

# CHAPTER 6

## SOLIDS

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### 1. SYMMETRY

Repetition of faces, edges and interfacial angles when rotated by  $360^\circ$

Three elements of symmetry:

#### 1. PLANE OF SYMMETRY

An imaginary plane which divides the crystal into two equal halves.

#### 2. AXIS OF SYMMETRY

An imaginary line through which crystal can be rotated.

#### 3. CENTRE OF SYMMETRY

The central point of a crystal which is equidistant from two opposite faces of a crystal.

A crystal may have a number of planes of symmetry or axis of symmetry but it can have only one centre of symmetry.



## 2. GEOMETRICAL SHAPE

- Crystalline solids have definite geometry (shape)
- The interfacial angles are always same for a given crystal.
- Upon grinding to very fine powder, the crystalline solids still retain their specific geometrical shapes.

## 3. MELTING POINT

- Crystalline solids have a sharp melting point which means transition from solid state to liquid state will happen suddenly over a fixed value of temperature, not over a range of temperature.

## 4. CLEAVAGE PLANE

- The breaking up of larger crystals into smaller ones with identical size and shape is called cleavage.
- The plane which contains direction of cleavage is called cleavage plane.
- Two adjacent cleavage planes intersect always at a definite angle.
- The magnitude of interfacial angle, after cleavage has taken place, may differ from solid to solid and is a characteristic of a given solid.
- Minerals have characteristic number of cleavages -
  - determined by counting the number of cleavage surfaces that are NOT parallel.



## 5. HABIT OF CRYSTAL

The shape in which crystal usually grows is called its habit

e.g NaCl has eubic habit

Two Factors affect habit:

1. Temperature
2. Addition of impurities

If impurity is added, the solid material changes its structure bcz new faces are produced in addition to original one.

If urea is added to NaCl, its habit becomes needle shaped.

## 6. CRYSTAL GROWTH

Crystals are usually prepared (or grown) by slow cooling of a substance in liquid state or hot saturated solution of the substance concerned.

→ The apparent shape of the crystal depends on method and condition of preparation.

→ NaCl with a cubic crystal habit, may grow into a cubic (3D), a flat shaped (2D) or a long needle-like structure (1D), depending upon conditions under which it is prepared.

→ A 10% urea present in its solution, as an impurity, compels it to grow in one dimension (needle-like)

The size of crystal is controlled by its rate of growth. A slowly growing crystal has a larger size.

## 7. ANISOTROPY

A substance which shows different intensity of properties in different directions is called anisotropic and this property as anisotropy.

Anisotropic Properties:

1. Electrical Conductivity
2. Thermal Conductivity
3. Refractive Index
4. Co-efficient of thermal expansion

\* As in amorphous materials such as glass, no long-range order exist; such properties are identical in all directions so these are isotropic materials.

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## 8. ISOMORPHISM

→ When two or more different compounds exist in the same crystalline forms they are said to be isomorphs of each other.

→ The formula units of different isomorphs have usually the same atomic ratio.

Isomorphs	Atomic Ratio	Crystal Structure
1. NaCl and MgO	1:1	Cubic
2. $KNO_3$ and $NaNO_3$	1:1:3	Rhombohedral
3. ZnO and CdS	1:1	Hexagonal
4. $KNO_3$ and $CaCO_3$	1:1:3	Rhombohedral

Physical and chemical properties of isomorphs are different from each other.

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## 9. POLYMORPHISM

Certain crystalline compounds exist in more than one crystalline form under different conditions.

This phenomenon is called polymorphism.

→ Polymorphs have the same chemical properties but different physical properties.

1.  $KNO_3$  : Rhombohedral and orthorhombic
2.  $AgNO_3$  : Rhombohedral and orthorhombic
3.  $CaCO_3$  : Trigonal and orthorhombic

These different forms are interconvertible into each other under different conditions of temperature.

## 10. ALLOTROPY

When an element exists in more than one crystalline forms, it is called allotropy

e.g

S<sub>8</sub> : Rhombic and Monoclinic

Oxygen : Oxygen molecule (O<sub>2</sub>) and ozone (O<sub>3</sub>)

Carbon : Diamond (cubic), Graphite (Hexagonal) and Bucky ball

Tin : Grey Tin (cubic), white tin (Tetragonal)

Polymorphism is for crystalline 'compounds' while allotropy is for elements

## 11. TRANSITION TEMPERATURE

The temperature at which one crystalline form of a substance changes to another form is called transition temperature.

e.g For,

S<sub>8</sub> : 95.5°C

Tin : 13.2°C

KNO<sub>3</sub> : 128.5°C

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# CRYSTAL LATTICE

The overall arrangement of particles in a crystal is called the crystal lattice or space lattice.

The smallest unit by volume of the crystal lattice having all the characteristic feature of the entire crystal is called a unit cell.

A unit cell may be described by the lengths of its edges  $a, b, c$  and the angles  $\alpha, \beta, \gamma$  between the edges. These six parameters (3 edges and 3 angles) of the unit cell are called unit cell dimensions or crystallographic elements of a unit cell.

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## CUBIC CRYSTAL LATTICE

A cubic system is one in which all the edge lengths are equal (i.e.  $a=b=c$ ) and all the interfacial angles are equal to  $90^\circ$  ( $\alpha=\beta=\gamma=90^\circ$ )

There are three types of cubic lattices:

### 1) SIMPLE CUBIC LATTICE

- The points are only at the corner of each unit.
- They have maximum vacant space and are rarely found in nature
- There are 8 corners in simple cubic system and each point occupying a corner of the cell is shared by 8 unit cells.



## 2. BODY CENTRED CUBIC LATTICE

- Each unit cell has one point at the centre of the cube in addition to the points at the corners
- Particles are packed more efficiently than simple cubic
- Each point at the centre of the cell is part of only one unit cell.

## 3. FACE CENTRED CUBIC LATTICE

- They have one point at each of the six faces of the cube, in addition to the points at the corners
- Maximum space is occupied by particles in this case.
- Each point at the corner is shared by 8 unit cells and each face is shared by two unit cells.

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## POINTS TO REMEMBER

- \* A particle (atom, molecule or ion) which is located at the corners of the lattice, is shared by 8 unit cells. Hence the contribution of an atom at the corner to a particular unit cell is one-eighth.
- \* An atom on the face of the unit cell is shared by two unit cells. Hence the contribution of a particle at the face to a unit cell is  $\frac{1}{2}$



\* The constituent particle at the edge center is shared by four unit cells in the lattice. Hence its contribution to only one particular unit cell is one-fourth.

\* An atom at the body center of a unit cell belongs entirely to that unit cell of the lattice. There is no sharing involved.

## CALCULATION OF CONSTITUENT PARTICLES IN DIFFERENT TYPES OF UNIT CELLS

### 1. SIMPLE CUBIC LATTICE

In primitive unit cell the constituent particles are only located at the corners of the unit cell.

As any particle at the corner of a unit cell contributes one-eighth of itself to one unit cell.

Now, in a cube there are a total of eight corners.

So

$$\frac{1}{8} (\text{contribution of corner atoms}) \times 8 (\text{number of corners}) = 1$$

### 2. BODY CENTERED UNIT CELL

$$\left(\frac{1}{8} \times 8\right) + (1 \times 1) = 2$$

↓  
Due to corners

↓  
Due to center

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### 3. FACE CENTERED UNIT CELL

$$\left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right) = 4$$

↓                      ↓  
Due to                  Due to  
corners                  face

~~NUMERICAL~~

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

- ✓ a.  $AB_3$
- b. AB
- c.  $A_3B$
- d.  $A_3B_3$

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Explanation:

$$\text{No. of A atoms} = \frac{1}{8} \times 8 = 1$$

$$\text{No. of B atoms} = \frac{1}{2} \times 6 = 3$$

So compound will be  $AB_3$



# NaCl STRUCTURE

- NaCl has face centred cubic arrangement and in the octahedral structure.
- The chloride ions occupy the corner and face centred positions, the sodium ions occupy the octahedral voids in cubic close structure.
- The unit cell of NaCl contains 4 chloride ions and 4 sodium ions.
- The co-ordination number of NaCl is 6.  
Co-ordination Number: The number of ions that surround another ion in the crystalline lattice is called co-ordination number.  
Co-ordination number of each ion is 6. Each  $\text{Na}^+$  ion is surrounded by 6  $\text{Cl}^-$  ions and each  $\text{Cl}^-$  ion is surrounded by 6  $\text{Na}^+$  ions.
- Distance b.w two consecutive  $\text{Cl}^-$  ions is  $5.63 \text{ \AA}$
- Distance b.w two adjacent ions of different kinds is  $2.815 \text{ \AA}$ . Thus the two ions are not touching each other bcz the sum of their ionic radii is  $2.76 \text{ \AA}$



# LATTICE ENERGY

Lattice energy is a type of potential energy that may be defined in two ways.

1) The lattice energy is the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. This definition causes the value of L.E to be positive, since this will always be an endothermic reaction.

OR

2) The lattice energy is the energy released when gaseous ions bind to form an ionic solid. This process will always be exothermic and thus the value of L.E will be negative.

→ Its values are usually expressed in  $\text{kJ/mol}$

## MEASUREMENT

Lattice energy cannot be measured empirically, but it can be calculated using electrostatics or estimated using the Born-Haber cycle.

## FACTORS AFFECTING LATTICE ENERGY

1. Charge of ions
2. Size (or radius) of ions

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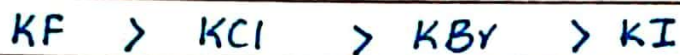
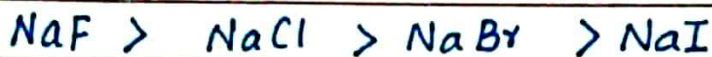
## 1. CHARGE OF IONS

As the charge of ions increase, lattice energy increase.

## 2. SIZE OF IONS

As the size of ion increases, the lattice energy decreases.

(Size increase down the group and decrease along the period)



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## \* CHARGE DENSITY

L.E depends on charge density. Greater the charge density, higher will be LE

$$\text{Charge Density} = \frac{\text{Charge}}{\text{Size}}$$

## \* L.E And SOLUBILITY

L.E is important in predicting the solubility of ionic solids in  $\text{H}_2\text{O}$ . Ionic compounds with smaller lattice energies tend to be more soluble in  $\text{H}_2\text{O}$



# TYPES OF CRYSTALLINE SOLIDS

Four types on basis of forces present between their particles.

## 1. IONIC CRYSTALS

The crystals in which components are ions and the attraction is ionic bond are called ionic ~~ion~~ crystals.

→ Electrostatic (Coulombic) force of attraction called the ionic bond.

TYPICAL PROPERTIES:

1. ~~Hardness~~ ~~very~~

2. Moderate to very high melting points

3. Non-conductors of electricity (but good electrical conductors in the molten state)

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EXAMPLES

$\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{MgO}$

## 2. METALLIC CRYSTALS

STRUCTURAL PARTICLES:

Cations plus delocalized electrons

INTERMOLECULAR FORCES:

Metallic bonds

TYPICAL PROPERTIES:

- Hardness varies from soft to very hard
- Melting point varies from low to very high
- Lustrous, ductile, malleable
- Very good conductors of heat and electricity

EXAMPLES

Na, Mg, Al, Fe, Zn, Cu, Ag

## 3. MOLECULAR CRYSTALS

STRUCTURAL PARTICLES:

Molecules (atoms of noble gases)

INTERMOLECULAR FORCES:

Vander Waal's Forces

TYPICAL PROPERTIES

- soft
- low melting points

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- Non conductors of heat and electricity
- sublime easily in many cases

EXAMPLES:

Noble-gas elements,  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{P}_4$ ,  $\text{S}_8$ ,  $\text{I}_2$ ,  $\text{H}_2\text{O}(s)$

## 4. COVALENT CRYSTALS

STRUCTURAL PARTICLES:

Atoms

INTERMOLECULAR FORCES:

Covalent bonds

TYPICAL PROPERTIES:

- Very hard
- Very high melting point
- Non conductors of electricity

EXAMPLES:

$\text{C}$  (diamond),  $\text{SiC}$ ,  $\text{SiO}_2$

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# STRUCTURE OF ICE

\* Ice - An example of polar molecular crystals.

\* In ice, oxygen atom of water molecule is surrounded by four H-atoms.

→ Each oxygen in ice is at the center of regular tetrahedron.

→ Two H-atoms are linked through covalent bond while the other two H-atoms are linked through Hydrogen bond. This is extended throughout, creating the empty spaces in the structure.

→ The structure of ice is like honey comb with hexagonal channels.

→ When water freezes it occupies 9% more space and its density decreases. That's why ice floats on the surface of water.

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## HYGROSCOPIC SALTS

Some salts absorb moisture from atmosphere. Such salts are called hygroscopic salts. Calcium Chloride ( $\text{CaCl}_2$ ) is a hygroscopic salt. The water molecules absorbed will become part of crystal of  $\text{CaCl}_2$  and may be called as water of crystallization. Such substances are called hydrates.  $\text{CaCl}_2$  can absorb a maximum of  $2\text{H}_2\text{O}$  to form  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . The water of crystallization attached will increase the mass of  $\text{CaCl}_2$ .