

Imperfection/defects in a crystal

The term imperfection or defect arise from the deviation of the ^{ideally perfect} crystal from the periodic arrangements of its constituents. Two types of the defects are (a) point defects (b) line defects.

A. POINT DEFECTS

→ Named after a displaced atom, missing atom or extra atoms. The main or most common point defects are Schottky defect and Frenkel Defect.

→ less common point defects metal excess and metal deficient defects.

Schottky defect: If some of the lattice points of crystals are unoccupied

The different ways by which each ion can be removed is given by $\frac{N!}{(N-n)! n!}$ missing or missing.

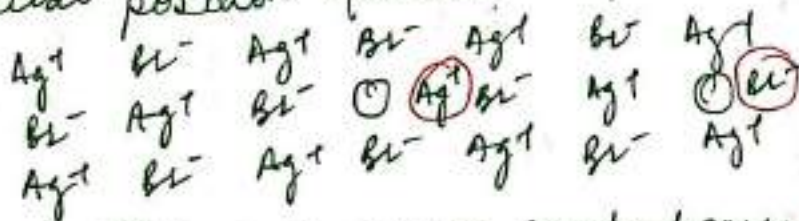


$$\frac{N!}{(N-n)! n!}$$

$N C_n$ ways.

$N \rightarrow$ total no. of ions.
 $n \rightarrow$ Schottky defects

Frenkel defects: when an ion occupies an interstitial position b/w lattice points



→ No. of ways n Frenkel defects can be formed in a crystal having N ions and N_i interstitial spaces in the cell.

$$n = \frac{N!}{(N-n)! n!} \times \frac{N_i!}{(N_i-n)!}$$

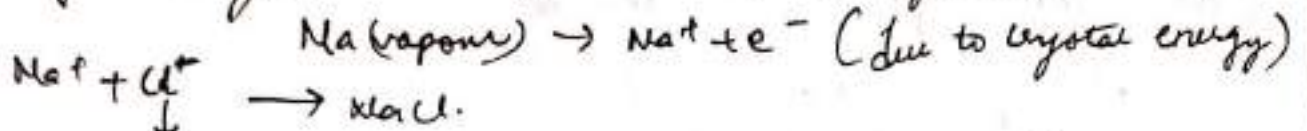
→ no. of Frenkel defects $n = N C_n \times N_i C_n$

(B) Metal Excess defects: - The colour centers

NaCl crystal + Heated in Na vapour \rightarrow Acquire yellow colour



Heating NaCl crystal in Na vapour. Cl^- is removed by Na^+ and is replaced by e^- .

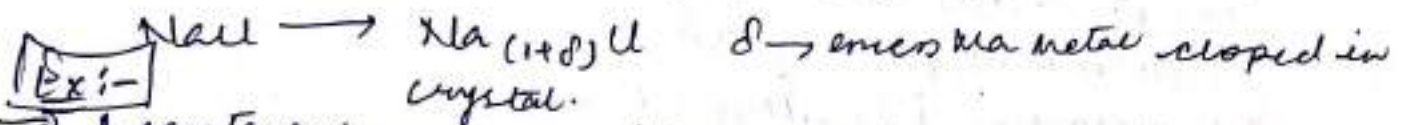


From crystal overall e^- neutrality of crystal is maintained

\rightarrow The extra e^- is shared b/w all Na^+ ions which implies that this e^- is not localized at the valant site of Cl^- .

\rightarrow this delocalized e^- absorb light and ~~promotes~~ to show a transition from ground to excited state.

\rightarrow The non stoichiometric form of NaCl appears coloured. Becor of this site occupied by extra electrons are known as colour centers also called f^- centers (f = false center) false = colour



Ex:- \rightarrow magenta colour of non stoichiometric compound of KCl by its exposure to K metal vapour.

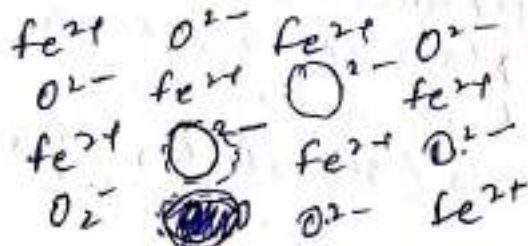
B. 2) Metal Deficiency defects:

When one $+ve$ ion is missing from its lattice site and $-ve$ charge is balanced by nearby metal ion.

\rightarrow this deficiency of metal ion but overall crystal remain neutral.

\rightarrow compounds of transition metals show this defect.

Crystals of FeO , FeS , NiO



metal deficient.

* All types of point defects result in creation of vacancies or holes in crystal lattice. The presence of holes, lowers density as well as lattice energy or stability of crystals. Too many holes in crystal may cause partial collapse of lattice.

(II) Line Defects: Dislocations.

Such imperfections in crystal occurs when periodicity of the atomic lattice array is interrupted along certain directions in crystals. These interruptions along lines of a crystal structure are called line defects. Most common line defect in crystal is dislocation.

(2) types of dislocations are Edge dislocations and Screw dislocations.

* Ionic Solids :-

Ionic solids are considered: ^(a) According to relative location adopted by ions

(b) energetics of resulting str.

(a) Structure :-

Coordination no. of ion is the no. of nearest neighbours of opp. charges. $(N^+ N^-) \rightarrow$ str. e.n. $N^+ =$ no. of cation
 $N^- =$ no. of anion.
 → Bcoz of ^{same size} ~~small~~ size of ions it is impossible to achieve 12-coordinate closed packed ionic str. ∴ they are less dense than metals.

* Best possible packing of ionic crystals achieved is (8:8) in CSL. one charge at the cubic center and at other 8 corners are counter ions. also by CaS (same size)

* When size of ions differs much the 8:8 is not achieved. the common type is (6:6) NaCl (Rock Salt Str) an ion is surrounded by 6 other counter ions.
 Ex: - MX type crystals (KBr, AgCl, MgO, SrO)

⇒ This structure difference is dependent on the value of radius ratio (γ)

$$\gamma = \frac{r_{\text{smaller}}}{r_{\text{larger}}}$$

So,

Radius Ratio

$$\gamma < 2^{-1/2} = 0.414$$

$$2^{-1/2} = 0.414 < \gamma < 0.732$$

$$\gamma > 3^{-1/2} = 0.732$$

Structural type ^{in = tetrahedral holes}

sphalerite (like ZnS)

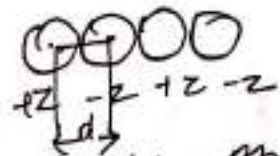
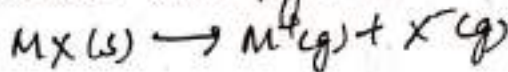
Rock salt

CSCl.

(b) Energetics: lattice energy of a solid is the difference in Coulombic PE of the ions packed together in solid and widely separated as gas.

high lattice energy ⇒ strong inter. b/w ions

lattice enthalpy MX



∗ Madelung Constant → how ions are arranged abt. one another.

$$E_p = - A \times \frac{|Z_A Z_B| N_A e^2}{4\pi \epsilon_0 d}$$

A = Madelung constant.

Z_A, Z_B = charge no. of ions.

d = dist b/w ions centers

d = $r_{\text{cation}} + r_{\text{anion}}$

E_p = Lattice energy, N_A = Avogadro's No.

Liquid crystals (mesomorphic state)

→ There are certain solids which when heated undergo two stage phase transformations one after the other.

Solid $\xrightarrow{\text{temp}}$ turbid liquids $\xrightarrow{\text{temp}}$ clear liquids.

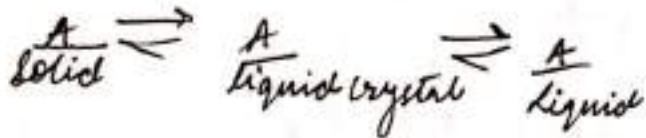
→ Turbid or translucent liquids, however show anisotropy (i.e. diff. arrangement in diff. direction).

→ These liquids are isotropic (same pattern in all directions)

* Since, turbid liquids are called liquid crystals.

→ ^{it is} the mesomorphic state (intermediate) state b/w solids & liquids

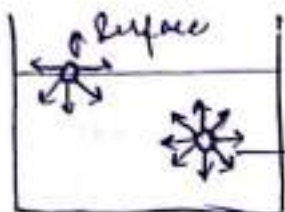
→ At first temp solid changes → turbid liquid (transition point)
Second temp. turbid liquid changes to clear liquid known as melting point.



Liquids

Surface Tension:-

The existence of strong intermolecular forces of attraction in liquids give rise to another imp. property.



→ Bulk molecule is equally attracted in all the directions by other molecules which surround it therefore, cancel the effect of one another.

* A molecule at the surface; The downward attractive forces are greater than the upward forces because there are more molecules of the liquid below than in the air above the surface. These unbalanced attractive forces acting downward tend to draw the surface molecules into the body of the liquid, therefore tend to reduce the surface to a minimum.

→ As attractive forces tend to ↓ the energy of the system.

attractive forces in bulk \gg surface
Bulk liquid has less energy than that of surface.

\therefore surface molecules \rightarrow bulk thus reduces the surface molecules and dist b/w the surface molecules inc. and it becomes larger than the dist b/w bulk molecules.

→ Consequently, the ~~bulk~~ surface molecules tend to move closer to one another in order to acquire a normal dist b/w them as before. As a result of this the drops of liquid or bubbles of gas are spherical in shape.

* Sphere has min. surface for a given volume. and the tendency to contract, surface of a liquid behaves as if it were in a state of tension. This force that tends to contract the surface of liquid is known as surface tension.

* Surface tension (Mathematically): The force in dynes acting at 90° angles to the surface of a liquid along one cm length of the surface.
(CGS) (SI) (N = 10⁵ dynes)
(γ) (dynes/cm) (N/m)
i.e. force in newtons acting at 90° angles to the surface of liquid along 1m length of the surface.

Surface Energy: S.T. reduces the surface area to a min.
 \therefore to \uparrow the S.A., we have to perform work against the force of surface tension. The work that is required to be done in order to extend the area of the surface of a liquid by 1 cm^2 is called surface energy of liquid.

units \Rightarrow (Energy/work) / Area \Rightarrow ergs/cm² or dynes/cm

Same as Surface tension

Surface tension equal to surface energy numerically as well as dimensionally.

$$(\text{work} = \gamma dA)$$

Affect of Temperature on Surface Tension

Molecular energy & Absolute temp.
 \rightarrow Rise in temp. accompanied by increase in energy of its molecules. As, intermolecular forces of attraction decreases with increase in temp.

\times Surface temp. tension of a liquid decreases with rise in temp.

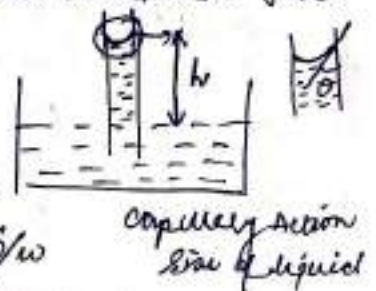
At critical temp, the surface of separation b/w liquid and its vapour disappears, the surface tension falls to zero.

Some effects of Surface Tension

1) S.T. reduces S.A. to minimum. a sphere has minimum S.A. for a given volume.

2) Rise of liquid in a capillary tube

\rightarrow depending upon density & S.T. the liquid rise in a capillary to height 'h' and contact angle b/w liquid and glass zero



\rightarrow Column of liquid in capillary is being supported by some force acting along the surface of the water. This force is known as force of surface tension.

* Stagnometer Principle

1) liquid density = ρ , rise level in capillary tube = h
 r = radius of tube
 $\gamma = s.t$ dyne/cm. / N/m.

\therefore Total force due to S.T, raising the liquid column upward
 $= \gamma \times$ inside circumference of capillary.
 $= 2\pi r \gamma$ (dynes/newton)

force of gravity pulling = weight of the liquid column.
 liquid downward

weight of liquid in column = $V\rho g$, $v =$ vol. of liquid in tube
 $V = \pi r^2 h$ (Cylinder)

hence, in equilibrium

$$2\pi r \gamma = \pi r^2 h \rho g \quad \gamma = \frac{r h \rho g}{2} \text{ dyne/cm.}$$

total force due to S.T. = weight of liquid in column.

\rightarrow till now the contact angle b/w liquid and glass $= 0$. (wetting is perfect)

2) Since, perfect wetting is not always available.

\therefore vertical component of upward force = $2\pi r \gamma \cos \theta$

$$\gamma = \frac{r h \rho g \cos \theta}{2}$$

\rightarrow Mercury \rightarrow Shows a depression in Capillary action.
 i.e. upper level is lower than surface of free liquid.

* Rise and fall may be well understood by the concept of Cohesion and adhesion :-

Cohesion \rightarrow intermolecular forces of attraction b/w like molecules in liquid

adhesion \rightarrow attraction b/w liquid and walls of the capillary.

adhesion $>$ cohesion (liquid wet the walls of capillary)

cohesion $>$ adhesion (liquid does not wet wall)

Same in case of Hg, cohesion is greater therefore a convex meniscus and spherical drop is obtained on a glass surface.

- 3) vapour pressure of liquid is greater when it is in form of small droplets than with that of a plane surface. this is according to kelvin eqn:- $P_0 = V.P. \text{ bulk sample}$

$$\ln(P/P_0) = \frac{2\gamma M}{R T r}$$

- the vapour pressure of P for very small droplet.
 → in sphere the surface of liquid is in a state of tension therefore, when heated immediately released to vapour.

Interfacial Tension

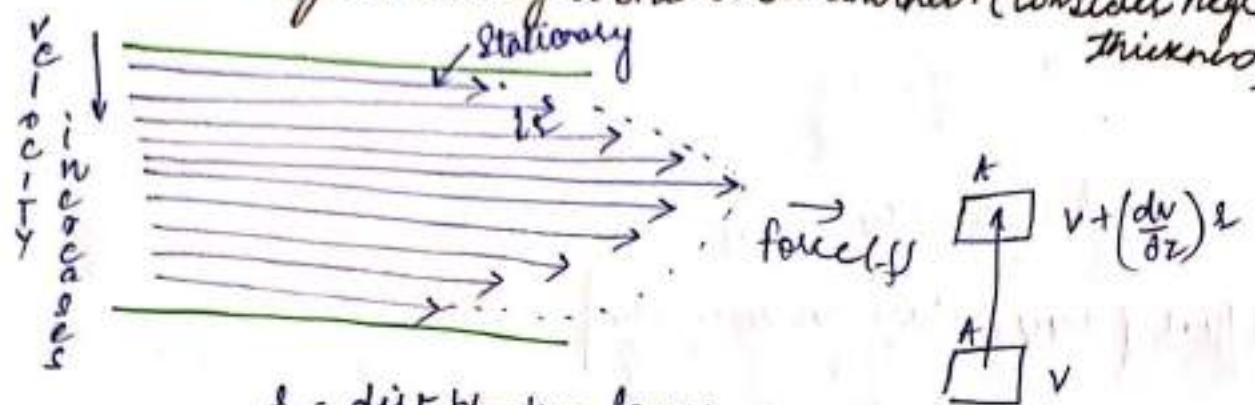
- for two immiscible liquids,
 → The force acting per unit length along the interface is called interfacial tension.
 → Interfacial tension < Surface tension
 as unbalanced forces on the surface of each liquid are partly compensated by the force of mutual attraction b/w the molecules of the two liquids.
 Surface tension → liquid & vapour.
 Interfacial tension → surface of separation b/w two immiscible liq.

Surface Active Agents

- Agents / substances when added lowers its surface tension. these are known as surfactants / surface active agents.
 → like methanol, ethanol, acetone, acetic acid (& water) lowers its surface tension
 → Soaps and detergents.
 As, soaps & detergents lowers the interfacial tension b/w water & grease so as to facilitate the mixing of the two.

VISCOSITY

- flow is characteristic of liquids
- flow of liquid molecules ^{in a tube} may be analyzed in terms of molecular laminae layers arranged one over another. (consider negligible thickness)



$z =$ dist b/w two layers
 $\frac{dv}{dz} =$ velocity gradient along z axis
 $v, v \rightarrow v + z \left(\frac{dv}{dz}\right)$
 slow moving layers faster moving layers
 momentum slower → faster
 viscous faster friction slower retards.

viscosity → may be defined as the resistance that one part of liquid flowing with one velocity offers to another part of liquid flowing with diff. velocity.

OR viscosity → a force of friction b/w two layers of a liquid moving past one another with different velocities.

⇒ to maintain velocity gradient force may be provided along y axis. force is dir. prop. to area and vel. gradient.

$$* f \propto A \left(\frac{dv}{dz}\right) \Rightarrow -\eta A \left(\frac{dv}{dz}\right)$$

Newton's law of viscosity

$A \Rightarrow$ area of contact b/w two layers. $\eta =$ coeff. of viscosity (const. of prop.)

⇒ fluid flows to which this equation applies is laminar or streamlined flow not to turbulent flows. which do not obey eqn. are called non-Newtonian liquids.

Newtonian liquids; η is independent of dv/dz
 non-Newtonian = η changes with dv/dz

Units of viscosity

$$\eta = f \frac{dv_x}{dy}$$

$$\Rightarrow \frac{\text{kg m s}^{-2} \text{ m}}{\text{m}^2 \text{ m/s}}$$

$$\eta = \text{poise} = \frac{\text{dyne sec}}{\text{cm}^2}$$

$$\text{kg/m/sec}$$

$$\text{kg/onscc.}$$

In S.I. $\eta = \frac{\text{kg}}{\text{m.s.}}$

$$\Rightarrow \phi (\text{fluidity}) = 1/\eta (\text{viscosity})$$

Effect of Temperature on viscosity

Oswald's viscometer

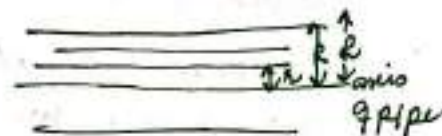
→ η decreases with rise in temp. being about 2 percent per degree rise in temp.

The hole theory:- there are holes and or vacancies in liquid through which the liquid molecules keep on moving continuously into these vacancies. Thus, vacancies keeps on moving cont. otherwise liquid will not be able to flow or move. Liquid molecules therefore need ^{activation} energy to move through these holes. On heating, All energy is supplied thus the liquid can flow easily and faster. Thus, η decreases appreciably with rise in temp.

$$\eta = A e^{+E_a/RT}$$

for gases however η increases with rising temp.

Effect of Pressure on η



η increases with rising pressure, this is in less in no. of holes. As pressure increases, it becomes more diff. for liquid to move thus, η increases.

Reynolds number flow of fluid through pipe of radius 'R'

has been directed by 'NR'

$$N_R = \frac{2R \bar{v} \rho}{\eta}$$

$$V = \frac{\pi R^4 (\Delta P) t}{8 \eta l}$$

$$\bar{v} = \frac{\Delta P (R^2 - r^2)}{4 \eta l}$$

length of pipe

$N_R < 2100$

\bar{v} = avg. bulk velocity of fluid
 ρ = density
 R = pipe radius
 $N_R > 4000$ (turbulent) flow
 $N_R < 2100$ (laminar)