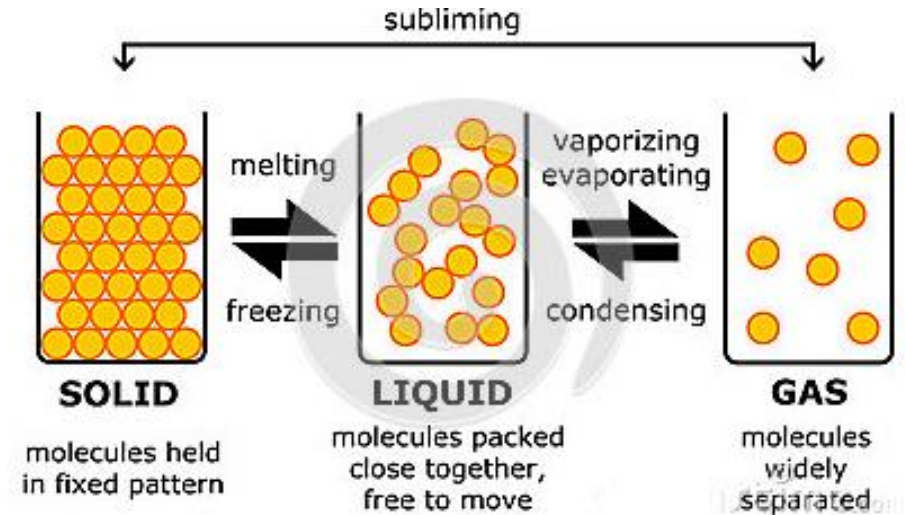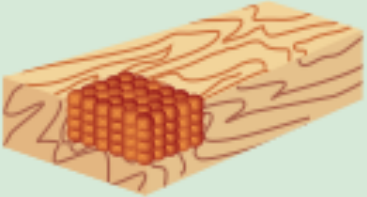# LIQUID STATE

- Intermediate state of matter between solid and gaseous states.

- Thermal energy and intermolecular forces are intermediate.

COMPARISON OF LIQUIDS WITH SOLIDS & GASES

1. **Intermediate attraction between particles.**

2. **More space between particles than solids.**

3. **Particles are not in a fixed position.**

4. **The attraction between particles keeps the volume of liquid constant.**

5. **Liquids will flow like gases.**

6. **Take the shape of the container.**

7. **Compressibility is limited and lower than gases**

	Properties	Solids	Liquids	Gases
1	Mass	Definite	Definite	Definite
2	Shape	Definite	Acquires the shape of the container	Acquires the shape of the container
3	Volume	Definite	Definite	Indefinite
4	Compressibility	Not possible	Almost Negligible	Highly Compressible
5	Fluidity	Not possible	Can flow	Can flow
6	Rigidity	Highly rigid	Less rigid	Not rigid
7	Diffusion	Slow	Fast	Very fast
8	Space between particles	Most closely packed	Less closely packed	Least closely packed
9	Interparticle force	strongest	Slightly weaker than in solids	Negligible

INTERMOLECULAR FORCES OF ATTRACTION

- The attractive or repulsive forces between molecules.
- Intermolecular forces are electrostatic in nature.
- Weaker than chemical forces.
- Operate over large distances.
- Intermolecular forces determine the properties of a substance

Attractive intermolecular forces:

van der Waals forces

- Dipole-Dipole Forces

- Dipole – Induced Dipole Forces

- Induced Dipole – Induced Dipole Forces

Ion – Dipole Forces

Hydrogen Bonding

- Intermolecular H-bonding

- Intramolecular H-bonding

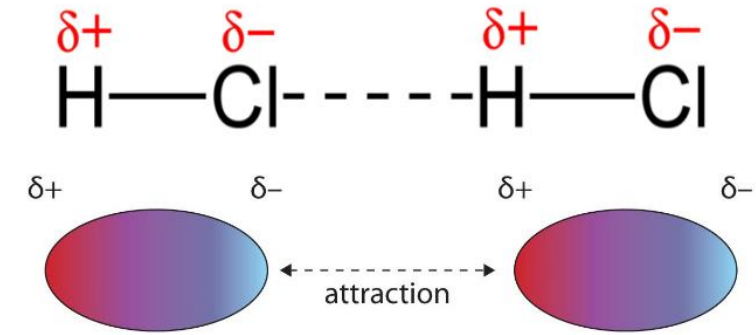**DIPOLE – DIPOLE FORCES: Keesom forces**

- **Attractive intermolecular forces between polar molecules.**

- **Opposite charges of two dipoles attract each other electrostatically.**

- **Molecules attain oriented arrangement.**

- **Strengths ranging from 5 to 20 kJ per mole.**

- **Interaction energy depends on the dipole moments of interacting dipoles.**

$$V = -\frac{2}{3kT}\left(\frac{\mu_1\mu_2}{4\pi\varepsilon_0}\right)\frac{1}{r^6}$$

- **More polar molecules interacts strongly.**

- **As the temperature is increased the dipole-dipole interaction decrease.**

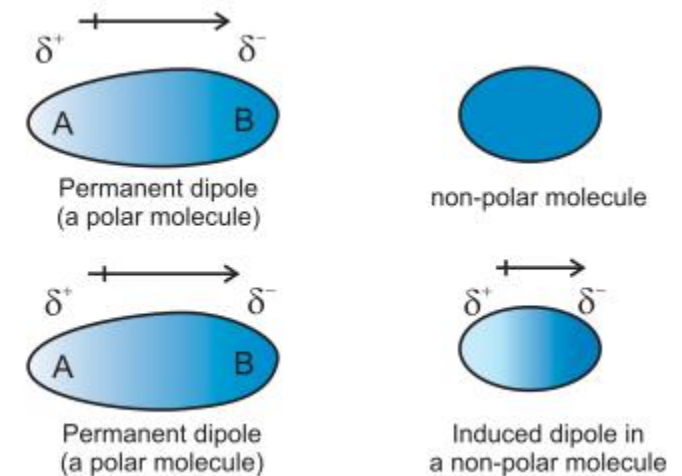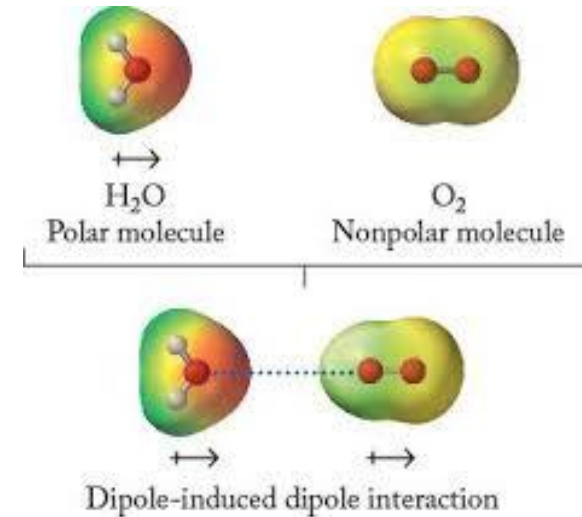- **Greater the dipole-dipole forces greater will be the melting and boiling points.**

  For example: B.P. of N_2 is -196 ^{0}C   & O_2 is -183 ^{0}C

  B.P. of NO is -151 ^{0}C

DIPOLE – INDUCED DIPOLE FORCES

- Attractive intermolecular forces between polar and non-polar molecules.

- Polar molecule polarizes the non-polar molecule and induces a dipole moment.

- The non-polar molecule is now said to be an induced dipole.

- Non-polar molecules of large size can be easily polarized.

- Opposite charges of two dipoles attract each other electrostatically.

- Interaction energy depends on the dipole moment of the polar molecule and polarizability of non-polar molecule.

$$V = -\frac{\mu_1^2 \alpha_2}{4\pi\varepsilon_0} \times \frac{1}{r^6}$$

- The dipole- induced dipole forces is responsible for the solubility of oxygen in water.


H_2O
Polar molecule

O_2
Nonpolar molecule

Dipole-induced dipole interaction

$\delta^+ \quad \delta^-$

A   B

Permanent dipole
(a polar molecule)

non-polar molecule

$\delta^+ \quad \delta^-$

A   B

Permanent dipole
(a polar molecule)

$\delta^+ \quad \delta^-$

Induced dipole in
a non-polar molecule

INDUCED DIPOLE – INDUCED DIPOLE FORCES : London Forces

- **Attractive intermolecular forces between non-polar molecules.**

- **Momentary distortions in the electron distribution constantly produces instantaneous dipoles.**

- **Attractive interactions between the instantaneous fluctuating dipoles produce London forces.**

- **Weakest van der Waal's forces (1 to 10 kJ per mole).**

- **Interaction energy depends on polarizability of non-polar molecule.**

$$V = -\frac{3}{2}\alpha_1\alpha_2\left(\frac{I_1 I_2}{I_1 + I_2}\right) \times \frac{1}{r^6}$$

   I_1 and I_2 are the respective first ionization energies of molecules.

- **These weak attractive forces exist in the sample of O_2 or N_2 or noble gases.**

- **Larger the molecules, greater the volume of space occupied by the electron clouds and the larger the momentary distortions in the electron cloud of the atoms - Hence large dispersion forces.**
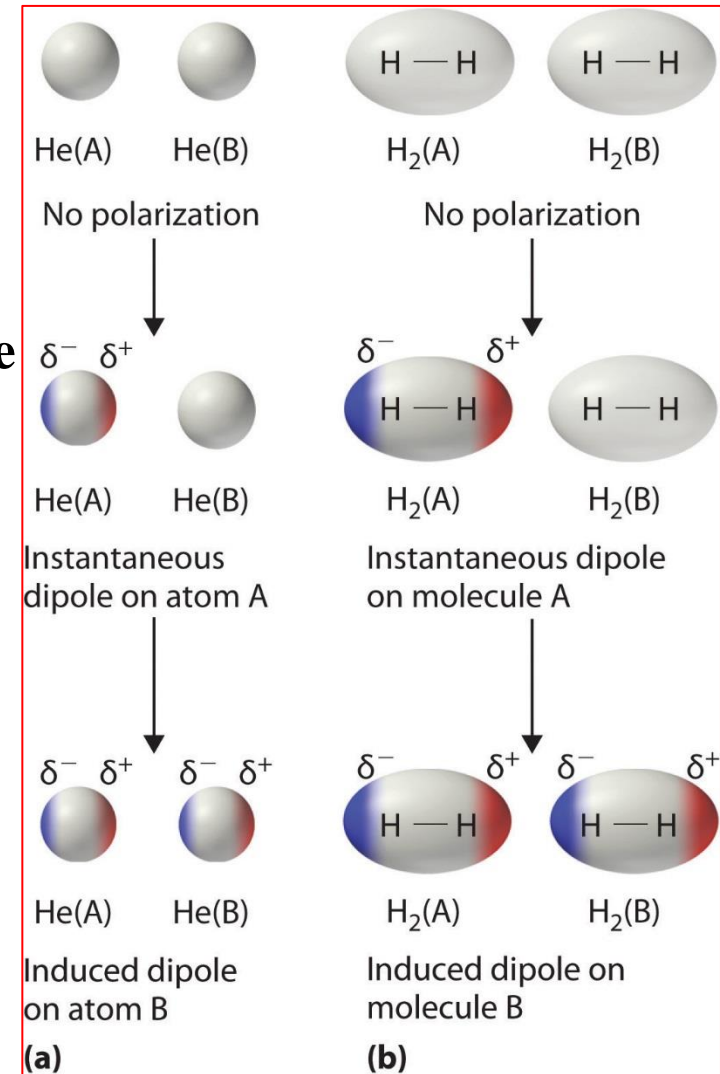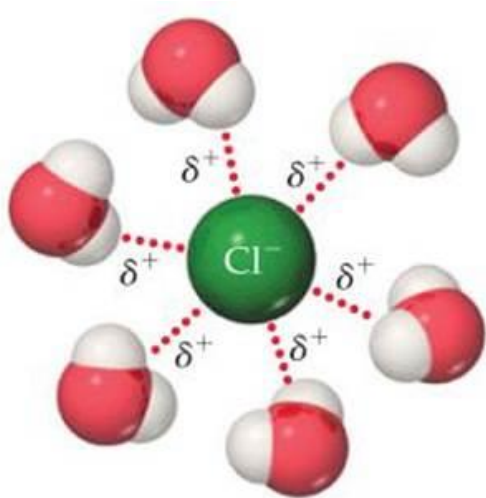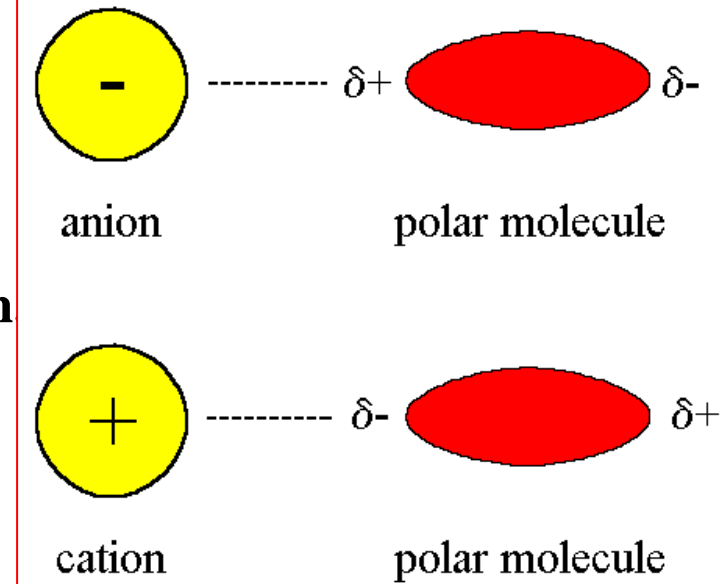
ION – DIPOLE FORCES

- **Attractive intermolecular forces between ion and dipole molecules.**

- **Opposite charges attracts each other.**

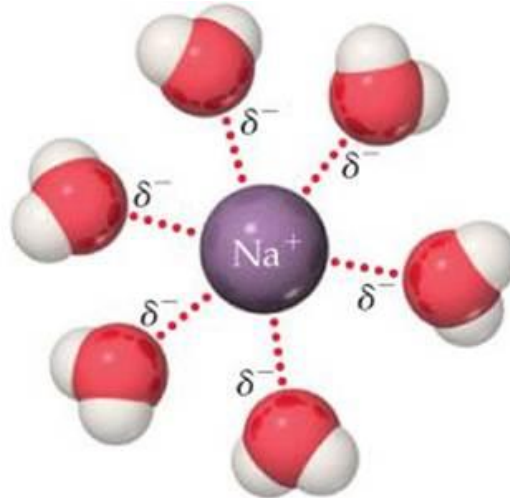- **Interaction energy depends on orientation of the dipole and charge of the ion**

$$V = -\frac{e\mu}{r^2}$$

    e **is the charge on the ion and μ is the permanent dipole moment.**

- **Responsible for the solvation of ions in water.**

anion   polar molecule

cation   polar molecule

Positive ends of polar molecules are oriented toward negatively charged anion

Negative ends of polar molecules are oriented toward positively charged cation

HYDROGEN BONDING

- **A special case of dipole-dipole interactions.**

- It results from the attractive force between a **hydrogen** atom covalently **bonded** to a very electronegative atom such as a N, O, or F atom and another very electronegative atom.
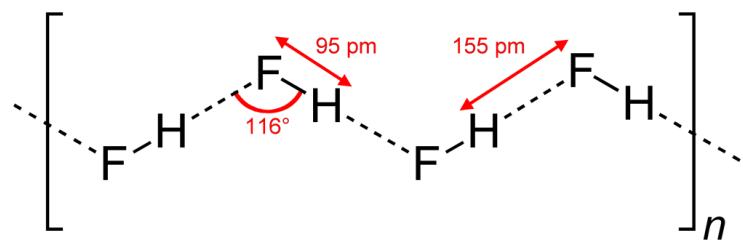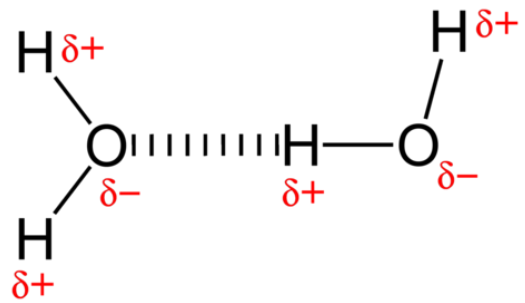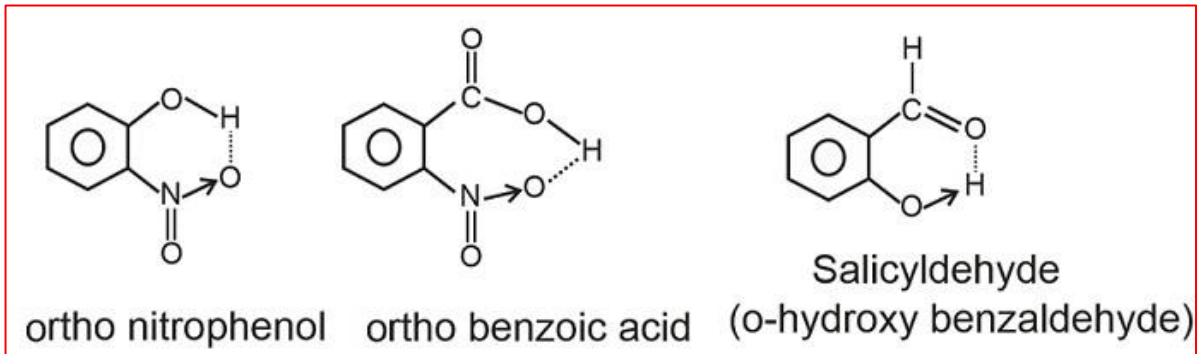

- **The energy of hydrogen bond is between 20 – 100 kJ per mole.**

INTRAMOLECULAR & INTERMOLECULAR HYDROGEN BONDING

ortho nitrophenol   ortho benzoic acid   Salicyldehyde (o-hydroxy benzaldehyde)
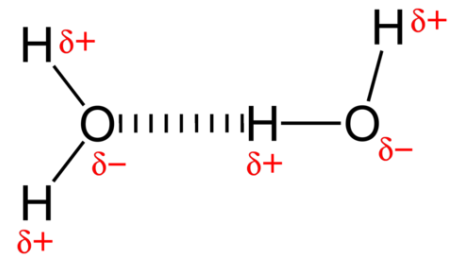
- Intermolecular H Bond – Association of molecules
- Physical properties changes

- H Bond within the molecule – Exist as discrete molecules
- No effect on physical properties.

VISCOSITY

- Viscosity is the **resistance** **o**ne part of a fluid offers to the flow of another part of it.

- It may be regarded as the **internal friction** operating within a fluid produced by the shearing effect, which results when one layer of fluid moves past another.

- *Viscosity of a liquid arise due to the intermolecular forces that hold its layers together* and thereby oppose the movement of layers past one another.

- Viscosity varies from liquid to liquid because the strength of intermolecular forces also varies from liquid to liquid.

- Liquids which offer less resistance to flow are said to be less viscous or said to have low viscosity. Similarly, liquids which offer greater resistance to flow are said to be more viscous or said to have high viscosity.
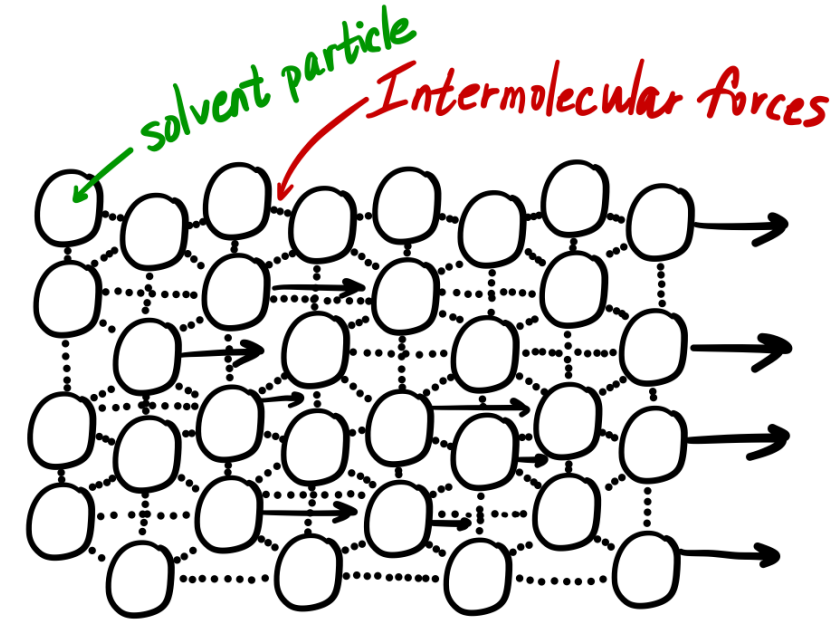
LAMINAR FLOW OF LIQUIDS:

- Consider the laminar or streamline flow of the layers of the liquid in which the adjacent layers of molecules move at different velocities.

- The moving of molecules in layers is called LAMINAR FLOW OR STREAMLINE FLOW.

- The velocity increases with increase in distance from the stationary surface. The intermolecular forces are responsible for the frictional force called **viscous drag** from adjacent slow moving layer.

- Retarding influence of the slower-moving layer on the adjacent faster-moving layer is manifested as resistance to flow or **viscosity**.

Zero velocity

Laminar flow

Highest velocity
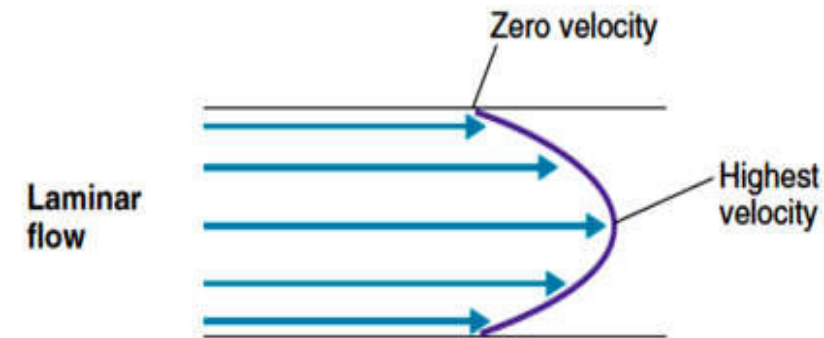
Viscosity & Intermolecular Forces:

The stronger the intermolecular forces, greater the resistance to flow and greater will be the viscosity.

Water - 10.08 milliPoise,

Ether – 2.33 milliPoise &

Glycerol – 10,000 milliPoise

The variation in viscosity values are due to variation in the extent of intermolecular forces.

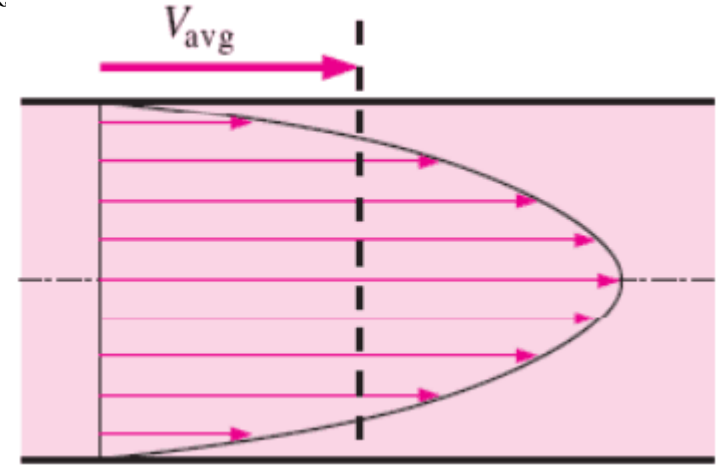Glycerol possess extensive H-bonding and consequently high viscosity.

Coefficient of Viscosity (η)

External force must be applied to overcome the viscous drag and maintain the movement. The viscous force is proportional to the area of contact (A) and velocity gradient (dv/dz).

$$F \propto \frac{dv}{dz} \qquad F \propto A$$

$$F \propto A \cdot \frac{dv}{dz}$$

$$F = \eta \cdot A \cdot \frac{dv}{dz} \qquad \text{where, } \eta = \text{coefficient of viscosity or viscosity.}$$

The negative sign indicates that the force tends to retard the flow.

$$\frac{F}{A} = \eta \qquad when \ \frac{dv}{dz} = 1$$

Hence, Coefficient of viscosity is defined as the force per unit area required to maintain a unit velocity difference between two adjacent parallel layers of a fluid unit distance apart.

Units of Coefficient of Viscosity (η)

Co-efficient of viscosity is given as $\quad \eta = - \cdot \dfrac{F}{A} \cdot \dfrac{dz}{dv}$

Substituting the suitable units, $\qquad \eta = - \cdot \dfrac{N}{m^2} \cdot \dfrac{m}{ms^{-1}} = Nm^{-2}s \qquad$ or, $\qquad Pa\ s$

Corresponding CGS unit is $\qquad dyne\ cm^{-2}\ s$

The unit $dyne\ cm^{-2}\ s$ is also known as Poise (P). One Poise is given by:

$1\ Poise = 0.1\ Pa \cdot s$

FLUIDITY

The reciprocal of viscosity is called the fluidity (ϕ). It is given by

$\phi = \dfrac{1}{\eta}$

Factors Affecting Viscosity

- **Temperature** : Increase of temperature decreases the viscosity

- Presence of colloidal matters increases the viscosity

- In a homologous series, as the molecular mass increases the viscosity increases.

- Viscosity increases as the branching of the alkyl chain increases.

- Viscosity increases due to intermolecular hydrogen bonding.

Viscosity & Temperature

- The kinetic energy of the molecules increases as the temperature increases.

- The increase in kinetic energy reduces the intermolecular forces of attraction. Consequently viscosity of the liquid decreases with temperature.

- **Arrhenius Equation**:

$$\eta = Ae^{E/RT}$$

Where, η is the coefficient of viscosity,

A and E are constants characteristics of the liquid.

$$\ln \eta = \ln A + \frac{E}{RT} \qquad\qquad \log \eta = \log A + \frac{E}{2.303RT}$$

If η_1 and η_2 are the viscosities of a liquid at two temperatures T_1 and T_2, then the above equation can be modified as:

$$\log \frac{\eta_1}{\eta_2} = \frac{E}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

This equation can be used to calculate the constant E.

Determination of Co-efficient of Viscosity:

- **_Ostwald's viscometer_** is used to measure the viscosity of a liquid and compare the viscosities of two liquids.

- In this method a fixed volume of the liquid is allowed to fall under its own weight and the time required for the flow is noted.

- The driving pressure (P) for the flow in this experiment is given by:

$$P = hdg$$

The Poiseuville's equation for coefficient of viscosity $\quad \eta = \dfrac{\pi P r^4 t}{8Vl}$
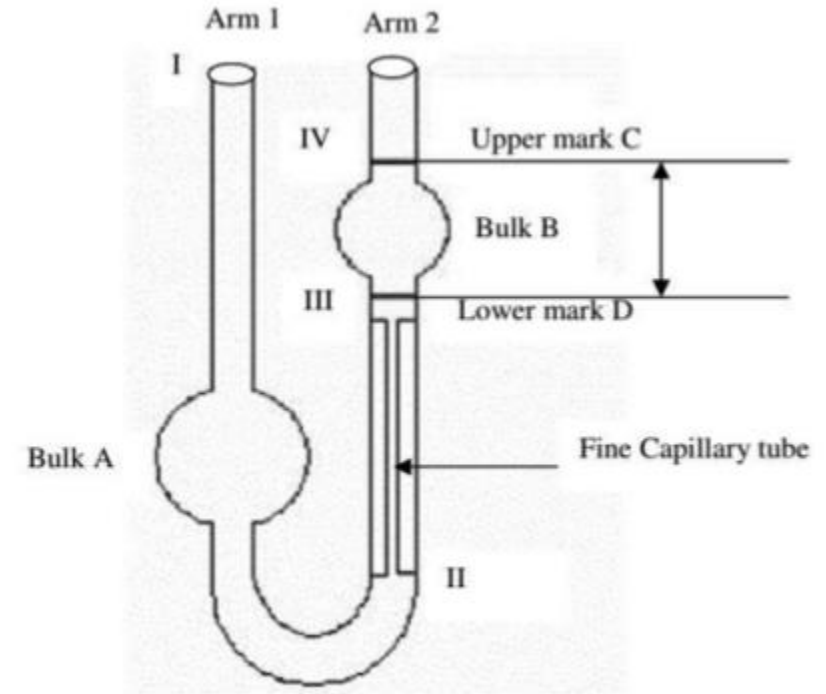
$$\eta = \dfrac{\pi r^4 hdgt}{8Vl}$$

If equal volumes of two liquids 1 and 2 are allowed to flow through the same tube under identical conditions of T and P, then the above equation can be modified as:

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

SURFACE TENSION

- It is a property related to intermolecular attractive forces within a liquid.

- A molecule in the interior - No resultant attractive force

- The molecules present at the surface - Pulled downward and sideways by other molecules

- *Due to the resultant inward pull - state of tension like a stretched elastic film or membrane – SURFACE TENSION*

Cause of Surface Tension:

- intermolecular attractive forces within a liquid

- Surface tension will be greater for liquids with greater intermolecular forces of attraction.

- **Surface Tension** *is the property of the surface of a liquid that allows it to resist an external force, due to the cohesive nature of its molecules."*
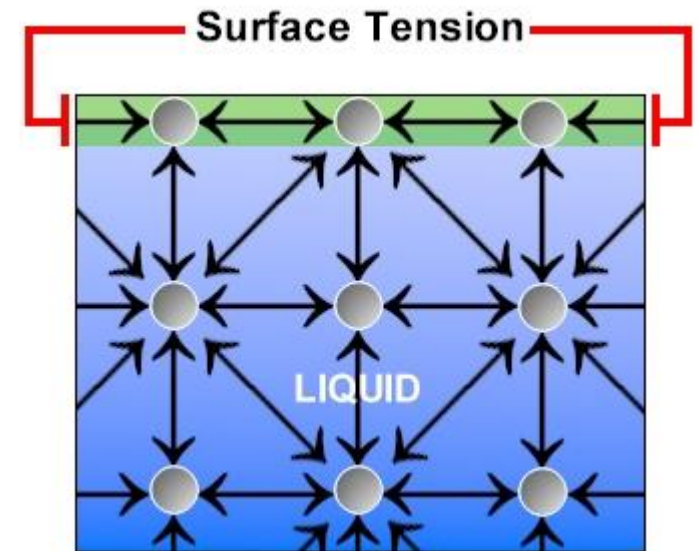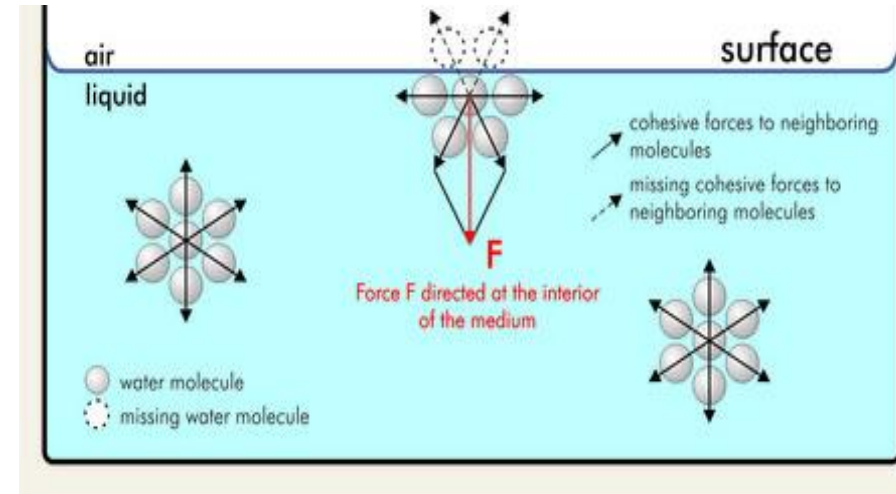
Definition and Unit of Surface Tension:

- The force acting at right angles to any line of unit length along the surface of the liquid.

$$\gamma = \frac{F}{l}$$

- Its unit is **Nm^{-1}** in the SI system and **dynes cm^{-1}** in the cgs system.

- **Surface energy** is a property related to surface tension, numerically as well as dimensionally.

- Surface energy is defines as the work or energy required to increase the surface area of a liquid by 1 unit.

- Its unit is Jm^{-2} in the SI system and ergscm^{-2} in the cgs system.
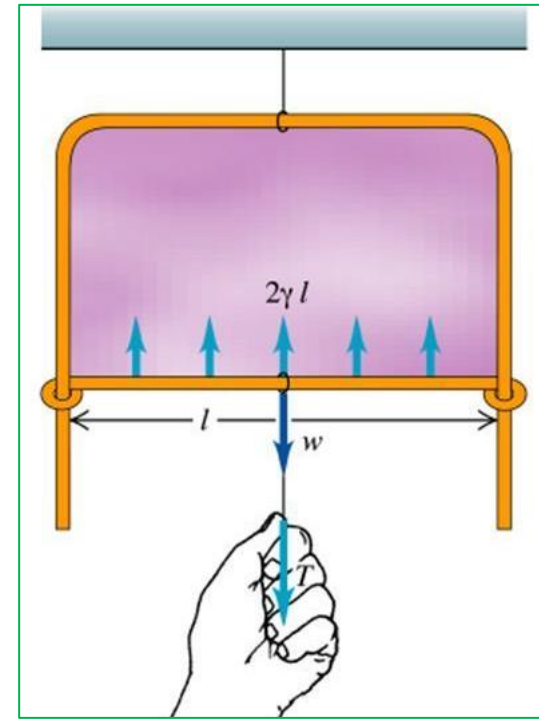
Liquid	Surface Tension (mJ/m² = mN/m)
n-Hexane = C_6H_{14}	18
Ethanol = CH_3CH_2-OH	23
Acetone = 2-Propanone	24
Ethylene glycol = 1,2-Ethanediol	48
Water	73

**Observable Consequences of Surface Tension:**

i) Spherical shape of liquid droplets:

The effect of surface tension is to reduce the surface area to a minimum. For a given volume of liquid, a sphere has the minimum surface area. Hence a liquid drop tends to assume a spherical shape.


Water droplet
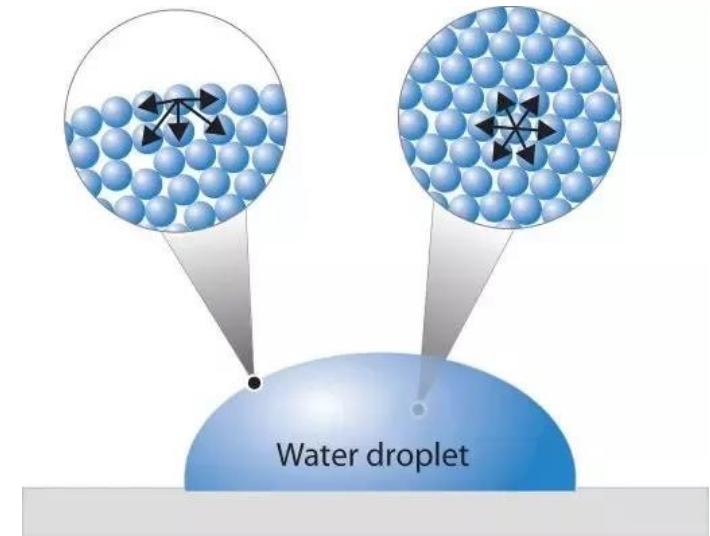
(ii) Capillarity and meniscus formation:

Capillary action is the ability of a liquid to move in a narrow spaced capillary tube. This phenomenon is related to surface tension.


H_2O Hg
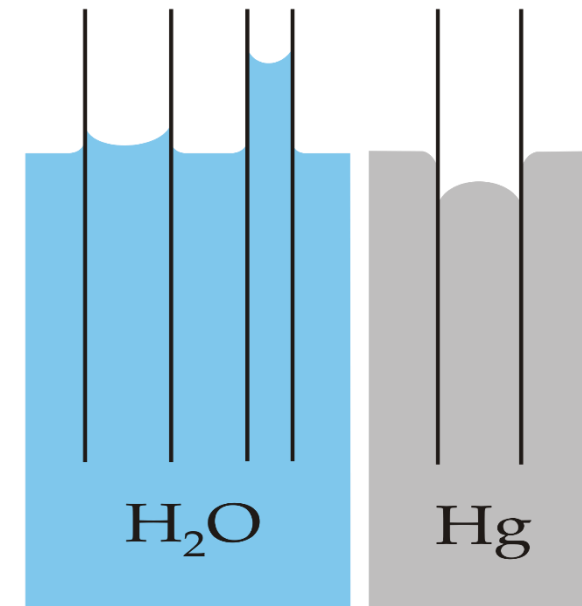
Capillary action of Water:

- *Adhesive forces* between water and glass.

- *Cohesive force* between water molecules. H-bonding

- Adhesive forces are stronger than the cohesive forces.

- a thin film of water creeps up the wall of the glass capillary.

- The cohesive forces that give rise to surface tension tend to reduce the surface area of this film and hence the water level begin to rise also.

- Consequently the meniscus, has its middle curved downward and its edges curved upward, ie, it has a *concave* shape.

- The final water level is a balance between the surface tension and the potential energy required to lift the water against gravity.
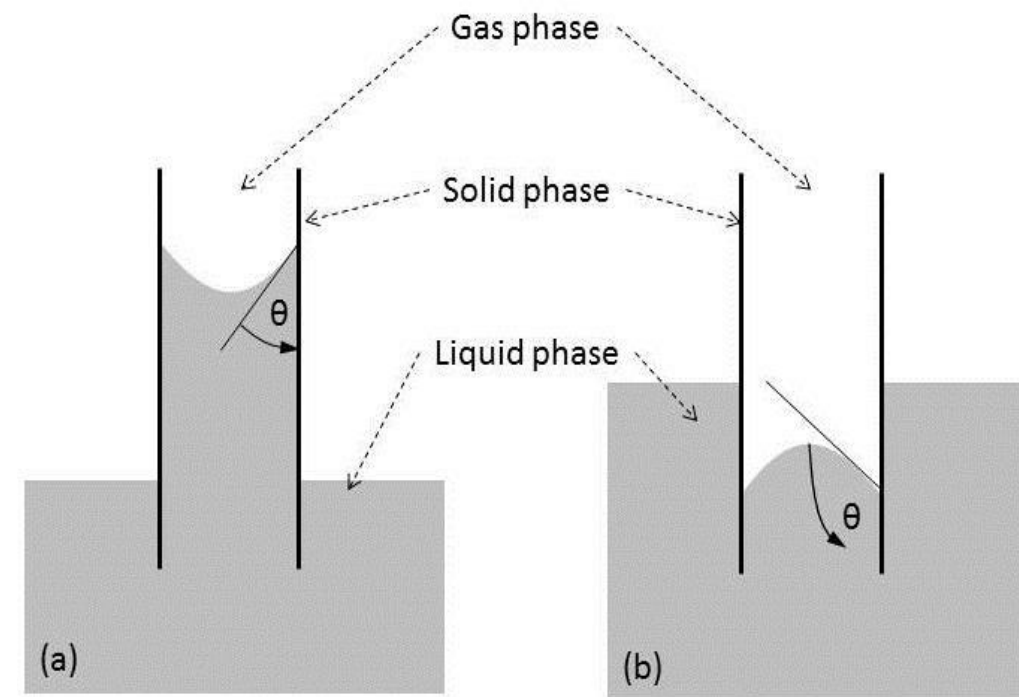
Capillary action of Mercury:

- Mercury has a much higher surface tension than water owing to stronger *cohesive forces* (*metallic bonding*).

- *A capillary fall or capillary depression* is observed.

- Also, the meniscus its middle curved upward and edges carved downward - *convex shape*.

- This behaviour of mercury results from the fact that the attraction (cohesive forces) between mercury atoms is greater than the attraction adhesive forces of mercury atoms for glass.

- The angle which the curved surface (*i.e.* meniscus) makes with the wall of the tube is called **contact angle (θ).**

- It is found by drawing a tangent at that point.

- For capillary rise shown by wetting liquids, $\theta < 90^0$ whereas for capillary fall shown by liquids that do not wet glass, $\theta > 90^0$.
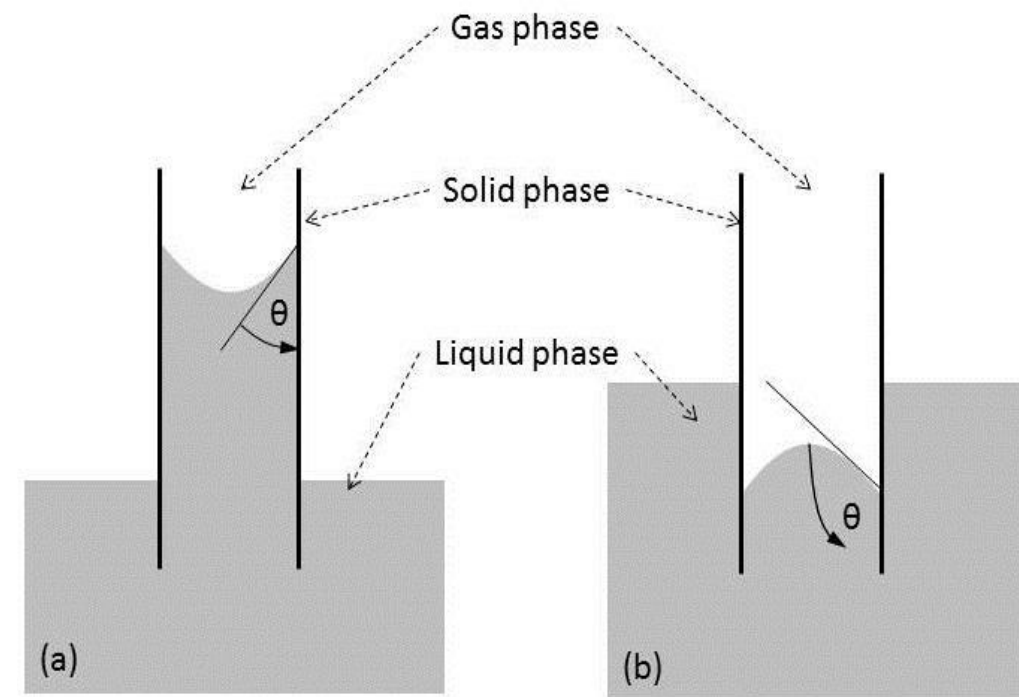
Cleansing Action of Soap – Surfactants:

- Surfactants are compounds that *lower the surface tension (or interfacial tension) between two liquids, between a gas and a liquid, or between a liquid and a solid*.

- Surfactants - Detergents, wetting agents, emulsifiers, foaming agents, or dispersants.


Hydrophobic

Short polar end
(Soluble in water)

Long non-polar end
(Soluble in oil)
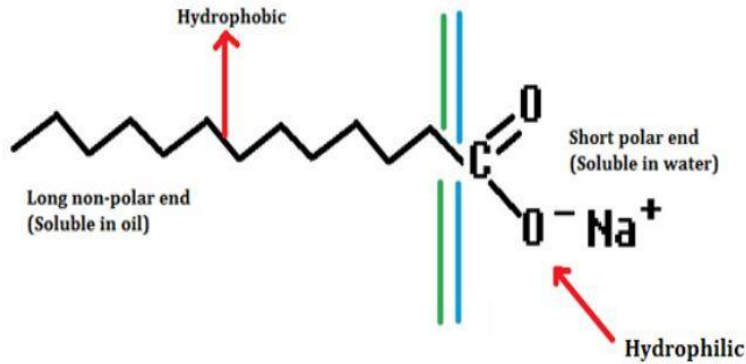
Hydrophilic

The structure of a surfactant:

Hydrophilic (water-loving) part and a hydrophobic (water-repelling) part.

Soaps (*e.g.* sodium stearate, $C_{17}H_{35}COO^-Na^+$) and detergents (*e.g.* sodium lauryl sulphate, $C_{12}H_{25}OSO_3^-Na^+$) are typical surfactants which can act as emulsifiers for stabilizing oil-in water emulsions.

Surfactants reduce the interfacial tension

- Cleansing action - ***Ascribed to the ability to emulsify grease (oil) with water***.

- The hydrophobic hydrocarbon chain of the surfactant (soap or detergent) gets attached to the oil (grease) and its hydrophilic polar head gets attached to water.

- Forms an *interfacial film, lowers the interfacial tension between grease and water.*

- Promotes emulsification.

- Dirt sticks to grease and is released from the cloth during rubbing.
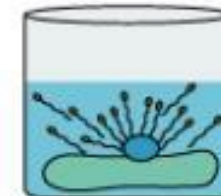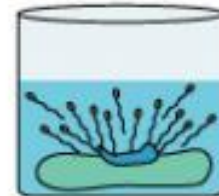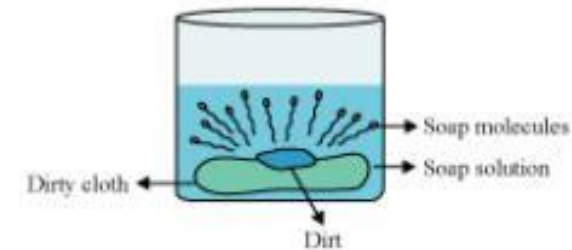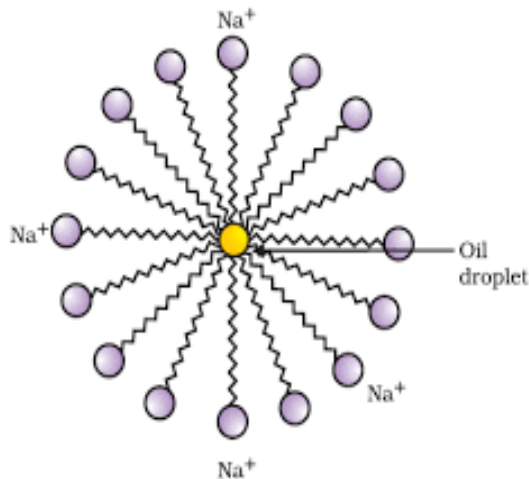
Effect of Temperature on Surface Tension:

- Increase in temperature increases the kinetic energy of the molecules and hence the intermolecular attraction decreases. Consequently the surface tension decreases. The dependence of surface tension on temperature is given by Ramsay-Shield equation.

$$\gamma \left(\frac{M}{\rho} \right)^{2/3} = k \left(T_c - T - 6 \right)$$

  Where, T_c is the critical temperature, ρ is the density of the liquid and k is a constant.

  Katayma modified the equation as:

$$\gamma \left(\frac{M}{\rho - \rho'} \right)^{2/3} = k' \left(T_c - T \right)$$

  Where, ρ' is the density of the vapour at T K.

Determination of Surface Tension – Capillary Rise Method

The surface tension of a liquid can be determined by the capillary rise of a liquid. Surface tension (γ) is related to capillary rise (h) as:

$$\gamma = \frac{1}{2} h \rho g r$$

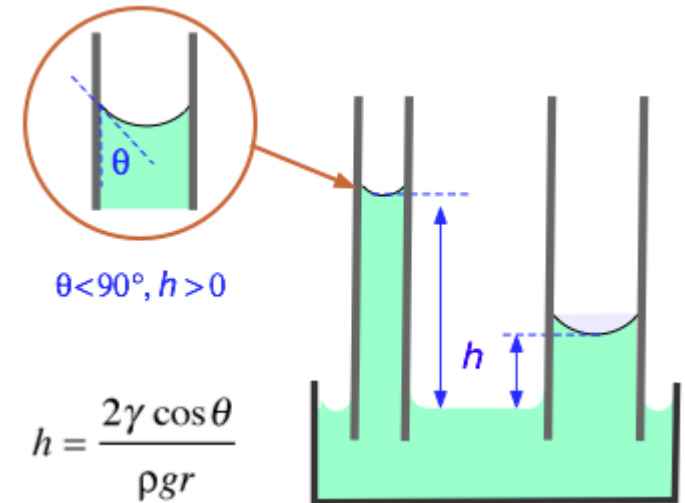Where, ρ is the density of the liquid and 'r' is the radius of the capillary tube.

Surface tension of a liquid can be determined by relative method using the above equation, by taking the two liquids in the same capillary tube.

Then, for liquid 1 we have; $\gamma_1 = \frac{1}{2} h_1 \rho_1 g r$

Then, for liquid 2 we have; $\gamma_2 = \frac{1}{2} h_2 \rho_2 g r$

Then, $\dfrac{\gamma_1}{\gamma_2} = \dfrac{h_1 \rho_1}{h_2 \rho_2}$

$\theta < 90°, h > 0$

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

PARACHOR AND CHEMICAL CONSTITUTION:

Parachor is a quantity, related to surface tension defined according to the formula:

$$P = \frac{\gamma^{\frac{1}{4}} M}{d}$$

Where, where γ is the surface tension, M is the molar mass, and d is the density.

- Parachor "**has been used in solving various structural problems**".

- Parachor is also defined as the molar volume of liquid when its surface tension is 1 unit.

- Parachor gives a measure of the molar volume at temperatures at which different liquids have the same surface tension.

- Parachor is an additive property and parachor of a compound can be determined as the sum of its atomic and structural parachors.

Atomic Parachor: Contributions of each atom present in a molecule.

Structural Parachor: Contributions of various bonds and rings present in a molecule.

C	4.8	S	48.2	triple bond	46.6
H	17.1	F	25.7	△	16.7
N	12.5	Cl	54.3	□	11.6
P	37.7	Br	68.0	⬠	8.5
O	20.0	I	91.0	⬡	6.1
O (esters)	60.0	double bond	23.2		

$$\overline{P}_{compound} = \sum n_i \overline{P}_i$$

I

II
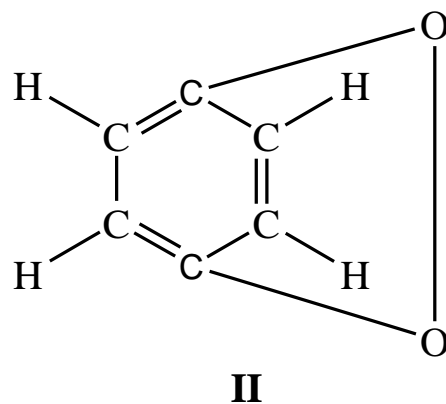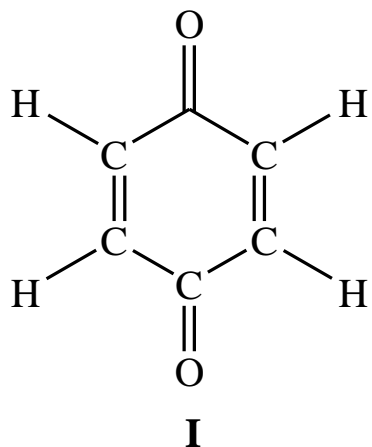
Structure I	Structure II
6 C : 6 × 4.80 = 28.8	6 C : 6 × 4.80 = 28.8
4 H : 4 × 17.1 = 68.4	4 H : 4 × 17.1 = 68.4
2 O : 2 × 20.0 = 40.0	2 O : 2 × 20.0 = 40.0
4 (=) : 4 × 23.2 = 92.8	3 (=) : 3 × 23.2 = 69.6
1 (6-membered ring) : 1 × 6.1 = 6.1	2 (6-membered ring) : 2 × 6.1 = 12.2
Total : 236.1	**Total : 219**

The experimental value of parachor is found to be 236.8. Since the parachor value of structure I is more close to the experimental value, Structure A represents quinone correctly.

STRUCTURE OF LIQUIDS

- Gas contains particles without any kind of order while the particles of a crystalline solid have a well-defined geometrical pattern.

- Crystalline solids possess along range order.

- The particles within a liquid are much more closer together than those in a gas, but are farther apart than those of a solid, because intermolecular forces in liquid are intermediate between those in a gas and solid.
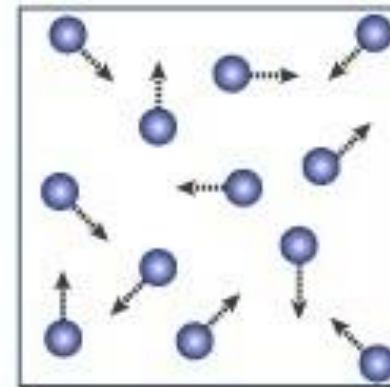
- The particles of liquid have a short-range order.

Liquid state is regarded as a condensed gas or molten solid.
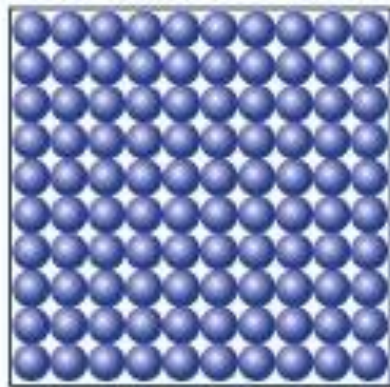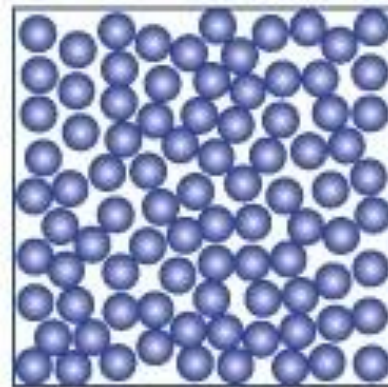

Solid   Liquid   Gas

The vacancy theory or hole theory of liquids:

- The vacancy theory on hole theory, put forward by Henry Eyring and Taikyune Ree in 1961, takes into consideration of the fact that the density of a liquid in generally less than that of the corresponding solid.

- This implies that the intermolecular space in a liquid is greater than that in a solid. According to Eyring and Ree, this intermolecular space in a liquid is comprised of a large number of vacancies or holes of molecular size.

- The theory considers a liquid as *a random congregation of large molecules and molecular size holes*. The molecules that can jump into neighbouring holes are conferred gas-like properties and the others solid-like properties.

The number of holes per mole of molecules $= \dfrac{V_l - V_s}{V_s}$

where V_l, and V_s, are the respective molar volumes of liquid and solid.
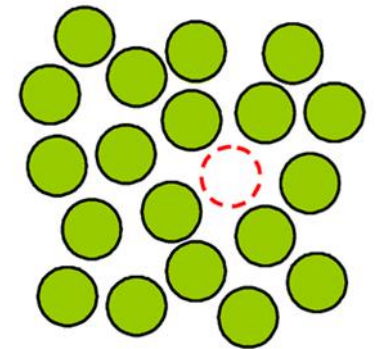
The Free Volume Theory:

- According to the free volume theory (Cohen and Turnbull, 1959), the hard-sphere molecules that constitute an idealized liquid exist in 'cages" formed by nearest neighbours.

- The particles move in an almost constant force field in a cage provided by the nearest neighbour particles surrounding them

- It is estimated that each molecule in a liquid is surrounded at a small distance by 10 to 12 neighboring molecules.

- Due to the existence of the cage' or 'cells of the surrounding molecules around it, the central molecule (with radius r) has to move only through a small distance to collide with any of its neighboring molecules, which is very small when compared to that for a molecule in a gas.

- Thus, the centre of the caged molecule can move only within the space limited by the volume of the cage. The volume available to a molecule within its centre can move is called the free volume. Thus, the total volume of the liquid can be divided into two components - % occupied volume and free volume.

caging
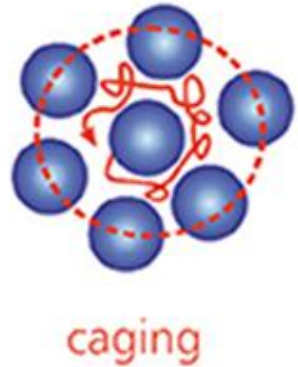
UNUSUAL BEHAVIOUR OF WATER

- Water shows some properties which are vital to the very existence of living organisms.

- Its unique and remarkable macroscopic behaviour - Polarity & H-bonding

- Each water molecule being able to engage in hydrogen bonding with four of its neighbours.

1) Water is an exceptionally good solvent:

- The great solvent power of water is the result of its polarity and exceptional H-bonding ability.

- It has a high dielectric constant and it dissolves ionic compound through ion-dipole forces that separate the ions from their crystals and dispense them in solution.

- Water also dissolves many polar non-ionic substances, such as ethanol and glucose by forming H-bonds with them.
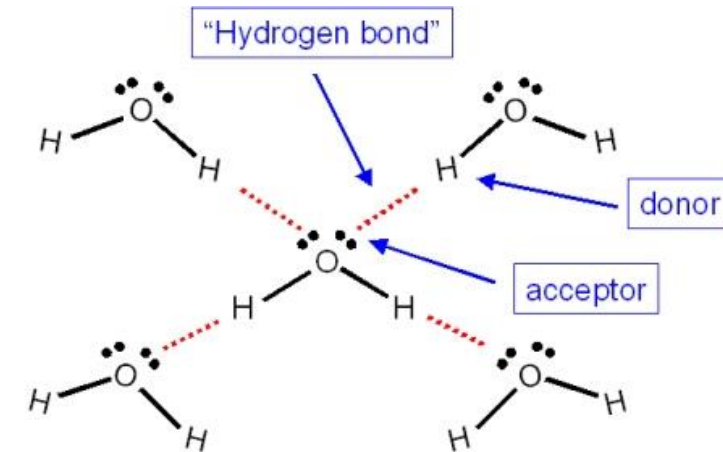
(2) Water has high specific heat and high heat of vaporization:

- The extensive association that it shows through H-bonding gives water an exceptionally high specific heat capacity, higher than almost any other liquid.

- Because the added heat gets utilized to break the hydrogen bonds instead of increasing the temperature.

- Such H-bonding also gives water an exceptionally high heat of vaporization.
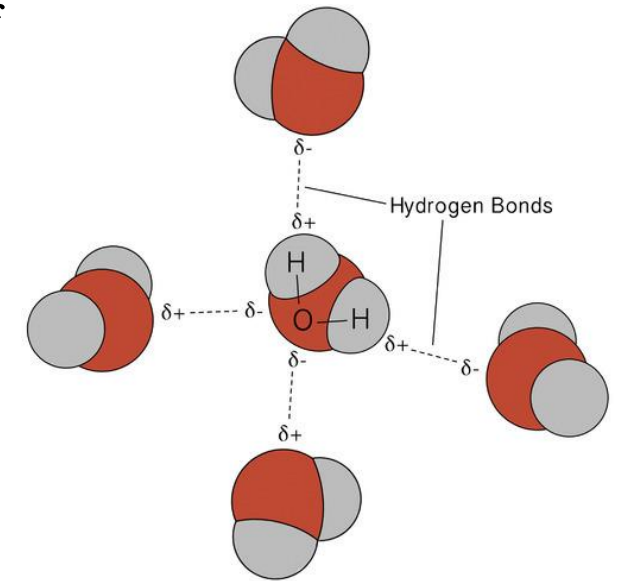
(3) Water shows high surface tension and high capillarity

- The extensive intermolecular H-bonding present in it is responsible for its high surface tension and high capillarity.

- The high capillarity of water is a result of its high surface tension, is crucial to land plants, because during dry periods, this enables the ground-water absorbed by the plant roots to rise by capillary action
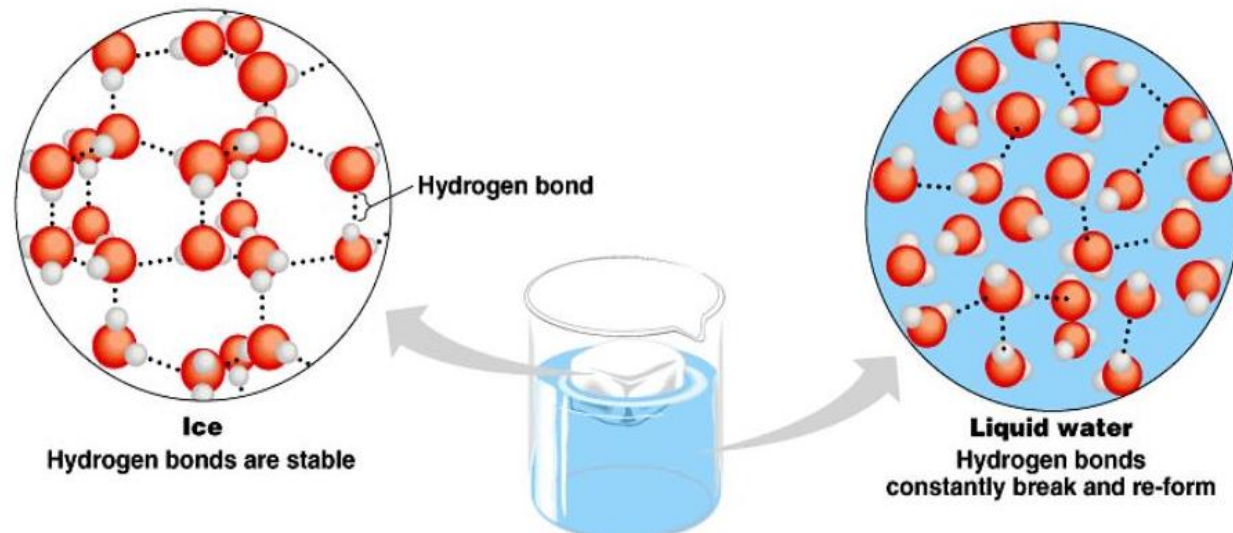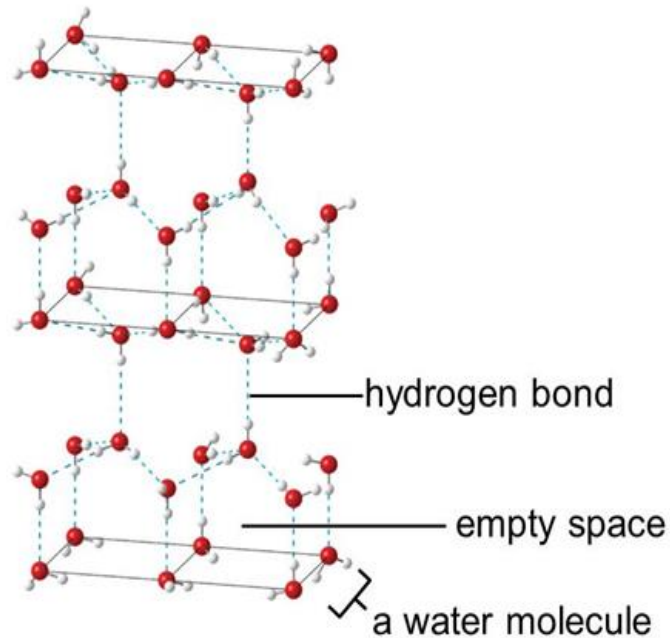
4) Water has the highest boiling point and melting point among the hydrides of group 16 elements:

- Among the group 16 hydrides, only water exists as a liquid at room temperature, others are gases.

- The extensive association of water molecules that takes place through intermolecular hydrogen bonding is, in fact, responsible for the unexpectedly high boiling point as well as melting point of water.

- Because a large amount of energy has to be expended to break these hydrogen bonds.

- Such association through hydrogen bonding is not present in H_2S, H_2Se and H_2Te. This is because, unlike oxygen, the elements S, Se and Te are not sufficiently electronegative to produce enough polarity to cause intermolecular hydrogen bonding in their hydrides.

- Consequently, H_2S, H_2Se and H_2Te have much lower melting and boiling points than water.
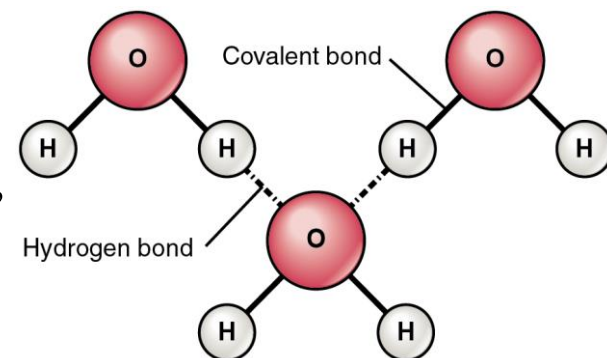
(5) Ice has a lower density than liquid water:

- Each water molecule gets connected to four other water molecules through intermolecular H-bonding, tetrahedrally.

- In ice, continuation of this tetrahedral pattern through many molecules in a ***fixed array*** leads to a rather open hexagonal three dimensional structure with several ***cavities or voids***. The large spaces within ice give ice a lower density than liquid water. As a result, ice floats on water.

hydrogen bond

empty space

a water molecule

Hydrogen bond

Ice
Hydrogen bonds are stable

Liquid water
Hydrogen bonds
constantly break and re-form

(6) *Water show anomalous variation of density between 0°C and 4°C*

- The density of water changes in anomalous manner.

- When ice melts at *0°C* its tetrahedral network arrangement breaks down, and the freed molecules pack much more closely, filing spaces in the collapsing cavity-filled solid structure and this decrease in volume continues up to about *4°C*.

- As a result, water shows its highest density (1.000 g/mL) at 4°C (more exactly, 3.98 °C).

- With further increase in met the density decreases through mal thermal expansion. In other words, water expands anomalously when it freezes.