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Chapter 11: Solids

Section 11.1: Structures and Types of Solids (Crystalline Solids)

Solids can be broadly classified as:

(a) amorphous solids

(b) crystalline solids

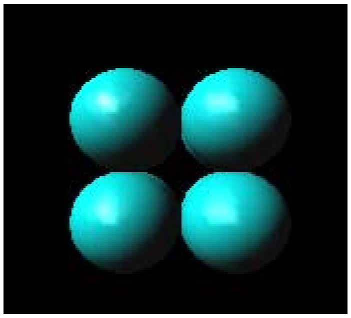
Amorphous and crystalline solids differ in the orderliness of the packing of their components. These components can be atoms, molecules or ions. A **crystalline** solid has a highly ordered arrangement of its components. In contrast, an **amorphous** solid exhibits total disorder in the packing of its components.

The components of a crystalline solid are packed in a three-dimensional periodical array, called a **crystal lattice**. Information about the structure of a crystalline solid is completely contained in the crystal **unit cell**. The unit cell is the smallest unit of a crystal, which makes up the crystal when it is repeated over and over in three directions.

Three common unit cells are found in a number of crystalline solids:

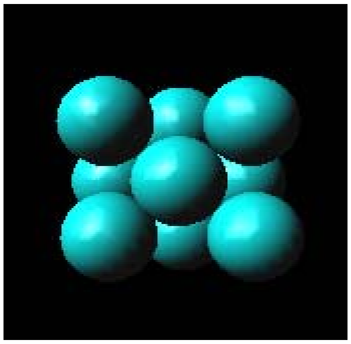
1. **Simple Cubic Cell**

   This cell is a cube containing eight atoms. The centers of these atoms are located at the corners of the cell. Atoms at adjacent corners of the cube touch one another.



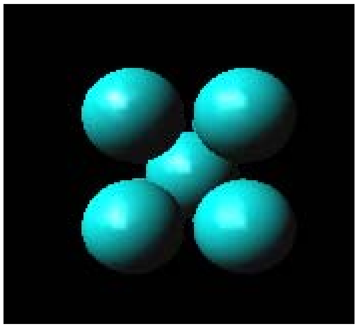
2. **Face-Centered Cubic Cell**

There is an atom at each corner of the cube and one in the center of each of the six faces of the cube. In this cell, the atom at the center of the face touches each of the four corner atoms on that face. Note: The atoms at the corners of the cube do not touch each other.



3. Body-Centered Cubic Cell

There is an atom at each corner of the cube and one in the center of the cube. The central atom touches each of the corner atoms. However, the corner atoms do not touch each other.



Crystalline solids can be broadly classified as:

(a) Atomic Solids

(b) Metallic Solids

(c) Molecular Solids

(d) Ionic Solids

(e) Network Covalent Solids

Section 11.2: Atomic Solids

The components of an atomic solid are atoms. Atomic solids are held together by dispersion forces. Recall: Dispersion forces are <u>weak</u> attractive forces resulting from the interaction between momentary induced dipoles. Hence, atomic solids have low melting temperatures and enthalpies of fusion. Only noble gases form atomic solids. Other elements do not form atomic solids, because these elements are not stable by themselves, as they do not have filled valence orbitals.

Section 11.3: Metallic Solids

The components of a metallic solid are the atoms of a metallic element. The structure of a metallic solid is best described as a lattice of cations held together by a sea of valence electrons. Because of the very strong coulombic forces between cations and electrons, metals tend to have relatively high melting points and enthalpies of fusion. Metals are characterized by high electrical and thermal conductivity.

These properties result from the fact that the valence electrons are not localized near the cations, but are free to move anywhere within the crystal lattice.

Section 11.4: Molecular Solids

The components of a molecular solid are molecules. Molecular solids are held together by Van der Waals forces. Recall: Van der Waals forces include dipole-dipole, dipole-induced dipole and induced dipole-induced dipole (or London dispersion) forces. Van der Waals forces between molecules are generally stronger than dispersion forces between atoms, but weaker than coulombic interactions between charged species. Hence, molecular solids generally have melting temperatures and enthalpies of fusion intermediate between those of atomic solids and those of metals or ionic solids.

Examples of common molecular solids are ice (H_2O), dry ice (CO_2), glucose ($C_6H_{12}O_6$), caffeine and aspirin crystals.

Section 11.5: Ionic Solids

Ionic solids are constituted by anions and cations. Ionic solids are held together by the strong electrostatic forces that exist between oppositely charged ions. Hence, ionic solids often have very high melting points and enthalpies of fusion.

Consider NaCl. Cl^- is a large anion, while Na^+ is a small cation. Na^+ and Cl^- ions are each located on their own face-centered cubic lattice. Each Na^+ ion is surrounded by Cl^- ions and each Cl^- ion is surrounded by Na^+ ions. This arrangement gives the maximum electrostatic force of attraction between Na^+ and Cl^- ions.

Other alkali halides, except those based on the Cs^+ ion, have the same structure as NaCl. Recall: As we go down in a group, the ionic radius increases. Thus, among alkali metal ions, Cs^+ has the largest radius. Because of its large size, the Cs^+ cation cannot occupy the center of a face but is located at the center of the unit cell. Hence, in CsCl, the anion is located on a faced-centered cubic cell and the Cs^+ cations are located on a body-centered cubic cell.

Section 11.6: Covalent Network Solids

In network covalent solids, the atoms are joined by a continuous network of covalent bonds. Hence, these solids are often regarded as one giant molecule. Depending on the nature of the bonding, these solids may be electrical conductors or insulators, hard or soft. Since these solids are held together by strong covalent bonds, they always have high melting points and are insoluble in common solvents.

Example: Graphite and Diamond

Carbon has two different crystalline forms or allotropes:

1. Graphite
2. Diamond

1. Graphite

The structure of graphite resembles a stack of staggered sheets of hexagonal carbon rings. Each carbon is sp^2 hybridized (σ and π bonds). While the covalent bonding within these sheets is very strong, the dispersion forces between sheets are relatively weak. Hence, it is very easy for individual sheets to slide past one another and, as a result, graphite is an excellent lubricant. Delocalization of the π bonding electrons over each graphite layer makes graphite an excellent conductor.

2. Diamond

In diamond, each carbon atom forms single bonds with four other carbon atoms. Thus, each carbon atom is sp^3 hybridized, and, the arrangement of carbon atoms is tetrahedral (σ bonds). Tetrahedral geometry and localization of bonding electrons in the σ bonds result in the unusual hardness and insulating properties of diamond. Diamond is used in cutting tools.

Example: Silicon Compounds

An example of the network covalent structure in a silicon compound is silica or SiO_2. Silica can exist at least in two forms:

1. Quartz
2. Glass

1. Quartz

Quartz is one of the crystalline forms of silica and is the major component of sand. In quartz, each silicon atom is bonded to four oxygen atoms, forming a tetrahedron. Each oxygen atom is shared by two silicon atoms. Hence, each tetrahedron contains one silicon and $4 \times ½ = 2$ oxygen atoms (1/2 because each oxygen belongs to two tetrahedrons). Thus, the structure SiO_2

2. Glass

When quartz is heated, it melts into a viscous liquid. This viscous liquid contains a disordered SiO_2 network structure. If we melt quartz and cool it rapidly, then, we obtain **glass**, an amorphous solid.

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