Chapter # 6

Solid

① Crystalline Solid:

Properties:

(*) Melting point: Sharp M.P b/c they have regular arrangement of particles

M.P → at which (Solid ⇌ Liquid)

→ less change in volume occur.

M.P ∝ attractive forces

M.P ∝ Symmetry

M.P ∝ $\frac{1}{\text{impurity}}$

other liquid

Solid ⇌ liquid

V ↓ V ↑

* P ↑↑ → V ↓↓ → Solid concentration ↑↑ (M.P ↑↑)

* ($P \propto \frac{1}{\text{Height}}$)

M.P ∝ external pressure

M.P ∝ $\frac{1}{\text{Height}}$

in Case of H_2O:

Solid ⇌ liquid

V ↑ V ↓

P ↑ V ↓ ⟹ Liquid Concent ↑ (M.P ↓)

M.P ∝ $\frac{1}{\text{pressure}}$

Test:

M.P is used to check purity of liquid.

⊛ Geometrical shape:

due to IMF.

⊛ Clevage plane:

* Real plane
* Crystal convert into Similar shape

Size → different
Crystal overall

* definite angle b/w Clevage plane
* weaken IMF
* Basal clevage ⇒ one clevage plane.
* Metallic solid has no clevage plane

Q# which one has zero clevage plane?

a) NaCl b) $H_2O_{(ice)}$ c) Zn d) All

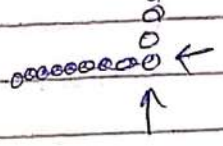
Zn → Metallic solid

⊛ Anisotropy:

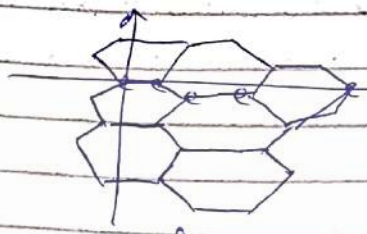
* direction dependant property.

⇓

b/c of different arrangement in different direction.



* Clevage plane
* adsorbance
* Chemical shift
* electrical Conductivity but in Graphite



→ horizontal (high conductivity)

vertical (low conductivity)

Liquid Crystal

* All Crystalline solid = anisotropic

except Cubic solid = isotrophic

(NaCl, MgO)

gas, liquid

Habitat of Crystal

* define internal shape of Crystal
* depend on interfacial angle

face

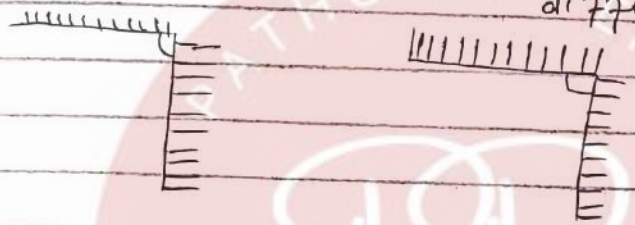
* independant of impurity & Method of preparation, concentration, P, T & V
* depend on
  - => interfacial angle
  - => Nature of Substance

Crystal growth

* Formation of Crystal
* define external shape of a Crystal
* depend on * impurity * P, T, V, concent
  * Methods of prep

⇓

b/c Relative growth of faces different



Symmetry

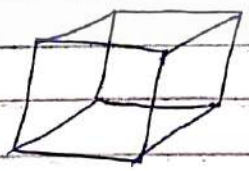
elements:

04

① Plane of Symmetry:

* imaginary plane
* divide Crystal = Equal halves
* donot week IMF
* each plane cover two faces, two edges or two Corners

For Cube: → plane of Symmetry = 09

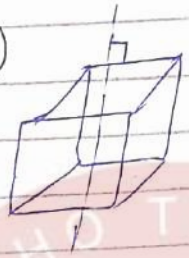


* each plane pass from the center of symmetry.

② Axis of Symmetry:

* imaginary line
* Rotate faces in such away that are indistinguishible.

Cube → Axis of Symmetry = (13)



* The angle b/w plane of axis of rotation is 90°
* Each line cover two faces or two corners or two edges

⇒ faces = $\frac{6}{2}$ = (3) ⇒ edge = $\frac{12}{2}$ = (6)

⇒ Corner = $\frac{8}{2}$ = (4)

③ Center of Symmetry:

* Imaginary point
* which is equidistance from all faces.
* plane of axis of Symmetry pass from it.

Cube → 1

④ Element of Symmetry (Cube):

23

④ Angle of Symmetry:

* Angle by which crystal rotate in such away that Same face is appear by a specific angle.

$$A.S = \frac{360^\circ}{\text{No \# face rotated}}$$

Cube → $\frac{360^\circ}{4} = 90^\circ$

Hexagonal → $\frac{360^\circ}{6} = 60^\circ$

Polymorphism

* valid for a Single Compound
  ↳ but having many shape

* KNO_3 → Rhombohedral
  → orthorhombic

Same:
* Composition
* chemical properties

different:
* Shape
* arrangement of particles.
* physical properties.

Isomorphism

* Valid for many Compounds
  - Same shape

Same:
- * Shape
- * Arrangement of particle.
- * Atomic ratio Same
- * Anion geometry Same

different:
- * Composition
- * Chemical property
- * Physical property.

Allotropy

* element (single)
* polymorphism of element is called allotropy

Same:
- * Composition
- * Chemical properties.

different:
- * physical properties
- * shape:

Transition Temperature

* Two Crystalline form exist
* above or below one form exist.
* White tin $\underset{\text{greater than } 13.2}{\overset{13.2^\circ C}{\rightleftharpoons}}$ Gray tin

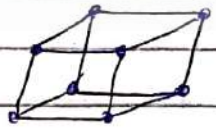
  Less than 13.2
* Valid for polymorphism & allotropy
* physical equilibrium → Solid – Solid equilibrium
* exist below the Melting point.

(#) Crystal lattice / Space lattice

* overall structure of a Crystal.
* made of unit Cell
* Shape depend on unit Cell
* May be one, two or 3 dimensional.

(#) lattice point or lattice spaces:

* position of atom in a Crystal.



* position of lattice point in such away that has ~~Min~~ P.E

Unit Cell

=> All features of Crystal present.

=> internal shape depend on

* interfacial

depend ← habit of Crystal

* External shape depend

face growth → Crystal growth

Unit Cell dimension / Unit cell parameter / Crystallographic element

unit cell parameters → 6 → (3) ~~edges~~ Angles

(3) Length.

Crystal System

on basis of unit cell dimension

* Cubic → most symmetrical ($a=b=c$, $\alpha \neq \beta \neq \gamma$)

Monoclinic

Triclinic → Most unsymmetrical ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$)

orthorhombic

Rhombohedral

Hexagonal

Tetragonal

Bravices lattice

on basis of position of particles

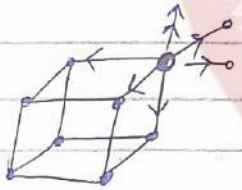
* primitive type
* face center
* Base Center
* Body Center

For 7 Crystal system = 14 Bravices lattice

Cube:

3 Bravices lattice

① simple Cubic:



* All atoms present at Corner
* Total atoms = 8
* density low
* packing efficiency = 52%
* wide " " = 48%

atoms around atom ← * Co-ordination Number = 6

* no # atoms per unit Cell =

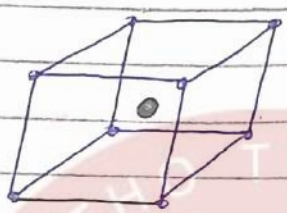
* Corner share by 8 unit Cell
* Contribution by unit cell = $\frac{1}{8}$
* No # atoms per unit Cell = $\frac{1}{8} \times 8$

= ①

* Most Metal => Simple Cubic

New Lec

Body Centered Cubic:



* Total atoms = 9
* density = intermediate
* packing = intermediate
* packing η = 68%
* Wide η = 32%
* Co-ordination number = 8 → 4 above, 4 below

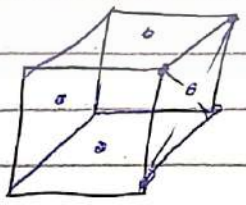
* No # atoms per unit Cell:

Corner = $\frac{1}{8} \times 8 = (1)$

Center = (1) Total atoms = (2) → per unit cell.

* Mostly in Binary Compound

Face Centered Cubic:



* Total atoms = 14
* Density = Maximum
* packing η = Max
* paking η = 74%
* wide η = 26%

* Co-ordination Number = 12

* No # atoms per unit Cell:

Corner = $8 \times \frac{1}{8}$ = (1)

Face = $6 \times \frac{1}{2}$ = (3)

No # atoms per unit cell = (04)

C. No # Ratio:

Simple Cub ..... B.C.C ..... F.C.C

6 : 8 : 12

3 : 4 : 6

No # atoms per unit Cell Ratio:

S.C : B.C.C : F.C.C

1 : 2 : 4

Sharing tendency:

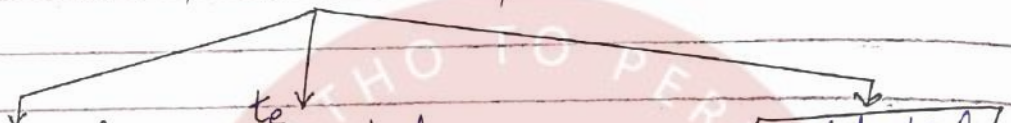
* Corner shared = (8) unit cell
* Face shared = (6) unit cell
* Center shared = Not shared.
* edges shared = (4) unit cell.

Contribution per unit Cell:

* Corner = $\frac{1}{8}$ * Face = $\frac{1}{2}$
* Center = 1 * edge = $\frac{1}{4}$

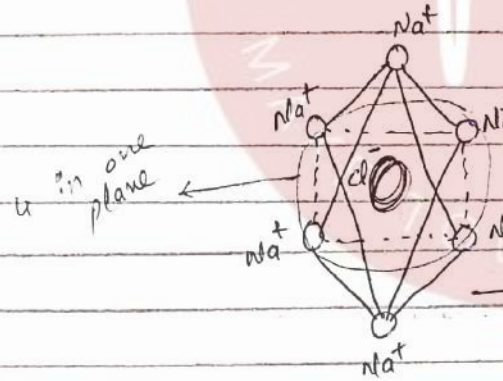
NaCl Crystal

* Crystal system:
  Cubic
* Bravice lattice:
  Face Center Cubic
* Structure:
  Octahedral (8 faces)
* Voids / interstitial spaces



present in NaCl

* Octahedral Voids: made of
  * 6 atoms/molecules



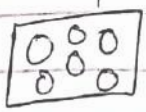
* Co-ordination:
  Cl^- is octahedrally surrounded by Na^+.
  OR
  Na^+ is octahedrally surrounded by Cl^-

  * C.N of Na^+ = 06
  * C.N of Cl^- = 06

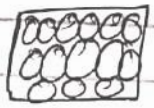
(Corner = 7aces)

* packing

open packing ⇓ spaces present



close packing ⇓ particles closely arranged



Cubic close packing ⇓ present in NaCl

1st layer Similar to 4th layer

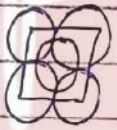
ABCABC

1231

below

above

middle



Hexagonal Close packing ⇓ 1st layer Similar to 2nd layer

ABAB

* No # Octahedral Voids:

No # O.V = No # atoms per unit Cell

b/c No # atom/cell = (4)

(4) → 1 at center

(4) → 3 at edges

* No # atoms / Cell:

① Na^+:

Corner = $8 \times \frac{1}{8} = 1$

Face = $6 \times \frac{1}{2} = 3$

→ 4 Na^+ per unit cell

if this face center cubic then why atoms to edges? (due to octahedral voidy)

② Cl^-:

edge = $12 \times \frac{1}{4}$ = (3)

Center = 1 = (1) → 4 Cl^- per unit cell

* Formula unit:

1 unit cell of NaCl contains (4) formula unit

$4\ Na^+ + 4\ Cl^- \longrightarrow$ (4) NaCl

* Mass of One unit Cell:

1 unit cell = 4 NaCl

= 4 (58.5)

1 unit unit of NaCl = 234 amu

* Mole " " " cell:

Mole " " " NaCl = 234 g

Q#: No # formula unit in 5 NaCl unit Cell? (20)

Sol: (F. unit = No # unit cell × 4) → For NaCl.

Q# if there is 40 formula unit of NaCl then No # unit Cell?

$\frac{40}{4} = (10)$

Q# 80g of X_A^{+-} is body Centered Cubic. NO # formula unit of X_A will be:
(M.mass of X_A = 40g)

Sol:

B.C.C ⟶ No# atoms per/cell = 2

↳ $X^+ + A^- \longrightarrow XA$ (1 formula unit)

Mole = 2 mole

1 mole B.C.C = 1 mole f.unit.

2 " " = 2 mole f.unit

= 2NA

Lattice energy

* Crystal energy
* Amount of energy release/absorb when ionic bond form or break
* KJ/mol
* endothermic/exothermic
* Cannot be find by directly
* Find by Bohn haber cycle.

Condition of L.E:

(Na — Na^+)

* ion ⟶ must be atomic ion.
* ion ⟶ in gaseous state
* ionic Compound ⟶ Solid state

Q# w.o represent L.E?

$Na^+_{(g)} + Cl^-_{2(g)} \longrightarrow NaCl_{(s)}$

$Na^+_{(g)} + Cl^-_{2(g)} \longrightarrow NaCl_{(s)}$

✓ $Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)}$

✗ $Na_{(g)} + Cl_{2(g)} \longrightarrow NaCl_{(s)}$

Factors:

* L.E $\propto$ charge

* L.E $\propto \frac{1}{\text{size}}$

Small size

Q# NaF > NaCl > NaBr > NaI

NaCl > KCl > CsCl → size ↑

For different Group Cy charge:

L.E $\propto$ $^{+3}_{-2}$ > $^{+2}_{-2}$ > $^{+2}_{-1}$ = or $^{-2}_{-1}$ > $^{+1}_{-1}$

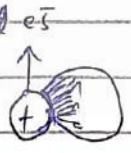
Q# $^{+3\ -2}Al_2O_3$ > $^{+2\ -2}MgO$ > $^{+2\ -1}MgCl_2$ > $^{+1\ -1}NaCl$

Note:

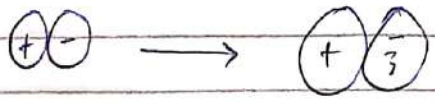
For Cation:

attract more es⁻

Seems share es



L.E $\propto \frac{1}{\text{C.char}}$



Comparison:

(4x)

if NaCl L.E is x then L.E of MgO is:

$Na^{+}Cl^{-}$ = 1 × 1 = (1x)

$Mg^{+2}O^{-2}$ = 2 × 2 = (4x)

Al_2O_3 = $Al^{+3}_2O^{-2}_3$ = 3 × 2 = (6x)

$\frac{Al_2O_3}{MgO} = \frac{6x}{4x} = \frac{3}{2} : 1.5$

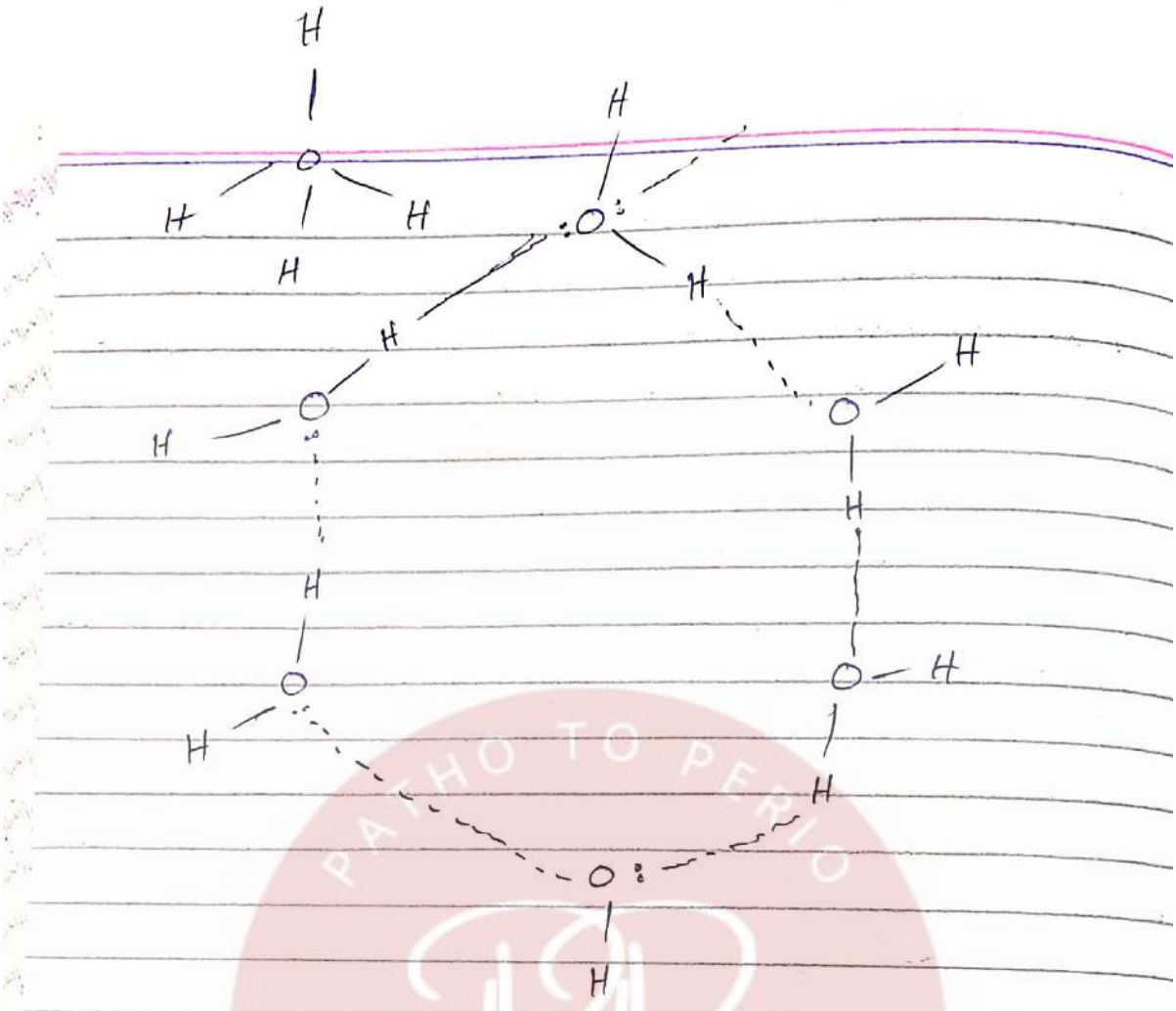
L.E of Al_2O_3 is 1.5 ↑↑ than MgO.

New Lec

Structure of ice

$H_2O_{(l)} \rightleftharpoons ice_{(s)}$

* Volume ↑↑
* 9% ↑↑ in volume
* Hexagonal → contain 6 H_2O
* oxygen in ice → tetrahedral
* H → joining the oxygen
* strong H. bonding



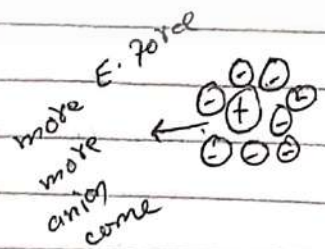
No # H. Bonding = of

Shape of ionic Solid

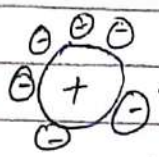
depend on

Concentration pressure impurity
Method of preparation

* electrostatic force
⇓
effect the Co-ordination number.



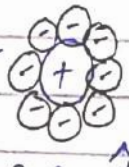
E. force α C.No

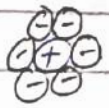


* Radius Ratio:

$$R.R = \frac{\text{radius of Cation}}{\text{radius of anion}}$$

$R.R \propto C.No$ | $R.R \propto$ stability | $R.R \propto \frac{1}{P.E}$





* R.R ↑↑
* C.No high
* Low E
* Stability high

* R.R ↓↓
* C.No low
* high E
* stability ↓↓

Note:

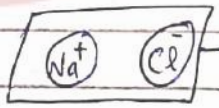
* For a structure R.R → wide / Not fixed
* R.R not depend on T, P, V
* R.R depend on Cation / Anion Nature

⊛ Poor Conductivity:

Na^+Cl^- → exist

poor Conductor ⇓ I.C will exist

Good Conductor → not exist.



→ then ionic Solid not exist.

Shape of ionic Compound exist → poor Conductivity

Types of Solid

- basis of arrangement of particle
  - Amorphous
  - Crystalline (7-Crystal System)
- on basis of forces
  - intermolecular
    - * Molecular Solid
  - intramolecular
    - * Metallic
    - * Ionic
    - * Covalent

Covalent solid	covalent bond (Non-metal)	insulator except (Graphite)	extremly high M.P
ionic solid	ionic bond * Metal & non metal * Non-metal	insulator (solid) Conductor (Molten)	very high
Metallic solid	Metallic bond * Metals	conductor in Solid form	high
Molecular solid	H.B, D.D.F, LDF Non-metal	insulator	Low