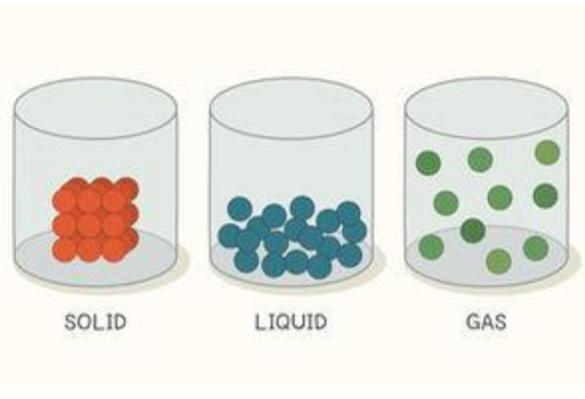


## Structure of Solid

### Introduction

In a solid, molecules are packed together, and it keeps its shape. Liquids take the shape of the container. Gases spread out to fill the container.

Solid is one of the three main states of matter, along with **liquid** and **gas**. Matter is the "stuff" of the universe, the atoms, molecules and ions that make up all physical substances. In a solid, these particles are packed closely together and are not free to move about within the substance. Molecular motion for the particles in a solid is confined to very small vibrations of the atoms around their fixed positions; therefore, solids have a fixed shape that is difficult to change. Solids also have a definite volume; that is, they keep their size no matter how you try to change them.



However, the main focus of this topic is to consider the solid phase of matter. A large majority of substances around us are solids. The distinctive features of solids are:

- They have a definite shape.
- They are rigid and hard.
- They have fixed volume.

These characteristics can be explained on the basis of following facts:

- The constituent units of solids are held very close to each other so that the packing of the constituents is very efficient. Consequently, solids have high densities.
- Since the constituents of solids are closely packed, it imparts rigidity and hardness to solids.
- The constituents of solids are held together by strong forces of attraction. This results in their having definite shape and fixed volume.

Information regarding the nature of chemical forces in solids can be obtained by the study of the structure of solids, i.e. arrangements of atoms in space.

## Classification of solids

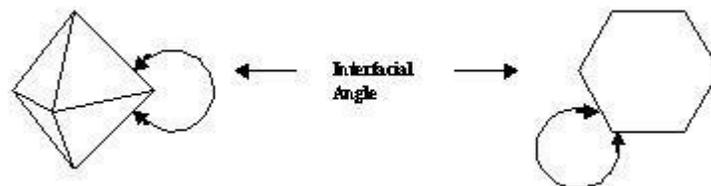
Solids are classified into categories:

- *Amorphous solids*
- *Crystalline solids*

The two types of solids have different characteristics.

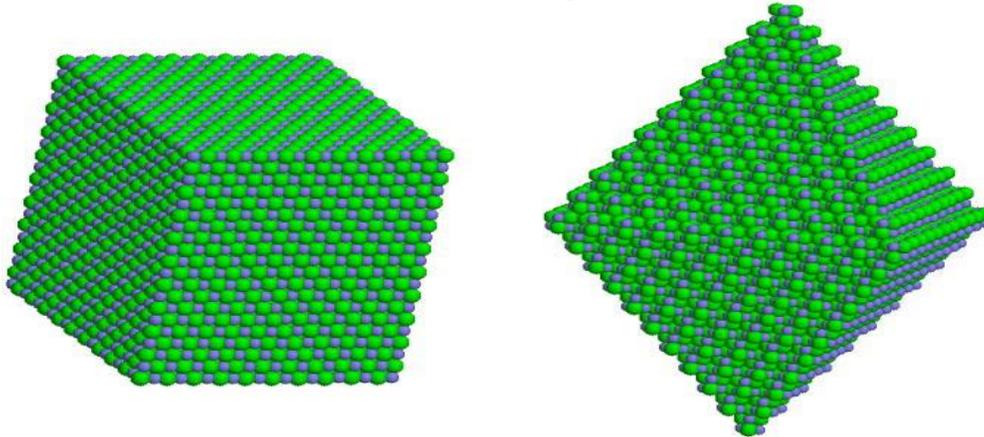
- *Amorphous Solids.* An amorphous solid is a substance whose constituents do not possess an orderly arrangement. Important examples of amorphous solids are glass and plastics. Although amorphous solids consist of microcrystalline substance but the orderly arrangement is restricted to very short distances. These distances are of the same order of magnitude as the interatomic distances.
- *Crystalline Solids.* A crystalline solid is a substance whose constituents possess an orderly arrangement in a definite geometric pattern. Some very common examples of crystalline substances are sodium chloride, sugar and diamond. The main characteristics of crystalline substances are:
  1. *Orderly arrangement.* The constituent units of crystalline solids are arranged in an orderly fashion which repeats itself over very long distances as compared to interatomic distances. The arrangement of bricks in a wall can be considered as an example. The arrangement is so well defined that the entire pattern can be repeated provided the arrangement of a few atoms is known.
  2. *Crystals are always bounded by plane faces.*
  3. *The faces of crystals always meet at some fixed angles.*

For any particular substances the angle between corresponding pair of faces is always the same in all crystals.



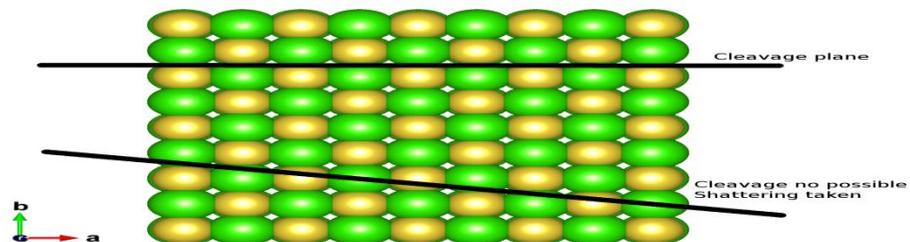
Different crystals of the same substance may sometimes appear to be different from outside, (either due to different rate of growth by different faces or due to some damage to the corners or edges) but the interfacial angle is always the same. For example, sodium chloride grows from

water solution as cubes but from 15% aqueous urea as an octahedran.



Two crystals of a single substance with the same lattice but different shapes are said to be of different *habit*. On habit modification, the relative areas of different faces change but the angles between such faces remain constant.

- Crystalline solids exhibit anisotropy in many of their properties.* It means all those properties which depend upon direction or angular orientation of crystals. These show different behaviour in non-parallel directions. One such consequence of anisotropy is the phenomenon of **cleavage**. In crystals the splitting is easier in some directions than others. For example, in a crystal of sodium chloride cleavage can only be achieved along planes parallel to cube faces. Any attempt to cleave such a crystal along any arbitrary plane will shatter it.



- The transition from the solid to liquid (i.e. melting point) for crystalline solids is sharp and distinct.* An amorphous substance, on the other hand, has no sharp melting point. The transition from solid to liquid in an amorphous solid does not take place at a define point but extends over a long range. The absence of sharp melting point suggests that most of amorphous solids may be best thought of as liquids.
- Crystalline solids exhibit definite heats of fusion.*

## Types of crystalline solids

There are four types of crystalline solids: ionic solids, molecular solids, network covalent solids and metallic solids.

### Ionic solids

Ionic compounds form crystals that are composed of oppositely charged ions: a positively charged **cation** and a negatively charged **anion**. Because of the strong attraction between opposite charges, it takes a lot of energy to overcome ionic bonds. This means that ionic compounds have very high melting points, often between 300 and 1,000 degrees Celsius (572 to 1,832 degrees Fahrenheit).

While the crystals themselves are hard, brittle and nonconductive, most ionic compounds can be dissolved in water, forming a solution of free ions that will conduct electricity. They may be simple binary salts like sodium chloride (NaCl), or table salt, where one atom of a metallic element (sodium) is bonded to one atom of a nonmetallic element (chlorine). They may also be composed of polyatomic ions such as  $\text{NH}_4\text{NO}_3$  (ammonium nitrate). Polyatomic ions are groups of atoms that share electrons (called **covalent bonding**) and function in a compound as if they constituted a single charged ion.

### Molecular solids

Molecular solids are composed of covalently bonded molecules attracted to each other by electrostatic forces (called Van der Waals forces). Because covalent bonding involves sharing electrons rather than outright transfer of those particles, the shared electrons may spend more time in the electron cloud of the larger atom, causing weak or shifting polarity. This electrostatic attraction between the two poles (dipoles) is much weaker than ionic or covalent bonding, so molecular solids tend to be softer than ionic crystals and have lower melting points (many will melt at less than  $100^0$  C, or 212 F). Most molecular solids are non-polar. These non-polar molecular solids will not dissolve in water, but will dissolve in a non-polar solvent, such as benzene and octane. Polar molecular solids, such as sugar, dissolve easily in water. Molecular solids are nonconductive.

Examples of molecular solids include ice, sugar, **halogens** like solid chlorine ( $\text{Cl}_2$ ), and compounds consisting of a halogen and hydrogen such as hydrogen chloride (HCl). Fullerene "buckyballs" are also molecular solids.

### Network covalent solids

In a network solid, there are no individual molecules. The atoms are covalently bonded in a continuous network, resulting in huge crystals. In a network solid, each atom is covalently bonded to all the surrounding atoms. Network solids have similar properties to ionic solids. They are very hard, somewhat brittle solids with extremely high melting points (higher than 1,000 C or 1,800 F). Unlike ionic compounds, they do not dissolve in water, nor do they conduct electricity.

Examples of network solids include diamonds, amethysts and rubies.

## **Metallic solids**

Metals are opaque, lustrous solids that are both malleable and ductile. Malleable means they are soft and can be shaped or pressed into thin sheets, while ductile means they can be pulled into wires. In a metallic bond, the valence electrons are not donated or shared as they are in ionic and covalent bonding. Rather, the electron clouds of adjacent atoms overlap so that electrons become delocalized. The electrons move with relative freedom from one atom to another throughout the crystal.

A metal may be described as a lattice of positive cations within a "sea" of negative electrons. This electron mobility means that metals are highly conductive of heat and electricity. Metals tend to have high melting points, though notable exceptions are mercury, which has a melting point of minus 37.84 degrees Fahrenheit (minus 38.8 Celsius), and phosphorous, with a melting point of 111.2 F (44 C).

An alloy is a solid mixture of a metallic element with another substance. While pure metals can be overly malleable and heavy, alloys are more workable. Bronze is an alloy of copper and tin, while steel is an alloy of iron, carbon and other additives.

## **Amorphous solids**

In **amorphous** solids (literally "solids without form"), the particles do not have a repeating lattice pattern. They are also called "pseudo solids." Examples of amorphous solids include **glass, rubber, gels and most plastics**. An amorphous solid does not have a definite melting point; instead, it melts gradually over a range of temperatures, because the bonds do not break all at once. This means an amorphous solid will melt into a soft, malleable state (think candle wax or molten glass) before turning completely into a liquid.

Amorphous solids have no characteristic symmetry, so they do not have regular planes of cleavage when cut; the edges may be curved. They are called **isotropic** because properties such as refractive index, conductivity and tensile strength are equal regardless of the direction in which a force is applied.

## **Seven Crystal Systems**

Since solid materials are of many different shapes, it may appear at first sight that there may be an infinite number of interfacial combinations. But this is not true. A careful examination of several thousand crystals of various substances reveals that there are only **seven** possible crystal symmetries exhibited by solids. Different solids which exhibit the same symmetry elements are all classified as belonging to the same system.

1. **Cubic system.** All three axes are of equal length and are mutually perpendicular to each other. Some typical examples are diamond, silver and cesium chloride.

2. **Orthorhombic system.** It is also called rhombic system. It consists of three mutually perpendicular axes of unequal lengths. Few are di mercury dichloride, ammonium sulphate and
3. **Tetragonal system.** To produce tetragonal symmetry, the cube is elongated in one direction. The axes are still at right angle to each other, but one axis is longer (or shorter) than the other two axes. One example is lead tungsten.
4. **Monoclinic system.** In monoclinic system the three axes are of unequal length and are no longer perpendicular to each other. Monoclinic system differs from rhombic symmetry in that one of axes does not make  $90^\circ$  with the plane of other two axes. Examples include potassium chloride and high temperature form of sulphur.
5. **Rhombohedral system.** It consists of three equal axes which are inclined to each other at same angle but it is not  $90^\circ$ . Some common examples are arsenic, antimony, bismuth and calcite.
6. **Triclinic system.** It consists of three unequal axes and none is perpendicular to any of the others. This system has the lowest symmetry. There is no simple axis or plane of symmetry. Boric acid is an example of this class.
7. **Hexagonal system.** In this type of symmetry the atoms are arranged in the form of hexagons and these unit cell has two edges of one above length ( $a=b$ ). The symmetry axis ( $c$ ) is at  $90^\circ$  to these two axes which make an angle of  $120^\circ$  with one another. Graphite is a common example of hexagonal symmetry.

### REVIEW QUESTIONS/ ASSIGNMENT

1. What are solids?
2. List and explain the distinctive features of solids
3. Amorphous solids and crystalline solids are the classification of solids. Briefly explain these two.
4. Mention the characteristics of crystalline substances.
5. List and explain the different types of crystalline solids.
6. What are the seven crystal systems?
7. Find out the structure of each of the seven crystal systems.