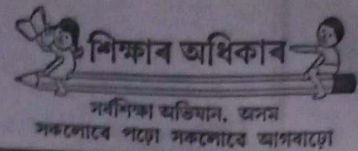


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Unit → 04



Liquids and Solids

Liquids :-

Surface tension -

The existence of strong intermolecular forces of attraction in liquids gives rise to important property known as surface tension.

Surface tension is the energy per unit area of the surface of a liquid, typically measured in units of millinewtons per meter (mN/m).

It arises from the imbalance of intermolecular forces at the liquid-vapour interface.

Factors affecting surface tension -

(1) Temperature — Surface tension decreases with increase in temperature.

(2) Purity — Surface tension can be affected by the presence of impurities or contaminants.

(3) Surfactants — Surface-active agents can significantly reduce surface tension.

Stalagmometer -

A stalagmometer is a device used to measure the surface tension of a liquid.

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It consists of :-

(a) A capillary tube \rightarrow A narrow tube with a precisely controlled diameter

(b) A reservoir \rightarrow A container to hold the liquid

(c) A graduated scale \rightarrow To measure the drop volume

Determination of surface tension using a stalagmometer -

The drop number method :-

Principle - The weight of each drop falling from the stalagmometer is proportional to the surface tension of the liquid. By comparing the numbers of drops formed by equal volumes of two different liquids, the surface tension can be determined.

Formula - If,

γ_1 = surface tension of liquid 1 (eg. water)

γ_2 = surface tension of liquid 2 (test liquid)

n_1 = no. of drops of liquid 1

n_2 = no. of drops of liquid 2

ρ_1 = density of liquid 1

ρ_2 = density of liquid 2

$$\therefore \frac{\gamma_2}{\gamma_1} = \frac{n_1 \cdot \rho_2}{n_2 \cdot \rho_1}$$

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\rightarrow This method is most commonly used for the determination of surface tension of liquids. The method is based on the principle that the weight of the drop, w falling from a vertically held capillary tube is approximately proportional to the surface tension of the liquid. Thus, if γ_1 & γ_2 be the surface tension of two liquids & w_1 & w_2 be the mean weights of their drops respectively falling from the same capillary,

$$\text{then - } \frac{\gamma_1}{\gamma_2} = \frac{w_1}{w_2}$$

The drop falls when its weight is equal to

$$w = 2\pi r \gamma$$

The apparatus used for this purpose consists of a pipette shaped tube with capillary. Flattening of the surface provides a larger dropping surface. It is more convenient to count the drops formed by a given volume of the liquid than to find the weight of drops.

Let n_1 & n_2 be the number of drops of two liquids for the same volume 'v' i.e.,

$$w_1 = \frac{V \cdot \rho_1}{n_1}$$

where ρ_1 & ρ_2 are the densities of two liquids

$$\& \quad w_2 = \frac{V \cdot \rho_2}{n_2}$$

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then, $w_1 = \pi r_1^2 h_1 \rho_1$
 $w_2 = \pi r_2^2 h_2 \rho_2$

Now, $\frac{y_1}{y_2} = \frac{w_1}{w_2}$

$$\Rightarrow \frac{y_1}{y_2} = \frac{\pi r_1^2 h_1 \rho_1}{\pi r_2^2 h_2 \rho_2}$$

$$\Rightarrow \frac{y_1}{y_2} = \frac{r_1^2 h_1 \rho_1}{r_2^2 h_2 \rho_2}$$

Procedure -

- (1) Clean and dry the stalagmometer
- (2) Fill it with distilled water and let a known volume drip through the tip.
- (3) Count the no. of drops formed between two marks.
- (4) Note the density of both liquids.
- (5) Repeat the process with the test liquid & use the formula to calculate the surface tension.

Precautions -

- (1) Ensure that the stalagmometer is clean to prevent error due to contamination.

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- (2) Maintain a constant temperature.
- (3) Avoid air bubbles in the liquid column.

Double Capillary Rise method -

This method is useful when the given liquid is available in a small quantity. If two capillary tubes of radii r_1 & r_2 ($r_2 > r_1$) are immersed in a same liquid whose surface tension is to be determined, then the liquid rises to different height in the tubes & difference in the height between the levels of the liquid in the two capillaries.

Let h_1 and h_2 be the heights of the liquid in two capillaries & r_1, r_2 their radii. Assuming that θ , the angle of contact, is negligible.

$$\text{Surface tension } = \gamma = \frac{r_1 h_1 \rho g}{2}$$

$$\Rightarrow \frac{\gamma}{r_1} = \frac{1}{2} h_1 \rho g \quad \text{--- (1)}$$

Similarly for 2nd capillary tube with radius

$$\gamma = \frac{r_2 h_2 \rho g}{2}$$

$$\Rightarrow \frac{\gamma}{r_2} = \frac{1}{2} h_2 \rho g \quad \text{--- (2)}$$

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Eq. ① - Eq. ② →

$$\gamma \left(\frac{1}{r_1} - \frac{1}{r_2} \right) = \frac{1}{2} (h_1 - h_2) \rho g$$

Viscosity of a liquid -

Viscosity is a measure of a liquid's resistance to flow. It arises due to internal friction between layers of the liquid. A highly viscous liquid flows more slowly (like honey), while a low-viscosity liquid flows easily (like water).

↳ The coefficient of viscosity (η) is defined as the force required to maintain a unit velocity gradient between two parallel layers of fluid one unit apart.

Determination of coefficient of viscosity using Ostwald viscometer -

↳ An Ostwald viscometer is a U-shaped glass capillary tube used to measure the viscosity of a liquid by comparing its flow time with that of a reference liquid (usually water).

Principle -

According to Poiseuille's law, the time required for a liquid to flow through a capillary tube under gravity is proportional

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to its viscosity & density.

$$\frac{\eta_1}{\eta_2} = \frac{t_1 \cdot \rho_1}{t_2 \cdot \rho_2}$$

where
 η_1 = coefficient of viscosity of liquid 1
 η_2 = coefficient of viscosity of liquid 2

t_1 = time taken by liquid 1

t_2 = time taken by liquid 2

ρ_1 & ρ_2 = density of the two liquids.

↳ The simplest apparatus for comparing viscosities of liquids was developed by the German physical chemist W. Ostwald. The Ostwald viscometer consists of two bulbs through a fine capillary tube. One bulb is bigger & another is smaller. Initially, the apparatus should be cleaned with chromic acid and dried. It is mounted vertically & a definite vol^m of water is introduced into bigger bulb & sucked into another bulb. 't' time is required to fall the water from one mark to another. The experiment is repeated with given liquid with 't₁' time also noted. Density of water (ρ_1 & ρ_2) are determined. η_1 & η_2 are coefficient of viscosity.

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$$\text{Now } \eta_1 = \frac{\pi r^4 h \rho_1 g t_1}{8 v l}$$

$$\& \eta_2 = \frac{\pi r^4 h \rho_2 g t_2}{8 v l}$$

$$\Rightarrow \frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

Procedure -

- (1) Clean the ostwald viscometer thoroughly.
- (2) Fill it with the reference liquid (eg. water) upto mark.
- (3) Suck the liquid above the upper mark using pipette & allow it to flow down.
- (4) Record the time taken.
- (5) Use the formula for calculation.

Precautions -

- (1) Keep the temp. constant for both liquids.
- (2) Ensure the viscometer is clean and dry before use.
- (3) Avoid air bubbles during suction.

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Effect of temperature on surface tension and viscosity -

(1) Surface tension

↳ As temp. increases, surface tension decreases

Reason -

With higher temp., the K.E of liquid molecule increases. This reduces the cohesive forces between molecules at the surface, causing the surface tension to decrease.

Graphically -

A plot of surface tension vs. temperature typically shows a downward sloping curve.

(2) Coefficient of viscosity

↳ As temp. increases, the coefficient of viscosity decreases for liquid.

Reason -

At higher temp, liquid molecules move faster reducing internal friction between layers & making it easier for the liquid to flow.

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Note:-

- ↳ For liquid, viscosity decreases with temp.
- ↳ For gases, viscosity increases with temp. (due to increased molecular collision)

Graphically -

A plot of viscosity vs. temperature also shows downward curve for liquids.

Solids :-

Solid

liquid and gas

- | | |
|-----------------------------------|--|
| (1) Definite volume and shape. | (1) does not have definite volume and shape. |
| (2) Incompressible and rigid. | (2) able to flow |
| (3) Hard, ductile, does not flow. | (3) Low intermolecular force. |

↳ Depending on nature of constituent particle and arrangement of constituent particle solids are broadly divided into two groups -
 (a) Crystalline and (b) Amorphous solids

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Crystalline

Amorphous

- | | |
|--------------------------------------|--|
| (1) They have a particular geometry. | (1) No particular geometry |
| (2) They have a sharp melting point. | (2) They melt over a range of temperature. |
| (3) True solid. | (3) Pseudo solid |
| (4) They are anisotropic in nature. | (4) Isotropic in nature. |

Ionic solid -

- ↳ constituent particles are ions (s-block elements always makes ionic compound, eg: BaCl_2 , NaCl etc)
- ↳ The force between the constituent particles is strong electrostatic force or Coulombic force
- ↳ they have high melting and boiling point.
- ↳ they are hard and brittle in nature.
- ↳ Insulator in solid state (neuron ions are not free)

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Covalent Solid —

- ↳ Constituent particles are atoms.
- ↳ Force between them is covalent bond.
- ↳ eg: diamond, graphite, silicon etc.
- ↳ They are very hard and high melting point and boiling point.

Molecular Solid :-

- ↳ Constituent particles are molecules.

Molecular solids are two types -

- (a) Polar molecular solid
- (b) Non-polar molecular solid

Polar molecular solid

- ↳ Constituent particles are molecules containing polar covalent bond between H & F, O or N atom.
- ↳ Force between them is H-bond.
- ↳ Non-conductor (insulator) of electricity.
- ↳ Generally volatile liquids or soft-solid under room temperature.

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(a) Polar molecular solid —

- ↳ Constituent particles are polar molecules & are formed by polar covalent bond.
- ↳ eg: HCl , NO_2 , SO_2 , SO_3 etc
- ↳ Force between them is dipole-dipole interaction.
- ↳ They are insulator & they exist as gas or liquid.
- ↳ They are soft.

(b) Non-polar molecular solid —

- ↳ Constituent particles are non-polar molecules
- ↳ eg: I_2 , H_2 , N_2 , Cl_2 , F_2 etc
- ↳ Force between them is dispersion force or London force (very weak force)
- ↳ They exist as gas & they are soft.
- ↳ They are insulator.
- ↳ They have very low melting point.

Different types of cubic unit cells —

There are mainly three types of cubic unit cells

- (a) Simple cubic (SC)
- (b) Body-centered cubic (BCC)
- (c) Face-centered cubic (FCC)

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(a) Simple unit cell / simple cubic —

When constituent particles are only present at the corners of the unit cell then it is called simple cubic unit cell.

↳ There are 8 particles present at corners.

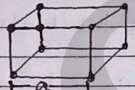
↳ Contribution of each particle at corner is $\frac{1}{8}$

↳ Total no. of particles present in simple unit cell $\approx 8 \times \frac{1}{8}$

↳ $a = 2r$ $\approx 1 \rightarrow$ (no. of effective atom per unit cell)

(b) Body centred cubic —

↳ In this type of unit cell, the constituent particles are not only present at the corners but also present in the body centre.



↳ There are 8 particles present at corners

↳ Contribution of each particle at corner is $\frac{1}{8}$.

↳ There one particle present at body centre &

↳ Contribution is 1.

↳ Total no. of particles $\approx 8 \times \frac{1}{8} + 1$

≈ 2

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Here, $a = \frac{4r}{\sqrt{3}}$

(c) Face-centred cubic —

In this type of unit cell, the constituent particles are not only present at the corners but also present at centre of each face.

↳ There are 8 particles present at corners & its contribution is $\frac{1}{8}$.

↳ There are 6 particles present at face centre and contribution of each is $\frac{1}{2}$.

↳ Total no. of particles $\approx 8 \times \frac{1}{8} + 6 \times \frac{1}{2}$

≈ 4

↳ $a = \frac{4r}{\sqrt{2}}$

Crystal systems —

Crystal systems are classification of crystal structures based on their symmetry and lattice parameters. There are seven crystal systems —

- (i) Cubic, (ii) Tetragonal, (iii) Orthorhombic
- (iv) Monoclinic, (v) Triclinic, (vi) Hexagonal,
- (vii) Trigonal

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Crystal system	Axial length	Axial angle	Example
(1) Cubic	$a=b=c$	$\alpha=\beta=\gamma=90^\circ$	$\text{NaCl, KCl, Cu, diamond etc.}$
(2) Tetragonal	$a=b \neq c$	$\alpha=\beta=\gamma=90^\circ$	$\text{CuSO}_4, \text{TiO}_2, \text{SnO}_2 \text{ etc.}$
(3) Orthorhombic	$a \neq b \neq c$	$\alpha=\beta=\gamma=90^\circ$	$\text{BaSO}_4, \text{KNO}_3, \text{Rhombohedral Sulphur}$
(4) Hexagonal	$a=b \neq c$	$\alpha=\beta=90^\circ, \gamma=120^\circ$	Graphite, ZnO
(5) Trigonal	$a=b=c$	$\alpha=\beta=\gamma \neq 90^\circ$	$\text{CaCO}_3, \text{HgS}$
(6) Monoclinic	$a \neq b \neq c$	$\alpha=\gamma=90^\circ, \beta \neq 90^\circ$	Sulphur, Na_2SO_4
(7) Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{CuSO}_4, \text{HgO}$

Calculation of no. of particle per unit cell -

(1) A particle present at corner is shared by 8 other unit cell. Hence contribution of each particle present at corners per unit cell is $\frac{1}{8}$.

(2) An atom present at face is shared by two unit cell and contribution of each atom present at face per unit is $\frac{1}{2}$.

(3) If an atom is present at the body centre is shared by no other unit cell. Hence its contribution is 1.

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Bravais lattice types -

There are 14 Bravais lattice types, which are grouped in 7 crystal systems. Bravais lattice are the distinct lattice types which describe the periodic arrangement of points (representing ions, atoms or molecules).

Here are the 14 Bravais lattices -

(1) Cubic - All angles $=90^\circ$, all sides equal ($a=b=c$)
 ↳ Cubic systems are classified into 3 parts -

- (i) Simple cubic
- (ii) Body-centered cubic. } Discuss earlier.
- (iii) Face-centered cubic

(2) Tetragonal - All angles $=90^\circ$, sides are $a=b \neq c$
 These are of two types -

- (i) Simple tetragonal :- Points at the corners of a rectangular prism where height differs from the base. Rare in nature.
- (ii) Body-centered tetragonal :-

↳ Corners + one point at the body corner.

(3) Orthorhombic - All angles $=90^\circ$, $a \neq b \neq c$
 These are of two types -

- (i) Simple orthorhombic :-
- ↳ Points only at corners. eg: Sulphur.

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(ii) Body centered orthorhombic :-
↳ corners + body center. eg: Uranium.

(iii) Face centered orthorhombic :-
↳ corners + centers of all faces. less common

(iv) Base centered orthorhombic :-
↳ corners + centers of two opposite faces.
eg: Gypsum.

(4) Monoclinic :- Two angles 90° , one angle $\neq 90^\circ$,
 $a \neq b \neq c$

↳ Two types are -

(i) Simple monoclinic :-
↳ points only at corners. eg: Monoclinic Sulphur

(ii) Base centered monoclinic :-
↳ corners + centers of two opposite faces.
eg: Cinnabar.

(5) Triclinic :- no angles 90° , $a \neq b \neq c$

↳ (i) Simple triclinic :-
Least symmetric, only corner points.
eg: Kyanite.

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(6) Hexagonal :- Two angles 90° , one angle 120° ,
Sides $\rightarrow a \neq b \neq c$

↳ (i) Simple Hexagonal :-
Points at corners of a hexagon repeated
vertically.
eg: Graphite, Zinc

(7) Rhombohedral (Rhombohedral)

all angles $\neq 90^\circ$, Sides: $a = b = c$

↳ (i) Simple Rhombohedral -
Skewed cube with equal sides but
non-right angles.
eg: Quartz.

Defects in crystals :-

Any departure or irregularities from perfect
ordered arrangements of constituents (particles)
in the crystal is called imperfection or defect

Types of defects :-

↳ There are two types of defects -

- (i) Point defects
- (ii) Line defects

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(1) Point defects: They are irregularities of deviation from ideal arrangement around a point or an atom in a crystal.

(2) Line defects: They are irregularities of deviation from ideal arrangement in entire row of the lattice points.

(1) Point defects :-

They are classified into three types.

- Stoichiometric defects.
- Non-stoichiometric defects.
- Impurity defects.

(a) Stoichiometric defects -

↳ These are the point defects that do not disturb the stoichiometry of the solid. i.e., the ratio betⁿ cation and anion remain same as represented by molecular formula.

Stoichiometric defects are of two types -

- Vacancy defects
- Interstitial defects.

↳ When some of the lattice sites are vacant, the crystal is said to have vacancy defect. This defect decrease the density of the solid. This is shown by non-ionic solids.

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↳ When some constituent particles occupy an interstitial site, the crystal is said to have interstitial defect. This defect increases the density of the solid.

~~Interstital defect~~

~~In this defect~~

(b) Non-stoichiometric defects :-

These are those defect in which the stoichiometry of the solid gets disturb i.e., ratio between different types of constituent particles is changes.

These are of two types -

- Metal excess defect.
- Metal deficiency defect.

↳ Metal excess defect produced due to presence of excess of positive ion (cation)

This can be achieved by two ways.

(i) Metal excess defect due to anion vacancy -

This defect shown by alkali metal halide like KCl, NaCl, KBr etc in which some of the negative ions missing from the lattice site leaving a hole & this holes are occupied by an extra free electron present in the crystal. This type defects shown by compounds showing Schottky defect.

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(b) Metal excess defect due to presence of extra cations at interstitial sites:

Metal excess defects can also be created if some extra cation occupied interstitial site and in order to maintain electrical neutrality same no. of anions are also occupied interstitial site. These defect shown by compounds showing Frenkel defect.

↳ Metal deficiency defect are many solids which are difficult to prepare in the stoichiometric composition & contain less amount of the metal as compared to the stoichiometric proportion.

(c) Impurity defects:

This defect arises when foreign atoms are present at the lattice site in place of host atoms or at the vacant interstitial sites.

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Schottky defect:

These are those stoichiometric defects in which equal no. of cation & anion missing from the lattice site in order to maintain electrical neutrality. eg: NaCl.

Properties:

- (1) Compound showing Schottky defect should have small difference between size of cation and anion.
- (2) Element showing Schottky defect should have high coordination number.
eg: NaCl, NaBr, AgBr, KCl etc

Frenkel defect:

In this defect an ion is dislocate from its lattice sites and occupy an interstitial site. The electrical neutrality as well as stoichiometry remain unchanged. This defect does not affect the density of the solid.

Properties:

- (1) Compound showing Frenkel defect should have large difference between size of cation and anion.
- (2) Element should have low coordination no.

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Q. Write difference betⁿ Schottky and Frenkel defect.

Ans:- Schottky defect

Frenkel defect

(1) These are those stoichiometric defects in which equal no. of cation & anion missing from the lattice sites.

(1) In this defect, an ion missing from the lattice site and occupies an interstitial site.

(2) This defect decrease the density of the solid.

(2) This defect does not effect the density of the solid.

(3) Element should have high coordination no.

(3) Element should have low coordination no.

(4) Alkali metal halide shows this effect.

(4) Alkali metal halide does not show this defect.

Line defects :- These are of two types :

- (a) Edge dislocations - Distortions along a line in the crystal lattice.
- (b) Screw dislocations - Helical distortions in the crystal lattice.

— X —

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