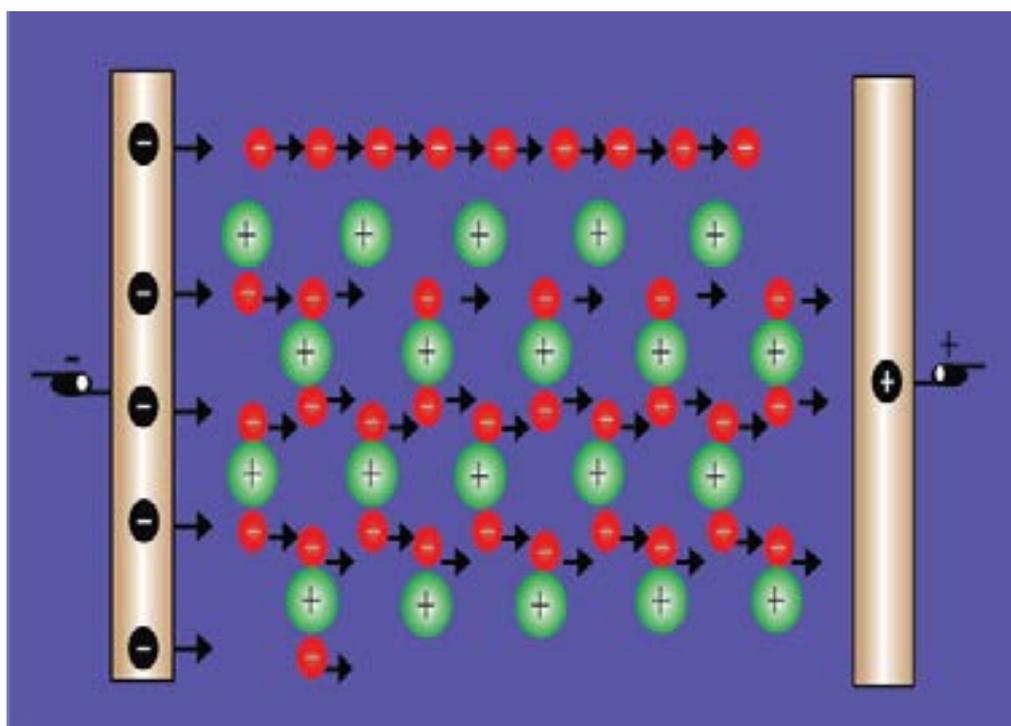
Fig (4.21a) Explanation of electrical conductivity of a metal

The rmal conductivity is another property associated with metallic solids. When a piece of metal is heated at one end, the mobile electrons at this end absorb heat energy and move very rapidly through the metallic lattice towards the cooler end. During the process they collide with adjacent electrons and transfer their heat energy to them.

Whenever the metals are freshly cut, most of them possess metallic luster which means that they have a shining surface. When light falls on the metallic surface, the incident light collides with the mobile electrons and they are excited. These electrons when deexcited give off some energy in the form of light. This light appears to be reflected from the surface of the metal which gives a shining look.

Metals are malleable and ductile whenever stress is applied on them. Their layers slip pass each other. The structure of the metal changes without fracturing as shown in the Fig. (4.21b).
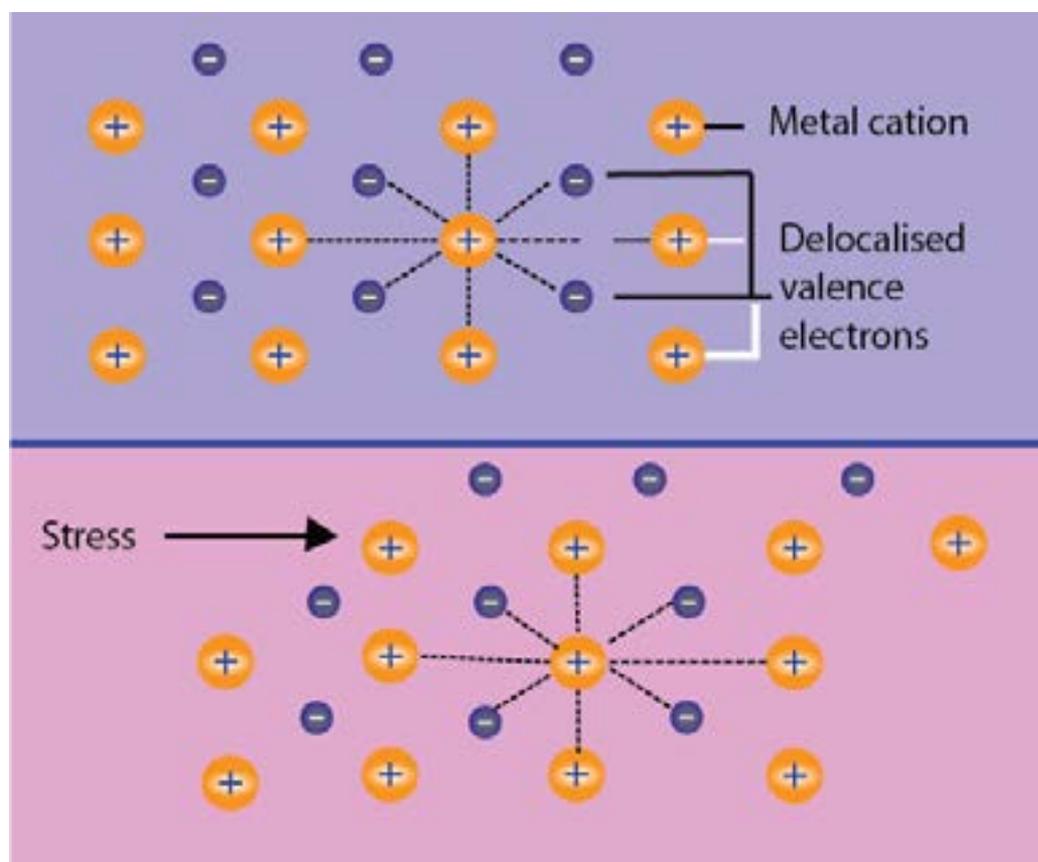
Fig(4.21b) Deformation of metal structures

Structure of Metals

In the previous article of metallic solids, we have learnt that metal atoms are arranged in definite pattern. Free electrons are roaming about in the crystal lattice. So a metal may be regarded as an assembly of the positively charged spheres of identical radii which are packed together to fill the space as completely as possible.

To understand the closed packing of atoms in metal structures, let us suppose that the metal atoms are like hard spherical balls. Take twelve spherical balls and pack in a box as shown in Fig (4.22 a).
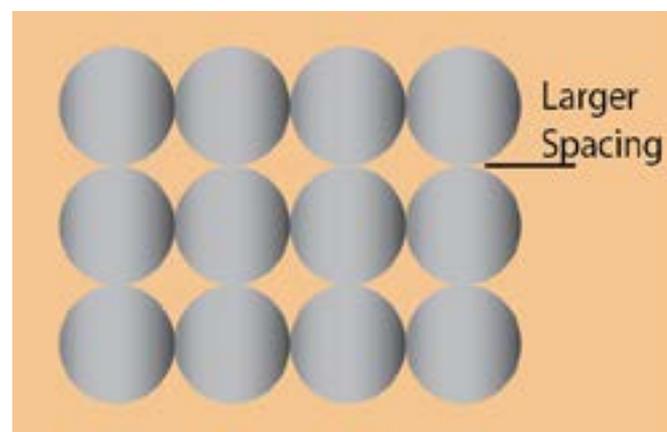

Fig (4.22 a) Packing of twelve sphere in a box (two dimensional view)

The spaces during the packing are larger. When the box is shaken, the balls will rearrange as shown in Fig (4.22 b). The arrangement of these balls are now stable and more closely packed. It is the natural tendency of the balls to have closely packed arrangement of eleven spheres after shaking.

Fig (4.22 b)Packing of eleven spheres in a box (two dimentional view)

In order to understand,how various unit cells of the crystal lattice are developed, consider three balls which join together in one plane. The fourth ball is inserted in the space created by the other three as a second layer. In this way tetrahedral structure is obtained Fig (4.22 c). Actually, the fourth ball of the second layer is placed in the depression created by the first three balls. These depressions are also called interstices or crevices or voids.

Consider the Fig (4.22 d) in which eleven balls of Fig. (4.22 b) are present in the first layer (circles with shade). The balls of the second layer (circle without shade) can fit into the depressions or interstices created by the first layer. When the balls of the second layer are arranged, then all the depressions of the first layer are not occupied. There are two types of depressions as 'a' and 'b'. The depressions marked 'b' are not occupied by the second layer and one can see the ground from looking at the top through depressions 'b'. The new depressions marked 'a' are created by the second layer. Through the depressions 'a', we can not see the ground, but balls of the first layer. Now arrange the balls of third layer in the depression of second layer. When the balls of the third layer are placed abov the second layer then there are two possibilities. Third layer balls may be accommodated in 'a'- type or 'b'-type interstices or depressions.
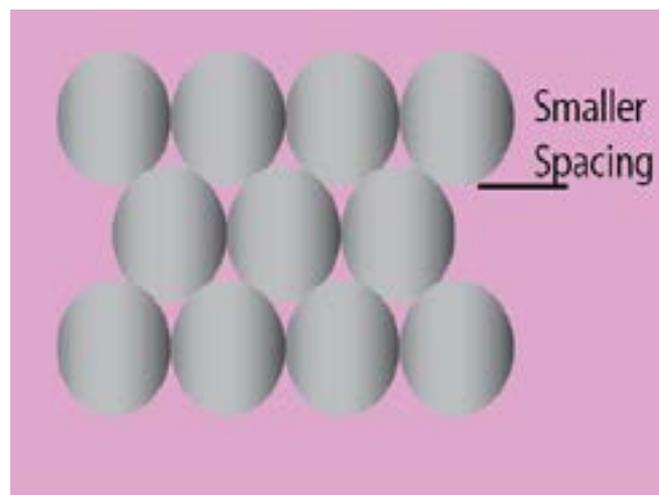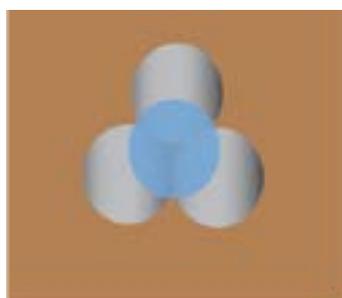

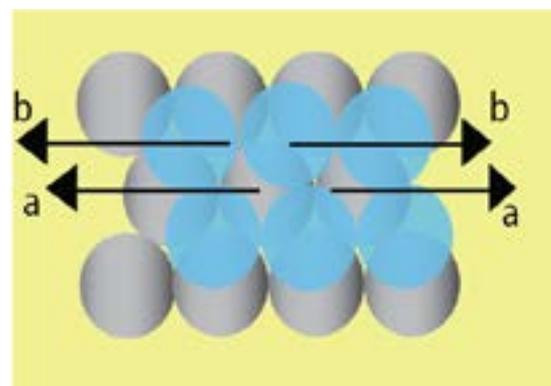Fig (4.22 c) The formation of a tetrahedral site, due to four balls

Fig (4.22 d) Close packing of spheres, showing 11 balls in first layer and 6 balls in second layer.

(i)   Cubic Close Packing

When the atoms of the third layer fit into the interstices marked b, then the atoms of the third layer will not lie directly above those of the atoms of first layer. This pattern of arrangement is called ABC ABC-------------- or 123 123-----------------. It is named as face centred cubic arrangement Fig. (4.23a). The balls of fourth, seventh and tenth layers will be in front of each other.
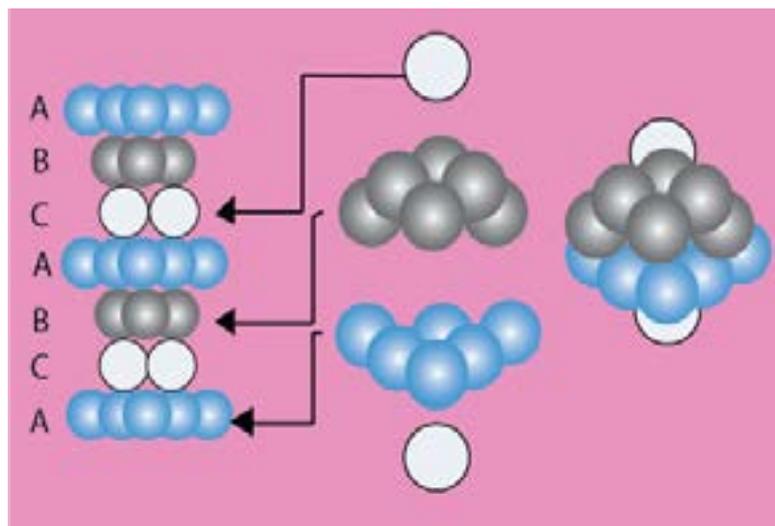
Fig (4.23 a) Cubic close packing or
Face centred cubic arrangement (ABCABC . . .)
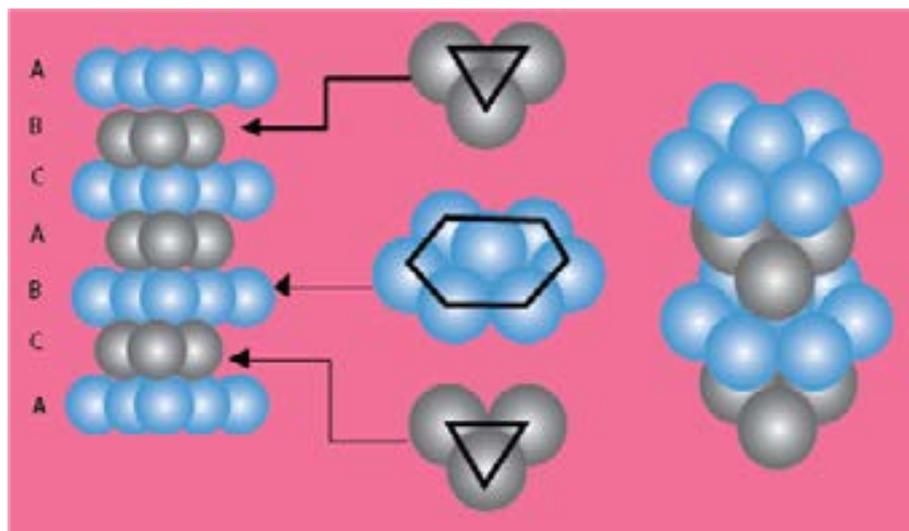
Fig (4.23 b) Hexagonal close packing (ABAB . . .)

(ii)   Hexagonal Close Packing

When the atoms of the third layer are arranged in such a way that they occupy the depressions created by the second layer i.e., in the 'a' types crevices then these atoms will directly lie above the atoms of first layer. This pattern of arrangement is usually written as ABAB ……. or 1212 . This pattern has been named as hexagonal close packing Fig(4.23b). The balls of third, fifth, seventh layers will be in front of each other.

Comparison of Properties of Various Types of Crystals

The following table gives a view to the comparison of properties of four types of crystals.

Table (4.9) Type of Crystalline Solids

Type of Solid	Structural Particles	Intermolecular Forces	Typical Properties	Examples
Metallic	cations plus delicalized electrons	metallic bons	hardness varies from soft to Very hard; melting points varied from low to very high; lustrous; ductile; malleable; very good conductors of heat and electricity	Na; Mg; Al Fe; Zn; Cu; Ag; W
Ionic	cations and anions	electrostatic attractions	hard; moderate to very high melting points: nonconductors of electricity　(but good electrical conductors in the molten state)	$NaCl$; $NaNO_3$, MgO
Molecular	molecules (atoms of noble gases)	Landon and/or dipole-dipole and/or hydrogen bonds	soft; low melting points: nonconductors of heat and electricity; sublime easily in many cases	noble-gas elements; CH_4; CO_2; P_4 S_8; I_2; H_2O
Network covalent	atoms	covalent bonds	very hard; very high melting points: nonconductors of elecrioity	C(diamonds); SiC; SiO_2

4.8 Determination of Avogadro's Number (N_A)

Avagadro number can be calculated in a number of different ways. One of the most accurate methods for determining this number is based on the study of crystalline solids.

In order to calculate this number, we need to know the volume of one gram-mole of a crystalline solid and the distance between its atoms or ions in the crystal lattice.

The volume of one gram-mole of a solid can be calculated from its density while the spacing between its atoms can be measured by X-rays.

The method of determining Avogadro' s number is explained with a help of following solved example which gives a reasonably good value of this number. The crystal of LiF is primitive cubic and can be used to calculate the Avogadro's number.

Example:

The density of LiF is 2.65 g cm^{-3}. It is made up of cubic array of alternate Li$^+$ and F$^-$ ions and the distance between these ions is 2.01 $\overset{o}{A}$ (2.01 x 10^{-8} cm). Calculate the Avogadro's number.

Solution:

The formula mass of LiF	=	6.939 + 18.9984
	=	25.9374 g mol^{-1}
Density of LiF	=	2.65 g cm^{-3}

From the density and molar mass, calculate the volume of 1 mole of solid LiF

The volume occupied

$$\text{by one formula unit of LiF} \quad = \quad \frac{25.9374 \text{g mol}^{-1}}{2.65 \text{g cm}^{-3}}$$

$$= \quad 9.788 \text{ cm}^3 \text{ mol}^{-1}$$

From this volume, we can calculate the edge length of the cube. For this, we suppose that 9.788cm^3 of LiF i.e., 1 mole of LiF, is present in the form of a cube. The cube root of this volume will give the length of one edge of cube.

Edge length of the cube $\quad = \quad \sqrt[3]{9.788\text{cm}^3}$

$\qquad\qquad\qquad\qquad\qquad\quad = \quad$ 2.139 cm

The number of ions of both Li^+ and F^- on one edge length can be calculated by dividing the edge length by distance between ions. Hence, the number of (Li^+ and F^-) ions along one edge length

$$= \quad \frac{2.139\text{cm}}{2.01\times10^{-8}\text{cm ion}^{-1}}$$

$$= \quad 1.064\text{x}10^8$$

When we take the cubes of these ions we get the total number of ions i.e. Li^+ and F^- in the cube.

Total number (Li^+F^-) of ions in the cube $\quad = \quad (1.064\text{x}10^8)^3$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad = \quad 1.204\text{x}10^{24}$

Since the cube of LiF crystal contains one Avogadro's number of Li^+ and one Avogadro's number of F^- , so the Avogadro's number will be

$$\frac{1.204x10^8}{2} \qquad =6.02\text{x}10^{23}$$

KEY POINTS

1. Among three states of matter i.e. gases, liquids and solids, the intermolecular attractive forces in the gases are negligible. In liquids intermolecular forces are strong enough to keep the molecules close together. Anyhow, the molecules in liquids are free to move with respect to one another. In solids the particles occupy specific locations in three dimensional arrangement. Molecules in liquids are free to move with respect to one another. In solids the particles occupy specific locations in three dimensional arrangement.

2. There are four types of intermolecular forces i.e. dipole-dipole forces, London dispersion forces, hydrogen bonding and Ion-dipole forces. The relative strengths of dipole-dipole and dispersion forces depend upon the polarity, polarisability, size and shape of the molecules. Hydrogen bonding occurs in compounds containing 0-H,N - H, H - F bonds.

3. The vapour pressure of a liquid measures the tendency of a liquid to evaporate. It is the pressure exerted by the vapours on the surface of a liquid when the rate of evaporation is equal to the rate of condensation. A liquid boils when its vapour pressure equals the external pressure.

4. Many crystalline solids melt to give a turbid liquid before melting to give a clear liquid. These turbid liquids possess some degree of order and are called liquid crystals. Liquid crystals have the fluidity of liquids and the optical properties of solids.

5. In crystalline solids the particles are arranged in a regular and repeating manner. The essential structural features of a crystalline solid can be represented by its unit cell. The three dimensional array of points representing atoms, ions or molecules is called crystal lattice. The points in the crystal lattice represent positions in the structure where they have identical environments.

6. The simplest unit cell is a cubic unit cell. There are seven crystal systems overall.

7. The properties of solids depend on the arrangement of particles and the attractive forces between them. Ionic solids are hard and brittle and have high melting points. Covalent solids consist of atoms held together by covalent bonds and these bonds extend throughout the solid. They are hard and have high melting points. Metallic solids consist of metal cations immersed in a sea of electrons and give a wide range of properties. Molecular solids consist of atoms or molecules held together by intermolecular forces.

8. The properties of solids depend on the arrangement of particles and the attractive forces between them. Ionic solids are hard and brittle and have high melting points. Covalent solids consist of atoms held together by covalent bonds and these bonds extend throughout the solid. They are hard and have high melting points. Metallic solids consist of metal cations immersed in a sea of electrons and give a wide range of properties. Molecular solids consist of atoms or molecules held together by intermolecular forces.

EXERCISE
(QUESTIONS OF LIQUIDS)

Q1. Choose the best answers from the given choices.

(i) London dispersion forces are the only forces present among the
(a) molecules of water in liquid state
(b) atoms of helium in gaseous state at high temperature
(c) molecules of solid iodine.
(d) molecules of hydrogen chloride gas.

(ii) Acetone and chloroform are soluble in each other due to
(a) intermolecular hydrogen bonding   (b) ion-dipole interaction
(c) instantaneous dipole   (d) all of the above

(iii) NH, shows a maximum boiling point among the hydrides of Vth group elements due to
(a) very small size of nitrogen   (b) lone pair of electrons present on nitrogen.
(c) enhanced electronegative character of nitrogen
(d) pyramidal structure of NH_3

(iv) When water freezes at 0"C, its density decreases due to
(a) cubic structure of ice   (b) empty spaces present in the structure of ice
(c) change of bond lengths   (d) change of bond angles

(v) In order to raise the boiling point of water upto 110°C, the external pressure should be
(a) between 760 torr and 1200 torr   (b) between 200 torr and 760 torr
(c) 765 torr   (d) any value of pressure

Q2. Fill in the blanks with suitable words
(i) The polarizability of noble gases_____down the group and results in the increase in their boiling points.
(ii) _____ is developed in acetone and chloroform when they are mixed together.
(iii) Exceptionally weak_____of HF is due to strong hydrogen bonding present in it.
(iv) The concept of dynamic equilibrium is the ultimate _____of all reversible systems.
(v) ΔH_v of C_6H_{14} should be_____ than that of C_2H_6.
(vi) During the formation of ice from liquid water there is a_____ % increase in volume.
(vii) The rate of increase of vapour pressure of water_____at high temperatures.
(viii) A layer of ice on the surface of water____the water underneath for further heat loss.
(ix) Evaporation is a _____process.
(x) Liquid crystals are used in the display of_____ devices.

Q3. Indicate true or false as the case may be
  (i)   Dipole-dipole forces are weaker than dipole-induced dipole forces.
  (ii)   The ion dipole interactions are responsible for the dissolution of an ionic substance in water.
  (iii)   The high polarizability of iodine is responsible for its existence in solid form and its difference from other halogens.
  (iv)   The strong hydrogen bonding in H_2S makes it different from water.
  (v)   Hydrocarbons are soluble in water because they are polar compounds.
  (vi)   The viscosities of liquids partially depend upon the extent of hydrogen bonding.
  (vii)   The state of equilibrium between liquid state and vapours is dynamic in nature.
  (viii) Heat of vapourization of liquids depend upon the intermolecular forces of attraction present between their molecules.
  (ix)   Ice does not show any vapour pressure on its surface at -1°C.
  (x)   Boiling point of a liquid is independent of external pressure.

Q4 (a) What type of intermolecular forces will dominate in the following liquids.
  (i)   Ammonia, NH_3 (ii)   Octane, C_8H_{18} (iii)   Argon, Ar
  (iv)   Propanone, CH_3COCH_3 (v)   Methanol, CH_3OH
  (b)   Propanone (CH_3COCH_3), propanol ($CH_3CH_2CH_2OH$) and butane ($CH_3CH_2CH_2CH_3$) have very similar relative molecular masses. List them in the expected order of increasing boiling points. Explain your answer.

Q.5 Explain the following with reasons.
  (i)   In the hydrogen bonded structure of HF, which is the stronger bond: the shorter covalent bond or the longer hydrogen bond between different molecules.
  (ii)   In a very cold winter the fish in garden ponds owe their lives to hydrogen bonding?
  (iii)   Water and ethanol can mix easily and in all proportions.
  (iv)   The origin of the intermolecular forces in water.

Q6   (a) Briefly consider some of the effects on our lives if water has only a very weak hydrogen bonding present among its molecules.
  (b) All gases have a characteristic critical temperature. Above the critical temperature it is impossible to liquefy a gas. The critical temperatures of carbon dioxide and methane are 31.14 °C and -81.9 °C, respectively. Which gas has the stronger intermolecular forces? Briefly explain your choice?

Q7   Three liquids have the properties mentioned against their names

		Water	Propanone	Pentane
(i)	Molecular Formula	H_2O	C_3H_6O	C_5H_{12}
(ii)	Relative molecular mass (a.m.u.)	18	58	72
(iii)	Enthalpy change of vapourization (kJ mol^{-1})	41.1	31.9	27.7
(iv)	Boiling point (⁰C)	100	56	36

(a)   What type of intermolecular force predominates in each liquid?
(i)   water   (ii)   propanone   (iii)   pentane
(b)   What do you deduce about the relative strength of these forces in the liquids?
        Justify your conclusions.
(c)   If the liquids are shaken together in pairs,
        (i)   Which pair would be unlikely to mix?
        (ii)   Explain this immiscibility in terms of the forces between the molecules.
        (iii)   Choose one of the pairs that mix and say whether the enthalpy change on mixing
                  would be positive or negative.

Q8   Describe the various forces responsible for keeping the particles together in the following
  elements and compounds and their effects on physical properties making use of the data
  below.

Substance	Formula	Molar Mass (a.m.u.)	M.P(°C)
Neon	Ne	20	-248
Argon	Ar	40	-189
Water	H_2O	18	0
Sodium fluoride	NaF	42	993
Diamond	C	12	3350

Q9   The boiiing points and molar masses of hydrides of some first row elements are tabulated
  below:

Substance	Boiling Point (K)	Molar Mass (g mol^{-1})
CH_4	109	16
NH_3	240	17
H_2O	373	18

Suggest reasons for the difference in their boiling points in terms of the type of molecules involved and the nature of the forces present between them.

Q10 Explain the term saturated vapour pressure. Arrange in order of increasing vapour pressure: ldm³ water, 1 dm³ ethanol, 50 cm³ water, 50 cm³ ethanol and 50 cm³ of ether.

Q11 While a volatile liquid standing in a breaker evaporates, the temperature of the liquid remains the same as that of its surrounding. If the same liquid is allowed to vapourize into atmosphere in an insulated vessel, its temperature falls below that of its surrounding. Explain the difference in behaviour.

Q12 How does hydrogen bonding explain the following indicated properties of the substances?
   (i)   Structure of DNA   (ii)   Hydrogen bonding in proteins
   (iii)   Formation of ice and its lesser density than liquid water
   (iv)   Solubilities of compounds

Q13 What are liquid crystals? Give their uses in daily life.

Q14 Explain the following with reasons.
   (i)   Evaporation causes cooling.
   (ii)   Evaporation takes place at all temperatures.
   (iii)   Boiling needs a constant supply of heat.
   (iv)   Earthenware vessels keep water cool.
   (v)   One feels sense of cooling under the fan after bath.
   (vi)   Dynamic equilibrium is established during evaporation of a liquid in a closed vessel at constant temperature.
   (vii)   The boiling point of water is different at Murree hills and at Mount Everest.
   (viii) Vacuum distillation can be used to avoid decomposition of a sensitive liquid.
   (ix)   Heat of sublimation of a substance is greater than its heat of vaporization.
   (x)   Heat of sublimation of iodine is very high.

(QUESTIONS OF SOLIDS)

Q1.   Multiple choice questions.

(i)   Ionic solids are characterized by
    (a)   low melting points.   (b)   good conductivity in solid state,
    (c)   high vapour pressures.   (d)   solubility in polar solvents.

(ii)   Amorphous solids
    (a)   have sharp melting points.
    (b)   undergo clean cleavage when cut with knife.
    (c)   have perfect arrangement of atoms.
    (d)   can possesses small regions of orderly arrangement of atoms.

(iii)   The molecules of CO_2 in dry ice form the
    (a)   ionic crystals   (b)   covalent crystals
    (c)   molecular crystals   (d)   any type of crystal

(iv)   Which of the following is a pseudo solid?
    (a) CaF_2 (b)   Glass   (c)   NaCl   (d)   All

(v)   Diamond is a bad conductor because
    (a)   it has a tight structure   (b)   it has a high density
    (c)   there are no free electron present in the crystal of diamond to conduct electricity
    (d)   is transparent to light

Q2.   Fill in the blanks
    (i)   In a crystal lattice, the number of nearest neighbours to each atom is called the_____.
    (ii)   There are_____ Bravis lattices.
    (iii)   A pseudo solid is regarded as_____liquid.
    (iv)   Glass may begin to crystallize by a process called_____ .
    (v)   Crystalline solids which exhibit the same _____ in all directions are called_____.
    (vi)   The branch of science which deals with the _____ of crystals is called crystallography.

Q.3   Indicate True/False as the case mav be
    (i)   There are five parameters in unit cell dimensions of a crystal.
    (ii)   Ionic crystals are very hard, have low volatility and very low melting and boiling points.

(iii)　The value of lattice energy of the ionic substances depends upon the size of ions.

(iv)　Molecular orbital theory of solids is also called band theory.

(v)　Ionic solid is good conductor of electricity in the molten state.

Q.4　What are solids? Give general properties of solids. How do you differentiate between crystalline solids and amorphous solids?

Q5

(a) Explain the following properties of crystalline solids. Give three examples in each case.

(i)	Anisotropy	(v)	Polymorphism
(ii)	Cleavage	(vi)	Transition temperature
(iii)	Habit of a crystal	(vii)	Symmetry
(iv)	Isomorphism	(viii)	Growing of a crystal

(b) How polymorphism and allotropy are related to each other? Give examples.

Q6

(a) Define unit cell. What are unit cell dimensions? How the idea of crystal lattice is developed from the concept of unit cell?

(b) Explain seven crystal systems and draw the shapes of their unit cells.

Q7

(a) What are ionic solids? Give their properties. Explain the structure of NaCl. Sketch a model to justify that unit cell of NaCl has four formula units in it.

(b) What are covalent solids? Give their properties. Explain the structure of diamond.

(c) What are molecular crystals? Give their properties. Justify that molecular crystals are softer than ionic crystals.

Q8

(a)Give different theories of a metallic bond. How does electron sea theory justify the electrical conductivity, thermal conductivity and shining surfaces of metals?

(b) Explain with the help of a diagram

(i)　　Cubic close packing in the structure of metals.

(ii)　　Hexagonal close packing in the structure of metals.

Q9　Crystals of salts fracture easily but metals are deformed under stress without fracturing. Explain the difference.

Q10 What is the coordination number of an ion? What is the coordination number of the cation in (a) NaCl structure and (b) CsCl structure? Explain the reason for this difference?

Q11 Give examples of ionic solids, molecular solids and covalent macromolecular solids. What are the factors which determine whether each of these types of solid will dissolve in water or not?

Q12   Explain the following with reasons:
(i)   Sodium is softer than copper, but both are very good electrical conductors.
(ii)   Diamond is hard and an electrical insulator.
(iii)   Sodium chloride and caesium chloride have different structures.
(iv)   Iodine dissolves readily in teterachloromethane.
(v)   The vapour pressures of solids are far less than those of liquids.
(vi)   Amorphous solid like glass is also called super cooled liquid.
(vii)   Cleavage of the crystals is itself anisotropic behaviour.
(viii) The crystals showing isomorphism mostly have the same atomic ratios.
(ix)   The transition temperature is shown by elements having allotropic forms and by compounds showing polymorphism.
(x)   One of the unit cell angles of hexagonal crystal is 120°.
(xi)   The electrical conductivity of the metals decrease by increasing temperature.
(xii)   In the closest packing of atoms of metals, only 74% space is occupied.
(xiii) Ionic crystals don't conduct electricity in the solid state.
(xiv) Ionic crystals are highly brittle.
(xv)   The number of positive ions surrounding the negative ion in the ionic crystal lattice depends upon the sizes of the two ions.