

Chapter-5

STATES II OF MATTER

Liquids

The state of matter that has definite volume but no definite shape is called liquid.

Kinetic Molecular Interpretation of Liquids:

Some of important postulates of kinetic molecular theory are:

- Liquid molecules have kinetic energy greater than solids and lesser than gases molecules.
- Intermolecular forces of liquid are stronger than gases but weaker than solids.
- Molecules of liquid are close to each other. Empty spaces among liquid molecules are negligible so liquids have definite volumes.
- Molecules of liquid are in constant motion. They slide one past other. So liquid have no definite shape and adopt shape of container.

Some Common Properties of Liquids:

Shape: Liquid has no definite shape.

Volume: Liquid has definite volume.

Compressibility: Liquids are comparatively less compressible because their molecules are closer.

Forces: Forces of attraction are stronger.

Diffusion: Liquids have little ability to diffuse into one another.

Fluidity: They are fluid i.e. they can flow very easily.

Density: Liquids have very more density than gases this is due to less volume of liquids e.g. $O_{2(l)}$ has density 1.149 g/cm^3 .

Evaporation: Liquids evaporate at all temperature.

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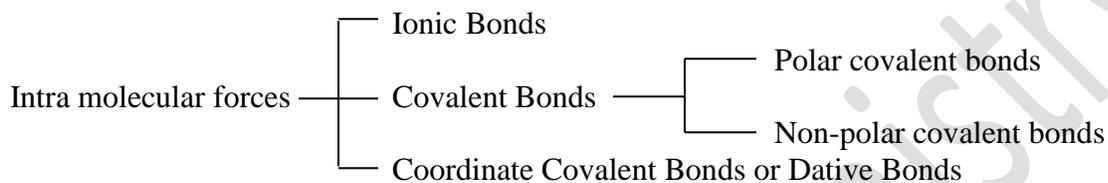
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Forces of attraction:

Two types of forces are present among molecules.

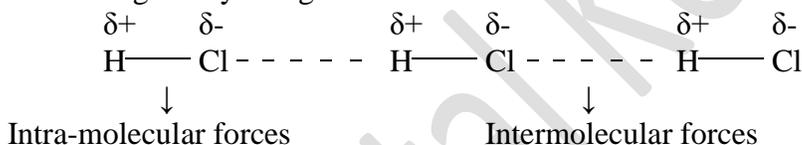
(i) Intra-molecular Forces:

The forces present between two atoms of same molecule are called intra molecular forces. They are also called Chemical Bonds. These are of three types.

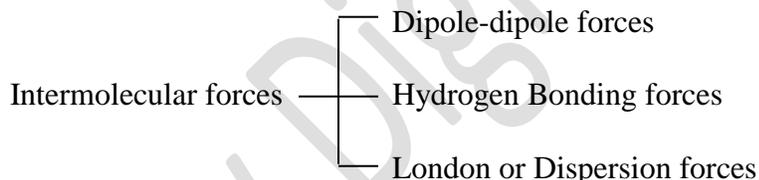


(ii) Intermolecular forces:

The forces of attraction between positively charged atom of one molecule and negatively charged atom of other molecule are called inter molecular forces.



Intermolecular forces are also of three types



- The intra-molecular forces are much stronger than intermolecular forces.

e.g. Heat of vaporization of water is 40.7 kJ i.e. $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)} \quad \Delta H = 40.7 \text{ kJ}$ which means that 40.7 kJ are required to convert one mole liquid water into gaseous water. This heat is used to overcome intermolecular forces among water molecules and to set them free.

Where as heat of decomposition of water is 920 kJ i.e. $\text{H}_2\text{O}_{(g)} \rightarrow 2\text{H} + \text{O} \quad \Delta H = 920 \text{ kJ}$ which means that 920 kJ are required to decompose water to hydrogen and oxygen atoms. This heat is used to overcome intra-molecular forces. As heat required for intra-molecular forces is higher than that required for intermolecular forces so intra-molecular forces are stronger than intermolecular forces.

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Presence of dipole-dipole forces:

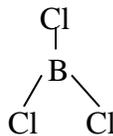
Dipole-dipole forces are not present in molecules consisting of alike/identical atoms e.g. O₂, H₂, N₂ etc.

Where as molecules consisting of dissimilar atoms may or may not possess d.d.f, as it further depends upon the geometry of molecules

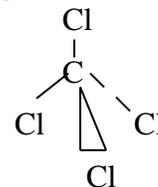
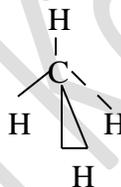
Cases of molecules consisting of dissimilar atoms that have no d.d.f:

(i) Tri atomic molecules having linear geometry and two bonds identical e.g. CO₂, CS₂ etc
O = C = O, S = C = S

(ii) Tetra atomic molecules having triangular planar geometry and three bonds identical e.g. BCl₃, BF₃ etc.



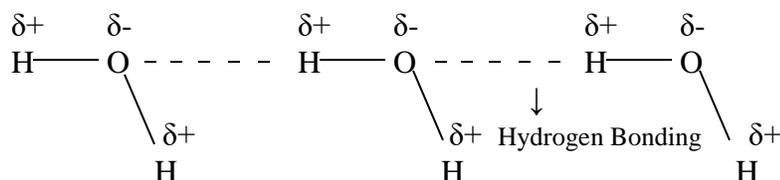
(iii) Penta atomic molecules having tetrahedral geometry and four bonds identical e.g. CH₄, CCl₄ etc.



(II) Hydrogen bonding:

It is actually a special case of dipole-dipole forces. In d.d.f there is no restriction of +ve & -ve poles but in hydrogen bonding there is restriction of +ve and -ve poles.

“The force of attraction between positively charged hydrogen atom of one molecule and negatively charged Fluorine or Oxygen or Nitrogen atom of other molecule is called Hydrogen bonding”.



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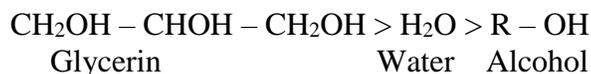
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Hydrogen bonding is the strongest intermolecular force. Due to greater electronegativity difference between H-atom and F/O/N-atom, sufficiently high +ve & -ve charge appears on these atoms respectively so stronger is the force.

Factors affecting strength of Hydrogen bonding:

- Number of OH or NH or HF groups: More is the number of OH or NH or HF groups stronger will be the force e.g. order of strength of hydrogen bonding in the following is:



- Ratio of lone pairs of electrons and hydrogen atoms: If ratio of lone pairs of electrons and hydrogen atoms is right ratio in molecules of a compound then hydrogen bonding in such molecules will be stronger e.g. water has strong hydrogen bonding than HF and NH₃. As lone pairs of electrons and H-atoms in water molecules are in right number (2:2) so every one of them is involved in hydrogen bonding, therefore, hydrogen bonding in water is stronger than that in HF and NH₃.
- Difference of electronegativity: Strength of hydrogen bonding also depends upon difference of electronegativities of atoms of the molecules e.g. HF has strong hydrogen bonding than NH₃ due to higher electronegativity difference in HF.

Presence of Hydrogen bonding:

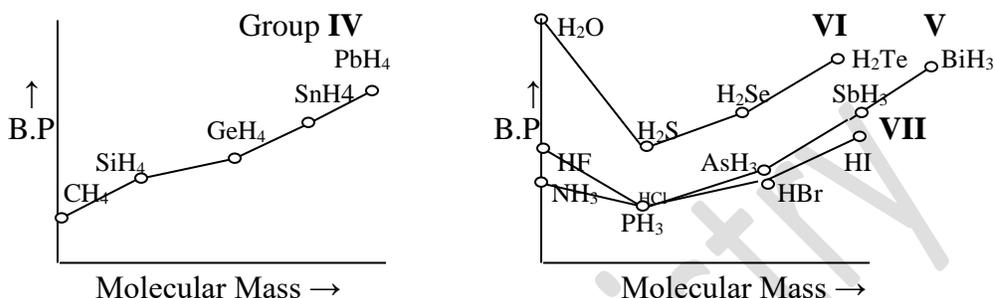
Hydrogen bonding exists in molecules in which hydrogen is directly attached to O or N or F-atom of molecule.

The Evidence for Hydrogen Bonding:

Many elements form Hydrides. Binary compounds of Hydrogen are called Hydrides.

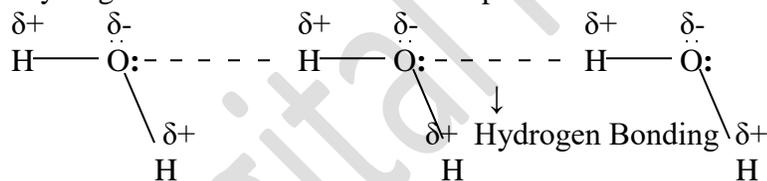
If we plot Boiling points of Group-IV hydrides against their molecular masses, we observe a regular increase in B.P with increasing size and number of electrons of Group-IV elements. It is due to increasing London forces with increasing number of electrons.

But in case of hydrides of Group-V, VI & VII elements, the hydride of first element in each group has extra ordinarily high boiling point. Other member shows normal trend of boiling points. Hydride of first element in these groups has hydrogen bonding which is a strong intermolecular force so the boiling point is high.



Origin of Hydrogen Bonding:

In H₂O, NH₃ & HF each of O/N/F atom to which hydrogen is attached has not only sufficiently high negative charge, but also has one or more lone pairs of electrons. These atoms have smaller size so they have high charge densities, due to which strong intermolecular force i.e. Hydrogen Bonding is developed between positively charged hydrogen of one molecule and lone pair of electrons of other molecule.



In water molecule there are 2 lone pairs of electrons and 2 hydrogen atoms so each water molecule make 4 hydrogen bonds.

- Strength of hydrogen bond is about one tenth 20 time less than strength of an average covalent bond. Its bond energy varies from 1- 40 kJ/mole. Bond length of a covalent bond in water is 0.96Å^o while that of hydrogen bond is 1.97Å^o. The bond energy of covalent bond in water is 464kJ/mole while that of hydrogen bond is 19kJ/mol. If covalent bond is considered to have a marriage status then hydrogen bond just has good friend status.

Properties of Hydrogen bonding:

- Hydrogen bonding is stronger than dipole-dipole and London forces.
Hydrogen bonding > dipole-dipole > London forces.
- Hydrogen bonding is approximately twenty times weaker than a covalent bond.
- Hydrogen bond is directional.
- Hydrogen bond results in the formation of long chains and network of molecules.
- Hydrogen bond does not bring chemical change in the substances.

Examples of Hydrogen Bonding:

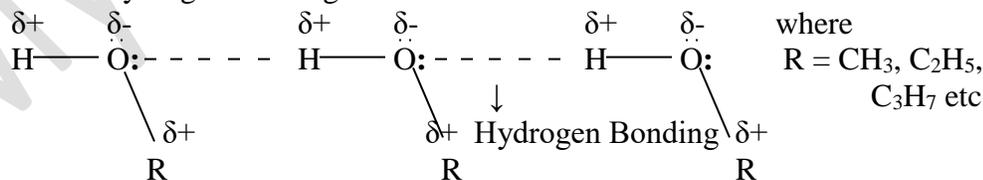
(i) Water:

In water molecule there are **2 lone pairs** of electrons and **2 hydrogen atoms** so each water molecule make 4 hydrogen bonds with four other water molecules. As lone pairs of electrons and H-atoms are in right number so every one of them is involved in hydrogen bonding. Thus hydrogen bonding in water is very strong and, therefore, H₂O is a perfect example of hydrogen bonding.

Bond length of a covalent bond in water is 0.96Å and bond energy is 464kJ/mol while that of hydrogen bond, bond length is 1.97Å and bond energy 19 kJ/mol.

(ii) Alcohols:

Alcohol molecule (e.g. ethyl alcohol) has "OH" group so it is capable of hydrogen bonding.



In alcohols although oxygen atom has two lone pairs of electrons but has only one hydrogen directly linked to O-atom so its hydrogen bonding is comparatively weaker than water.

Thus the boiling point of water is higher than methyl alcohol and ethyl alcohol, boiling points are 100°C , 64.7°C and 78.4°C respectively.

The boiling points of alcohols are higher than corresponding (having same molecular masses) alkanes and ethers as the later do not have hydrogen bonding.

<u>Compound</u>	<u>Structural formula</u>	<u>Boiling point</u>
n-pentane	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	36.3°C
Diethyl ether (Ethoxy ethane)	$\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$	34.7°C
n-Butyl alcohol (Butan-1-ol)	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$	117°C
Isobutyl alcohol (2-Methylpropan-1-ol)	$\begin{array}{c} \text{CH}_3\text{-CH-CH}_2\text{-OH} \\ \\ \text{CH}_3 \end{array}$	108°C

Both n-butyl alcohol and isobutyl alcohol have equal hydrogen bonding but the additional London forces are comparatively stronger in n-butyl alcohol so its boiling point is higher than isobutyl alcohol.

(iii) Ammonia, Methyl amine and DNA:

Molecules having hydrogen directly attached to N-atom also shows hydrogen bonding.

NH_3 has one lone pair of electron and three H-atoms attached to nitrogen so its hydrogen bonding is weaker than water.

Methyl amine ($\text{CH}_3\text{-NH}_2$) has one lone pair of electron and two H-atoms attached to nitrogen so its hydrogen bonding is also weaker than water.

Two strands of alpha-helix in DNA are attached to one another by hydrogen bonding.

(iv) Hydrogen Fluoride:

HF has three lone pairs of electron and one H-atoms attached to fluorine so its hydrogen bonding is weaker than water.

(v) Other examples:

Hydrogen bonding also exists in proteins, honey, fibers of hair, silk, muscles, carbohydrates (like glucose, fructose, sucrose etc), paints, glue, dyes etc.

Applications of Hydrogen bonding:

Various phenomenon and facts can be explained by hydrogen bonding.

- (i) **Strength of acids:** HF is a weak acid in the halogen acids series. There is hydrogen bonding between HF molecules, which make the molecule difficult to donate proton, and hence it is weak acid than other halogen acids.
- (ii) **Solubility:** Hydrogen bonding also explains solubility e.g. lower alcohols (like CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ etc), lower carboxylic acids (like CH_3COOH) lower aldehydes (like HCHO) and lower ketones (like CH_3COCH_3) are soluble in water due to their ability to form Hydrogen bonding with water. On other hand hydrocarbons have no ability to form hydrogen bonding with water so they are not soluble in water.
- (iii) **Cleaning action:** Cleaning action of soap and detergents is because of hydrogen bonding. Polar part of soap or detergent makes hydrogen bonding with water while non-polar part of their molecules attaches to dirt molecule. Due to which dirt is removed from fibers of clothes.
- (iv) **In Biological compounds:** Fibers, hairs, muscle proteins consist of long chains of amino acids and they are stabilized due to hydrogen bonds between them.
- (v) **DNA in cells:** Two strands of alpha-helix in DNA are attached to one another by hydrogen bonding.
- (vi) **Paints and Dyes:** The adhesive nature of certain paints and dyes is due to hydrogen bonding.
- (vii) **Action of Glue:** The sticky action of glue due to which it repairs broken parts of a machine is due to hydrogen bonding.
- (viii) **Viscosity of Honey:** High viscosity of honey is due to hydrogen bonding.
- (ix) **Food Material:** Carbohydrates e.g. glucose, fructose, sucrose are stabilized due to hydrogen bonds between them.
- (x) **Structure of Ice:** In liquid H_2O , molecules form hydrogen bonding with each other. But as molecules are mobile so bonds are broken and reformed. Hence, there is less regularity and less free space. However, when temperature of H_2O is lowered below 4°C , its molecules become regular and form permanent hydrogen bonds. Thus empty spaces are developed between the molecules. As a result, its volume increases below 4°C . At 0°C when water freezes to ice, arrangements of molecules become very orderly and ice occupies more space than liquid water. Therefore, density of ice become less than that of water, hence it floats over water.

(xi) **Boiling points of halogen acids:**

HF=19.4 °C, HCl= -85 °C, HBr= -66.38 °C, HI= -35.5 °C

The unusual higher boiling point of HF is due to hydrogen bonding. Other halogen acids have dipole-dipole forces, which are weaker than hydrogen bonding.

(xii) **Trend in boiling points of hydrides of Group-V, VI& VII elements:**

In case of hydrides of Group-V, VI& VII elements, the hydride of first element in each group has extra ordinarily high boiling point. Other member shows normal trend of boiling points. Hydride of first element in these groups has hydrogen bonding which is a strong intermolecular force so the boiling point is high. Other members do not have hydrogen bonding.

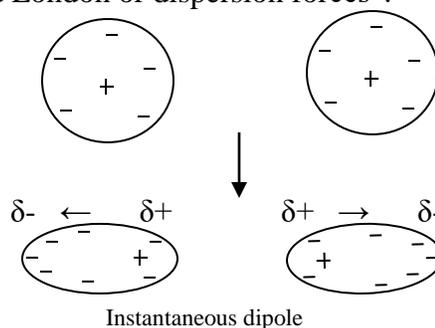
(xiii) **Trend in physical properties:** Trend in other physical properties like viscosity, surface tension, heat of vaporization, evaporation, vapour pressure etc can also be explained by hydrogen bonding.**(III) London or Dispersion or Dipole-Induced dipole forces:**

A German physicist Fritz London introduced these forces in 1930.

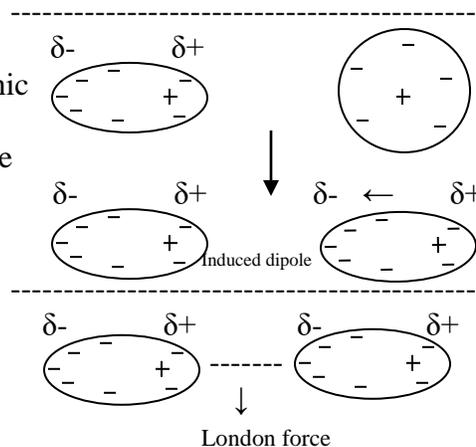
“The forces of attraction between two temporary dipoles created due to electronic cloud displacement OR forces of attraction between temporary i.e. instantaneous and induced dipoles are called London or dispersion forces”.

These forces generate due to two reasons:

(i) When two atoms or molecules come closer, their electronic clouds influence each other i.e. they repel each other. So electronic clouds of the two, move away and as a result instantaneous dipoles are created.



(ii) When an instantaneous dipole comes closer to a symmetrical molecule its electronic cloud repels or its nucleus attracts the electronic cloud of the symmetrical molecule and as a result a dipole is induced in it. This dipole is called induced dipole.



A force of attraction is generated between instantaneous dipole and induced dipole, which is known as London force or dispersion force or dipole-induced dipole force.

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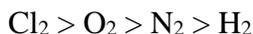
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- These forces are short range and short-lived forces.

Factors affecting strength of London dispersion forces:

- (i) Number of electrons: More is the number of electrons stronger will be London forces e.g. order of strength of London forces in the following is



Number of electrons 34 18 14 2

- (ii) Size of molecules: Bigger are the molecules stronger will be London force e.g. London forces among hydrogen molecules (H_2) are stronger than that in helium molecules (He). Both molecules have two electron but size of H_2 molecule is larger than that of He molecule so H_2 have stronger forces than He .

More is the number of electrons or larger is the molecular size stronger will be the London forces and vice versa. The following table

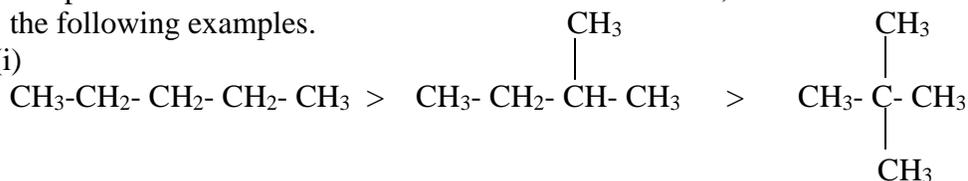
shows that going down a non-metal group, molecular size as well as number of electrons increases so London forces increase and in turn boiling points increase.

Zero Group	B.P (°C)	Group VII-A	B.P (°C)
He	-268.6	F_2	-188.1
Ne	-245.9	Cl_2	-34.6
Ar	-185.7	Br_2	58.8
Kr	-152.3	I_2	184.4
Xe	-107.1	At_2	-
Rn	-61.8	-	-

(iii) Molecular Shape:

London forces are stronger in long and straight chain molecules as compared to that in short and branched chain molecules, which is evident in the following examples.

e.g. (i)



n-pentane (B.P=36.1°C)
(pentane)

iso pentane (B.P=27.9°C)
(2-methyl butane)

neo pentane (B.P=9.5°C)
(2,2-dimethyl propane)

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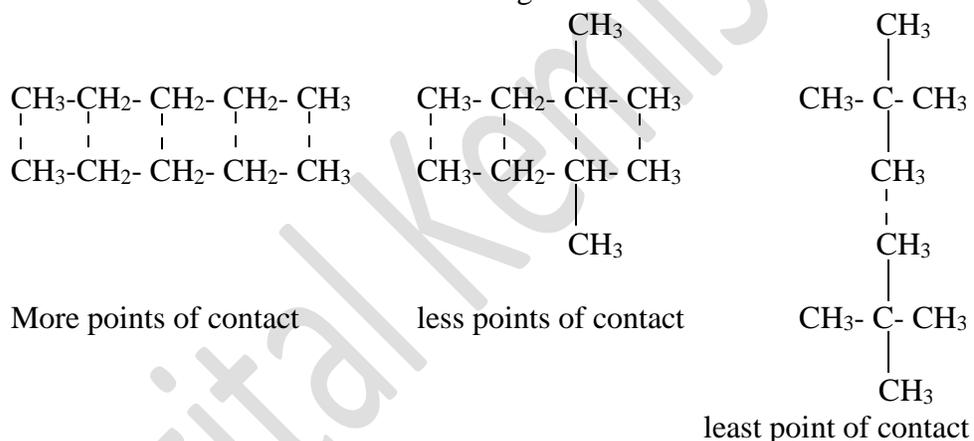
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n-pentane is straight chain molecule so dispersion forces in it are stronger than the other two isomers, so its boiling point is comparatively high. The other two isomers are branched chain molecules so their boiling points are less, furthermore neo pentane is more branched so its boiling point is least.

e.g. (ii) n-butane also called butane has boiling point higher than that of iso butane (also called 2-methyl propane). The boiling points of the two are -0.5°C and -11.7°C respectively.

Long straight chain molecules can come closer to each other as compared to branched chain molecules so London forces are more operative in straight chain compounds. In branched chain molecules there are less points of contact of molecules with each other so London forces in them are less operative and are weak. Thus the boiling points of branched chain molecules are lower than that of straight chain molecules.



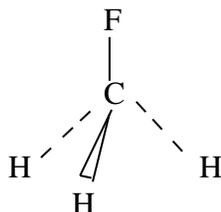
Presence of London Dispersion forces:

London forces are the only forces that exist in all molecules. Although they are present in all kind of molecules but are more prominent in molecules, which have no other forces e.g. Cl_2 , H_2 , O_2 , noble gases etc.

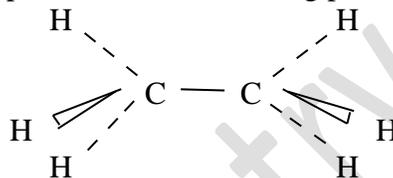
Comparison of Strength of Intermolecular forces:

- (i) In case of hydrides of Group-V, VI & VII elements, the hydride of first element in each group has extra ordinarily high boiling point. Hydride of first element in these groups has hydrogen bonding which is a strong intermolecular force so the boiling point is high. Other hydrides have dipole-dipole forces, which are comparatively weak so their boiling points are low.

- (ii) Boiling point of water is higher than ethyl alcohol. Although both have hydrogen bonding but that of water is stronger than that of ethyl alcohol due to more number of "O-H" groups in water. Hence boiling point of water is higher than that of ethyl alcohol.
- (iii) Fluoromethane and ethane both have equal number of electrons so London forces in the two compounds are equal but fluoromethane in addition to London forces also have dipole-dipole forces so its boiling point is slightly higher.



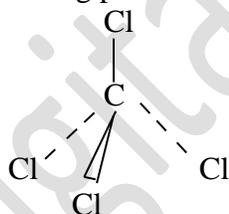
Fluoromethane

B.P= 194.7K or -78.3°C 

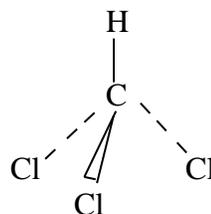
Ethane

B.P= 184.5K or -88.5°C

- (iv) Trichloromethane (Chloroform) is polar molecule so it in addition to London forces also has dipole-dipole interactions where as tetrachloromethane is non-polar so it has only London forces. But tetrachloromethane (Carbon tetra chloride) has more number of electrons than trichloromethane so the later has stronger London forces than the former. London forces of tetrachloromethane dominate the dipole-dipole forces of trichloromethane It is this reason that trtrachloromethane has higher boiling point than trichloromethane.



Tetrachloromethane

B.P= 349.8K or 76.8°C 

Trichloromethane

B.P= 334.2K or 61.2°C

- (v) London forces are stronger in n-butane than that in isobutane. Long straight chain molecules can come closer to each other as compared to branched chain molecules so London forces are more operative in straight chain compounds. In branched chain molecules there are less points of contact of molecules with each other so London forces in them are less operative and are weak. Thus the boiling points of straight chain molecules are higher than that of branched chain molecules.

Van der Waal's Forces: Dipole-dipole interactions and London dispersion forces collectively called Van der Waal's forces. These are weaker than hydrogen bondings.

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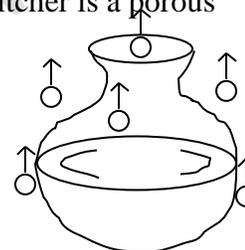
Evaporation:

“Spontaneous escaping of molecules from a liquid surface at any temperature is called evaporation.”

- It is a surface phenomenon and takes place at all temperatures.
- All molecules in a liquid do not possess equal energies at any temperature so they move with different velocities. When high-energy molecules hit molecules on surface of liquid they give part of their energy to surface molecules, which become able to overcome forces of attraction and thus leave liquid surface. In this way evaporation takes place.
- As high-energy molecules escape from liquid surface, therefore, average kinetic energy of remaining molecules decreases and hence temperature falls. It is this reason that evaporation causes cooling.

e.g. water remain cool in clay-pitcher (Mangai). The clay-pitcher is a porous container

from which water slowly comes out and evaporates due to which water in the pitcher get cooled and due to continuous evaporation remains cool then.



Factors Affecting Evaporation:

(i) Intermolecular forces:

Stronger are the intermolecular forces less will be evaporation and vice versa. Strong forces firmly hold molecules together and thus liquid will evaporate slowly. e.g. water is less volatile than ether and gasoline. Water has strong hydrogen bonding while other two have weak London forces so water evaporates slowly.

$$\text{Rate of evaporation} \propto 1/\text{Intermolecular forces}$$

(ii) Temperature:

Higher is the temperature high will be the rate of evaporation and vice versa. At higher temperature energy of molecules will be high and they can easily overcome forces of attraction and will evaporate rapidly e.g. wet clothes soon get dried in summer than in winter.

$$\text{Rate of evaporation} \propto \text{Temperature}$$

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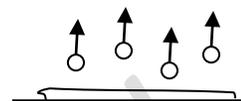
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(iii) Surface Area:

Evaporation is a surface phenomenon so it depends upon surface area, more is surface area more will be the evaporation

and vice versa. e.g. water present in a glass takes more time to evaporate than if it is spread on floor.

**(iv) Wind:**

If wind is blowing evaporation rate will be fast.

(v) Impurities:

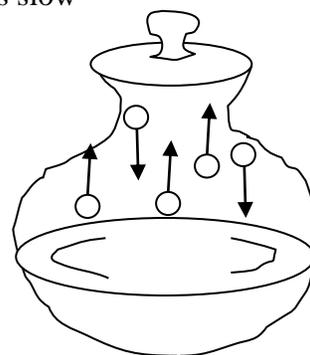
If non volatile impurities are present, rate of evaporation will be slow.

Vapour Pressure:

“The pressure exerted by vapours of a liquid at a given temperature when equilibrium is established between evaporation and condensation, is called vapour pressure”.

Consider a liquid in a close container.

At the beginning rate of evaporation will be very fast where as no condensation. But with the passage of time evaporation rate becomes slow and slow while condensation rate becomes fast and fast and ultimately the two rates become equal i.e. equilibrium will be established and number of vapours becomes constant. The pressure exerted by vapours at equilibrium is called vapour pressure.



Factors Affecting Vapour Pressure:

(i) Intermolecular forces:

Vapour pressure depends upon nature of liquid. Different liquids have different intermolecular forces. The liquid having stronger intermolecular forces show low vapour pressures and vice versa e.g. water has lower vapour pressure than ether and spirit at same temperature. Water has strong hydrogen bonding spirit also has hydrogen bonding but weaker than water while ether has London forces. So intermolecular forces in water are stronger and therefore its vapour pressure is lower than other two.

$$\text{Vapour Pressure} \propto 1/\text{IMF}$$

Vapour Pressure→ Compound ↓	Vapour Pressures at						
	0°C	20°C	40°C	60°C	80°C	100°C	120°C
Diethyl ether (B.P.=34.7°C)	185	442	920	1730	3000	4865	7495
Chloroform (B.P.=61.6 °C)	-	170	362	734	-	-	-
Carbon Tetrachloride (B.P.=76.8 °C)	32.9	87	224	448	843	1463	
Ethyl alcohol (B.P.=78.5 °C)	12	43	132	347	814	1780	3535
Water (B.P.=100 °C)	5	18	55	149	355	760	1489
Glycerin (B.P.=290 °C)	-	0.0016	-	-	-	-	-
Mercury (B.P.=356.58 °C)	0.00018	0.0012	0.0061	0.0252	0.0888	0.2729	0.7457

Negi82,Soni303,Lange1453,other

The order of strength of intermolecular is:

Mercury > Glycerin > Water > Ethyl alcohol > Carbon tetrachloride > Chloroform > Diethyl ether

(ii) Temperature:

Higher is the temperature more will be the kinetic energy of molecules and more will be the vapours produced. As a result high will be the vapour pressure. Reverse is true for lower temperature.

$$\text{Vapour Pressure} \propto \text{Temperature}$$

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(iii) Impurities:

If impurities are present in a liquid, less vapour will be formed and thus low will be the vapour pressure.

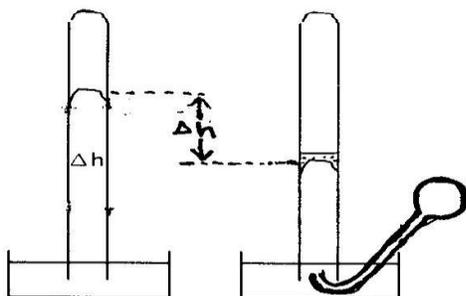
Measurement of Vapour Pressure:

There are two methods of measuring vapour pressure.

(i) Barometric Method:

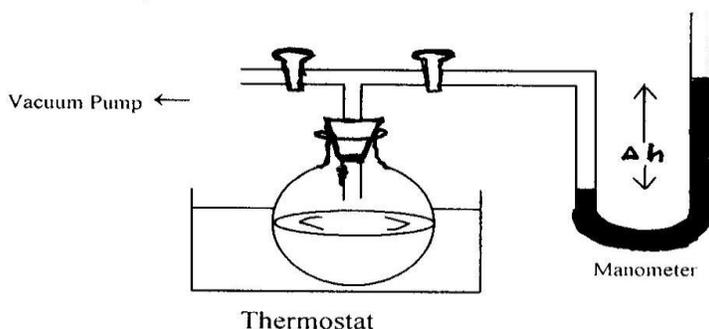
This is a convenient method of determining vapour pressure. Height of mercury column is noted. Then 1-2 drops of test liquid are introduced into barometric tube through its lower end by help of a dropper. The liquid rise above surface of mercury. A part of liquid vaporize. Due to pressure exerted by vapours height of mercury column falls and when becomes constant it is noted. The difference of height (Δh) gives vapour pressure.

Although this method is very convenient but is not much accurate.



(ii) Manometric Method:

This method is comparatively accurate. The test liquid is taken in a round bottom flask. A T-shaped tube is attached to it whose one end is connected to a vacuum pump and other end is connected to a manometer. The liquid is boiled to remove dissolved air in it. Liquid is then frozen and the air on it is removed by vacuum pump.



Liquid is again boiled to remove more air and is again frozen, the air on it will be removed by vacuum pump. This procedure is repeated again and again to remove maximum air dissolved in liquid. Now the flask is placed in a thermostat and desired temperature is set. The vapours of liquid are allowed to enter into manometer by opening the stopper. Mercury column in manometer facing vapours is depressed while that faces atmospheric pressure, rises.

Difference in heights of mercury columns in two limbs is noted from which then vapour pressure is determined.

$$P_{\text{vap}} = P_{\text{atm}} + \Delta h$$

Boiling Point:

“The temperature at which vapour pressure of a liquid becomes equal to atmospheric or external pressure is called boiling point”.

The phenomenon of conversion of liquid at its boiling point is called boiling.

With increase in temperature vapour pressure increases and ultimately reaches to atmospheric pressure or external pressure, at this stage boiling starts. At boiling temperature remains constant although heat is continuously supplied. Before boiling point heat supplied is partly used to increase P.E and partly used to increase K.E. Due to increase in K.E temperature increases. But at boiling point all the heat supplied is used to increase P.E and K.E remains constant so temperature remains constant.

Boiling points of some liquids are:

Liquid	B.P (°C)	Liquid	B.P (°C)	Liquid	B.P (°C)
Carbon disulphide (CS ₂)	46.30	Ethanol (C ₂ H ₅ OH)	78.40	Water (H ₂ O)	100.00
Carbon tetrachloride (CCl ₄)	76.80	Benzene (C ₆ H ₆)	80.10	Acetic acid (CH ₃ COOH)	118.10

Lange

Factors Affecting Boiling Point:

(i) Intermolecular forces:

Strength of intermolecular forces influences the boiling points of liquids. Stronger are the intermolecular forces low will be the vapour pressure and high will be the boiling point of the liquid and vice versa. Thus boiling point is the measure of hydrogen bonding. e.g. boiling point of H₂O is higher than that of H₂S, H₂O has strong hydrogen bonding while H₂S has dipole-dipole forces which are weaker than hydrogen bonding, so the H₂O of water is higher.

Vapour pressures of some compounds:

Compound	Formula	Vapour pressure at 293K/20°C
Isopentane	CH ₃ -CH ₂ -CH (CH ₃)-CH ₃	580 Torr
Chloroform	CHCl ₃	170 Torr
Carbon tetrachloride	CCl ₄	87 Torr
Water	H ₂ O	18 Torr
Mercury	Hg	0.0012 Torr

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Order of Strength of I.M.F	$\text{Hg} > \text{H}_2\text{O} > \text{CCl}_4 > \text{CHCl}_3 > \text{CH}_3\text{-CH}_2\text{-CH (CH}_3\text{)-CH}_3$
Order of Vapour pressures	$\text{CH}_3\text{-CH}_2\text{-CH (CH}_3\text{)-CH}_3 > \text{CHCl}_3 > \text{CCl}_4 > \text{H}_2\text{O} > \text{Hg}$
Order of Boiling points	$\text{Hg} > \text{H}_2\text{O} > \text{CCl}_4 > \text{CHCl}_3 > \text{CH}_3\text{-CH}_2\text{-CH (CH}_3\text{)-CH}_3$

This shows that liquid having higher vapour pressures have weak intermolecular forces and in turn low boiling points and vice versa.

(ii) External Pressure:

Liquid boils when its vapour pressure becomes equal to external pressure, thus boiling point depends upon external pressure. When external pressure is high liquid requires more heating to equalize its vapour pressure to external pressure and thus boils at higher temperature and vice versa. Similarly when external pressure is low, liquid needs less heating to equalize its vapour pressure to external pressure and thus boils at lower temperature e.g. (i) Water boils at Karachi (atmospheric pressure = 760mmHg) at 100°C while it boils at Murree hills (atmospheric pressure = 700mmHg) at 98°C. Mount Everest is still higher peak where atmospheric pressure is around 225mmHg so water boils at 69°C there.

(iii) Impurities:

Impure liquid boils at slightly higher temperature i.e. presence of solute in a liquid increases its boiling point. Increase in boiling point depends upon the number of particles of the solute. e.g pure water boils at 100°C but when 180g of Glucose or 342g of sucrose are dissolved in 1kg of water then it boils at 100.51°C.

Applications:

- (h) **Pressure cooker:** It is a closed container so the vapours as well air in it cannot escape and thus pressure inside it increases. Due to increase in pressure boiling point of water increases. So more heat will be absorbed by water and as a result food will be cooked quickly.

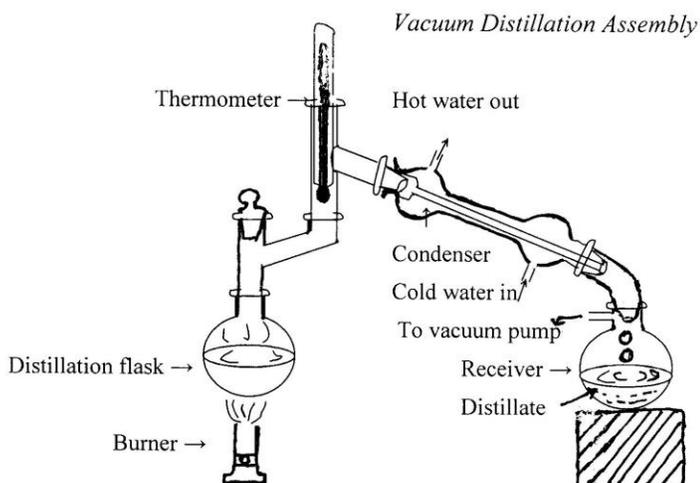
(ii) Vacuum distillation: The technique used to purify a liquid sample by first boiling and then condensing the vapours of to get pure liquid is called distillation.

“The distillation that is carried out at reduced or lower pressure is called vacuum distillation”.

By lowering the external pressure boiling point lowers. Thus in vacuum distillation boiling take place at a temperature lower than normal boiling point by reducing the external pressure.

Vacuum distillation is carried out:

- To Avoid Decomposition:** Some liquid decompose near their normal boiling point so their vacuum distillation is carried out. e.g. Glycerin boils at 290°C at 760 mmHg pressure but it decomposes at this temperature where as it boils at 120°C at 50 mmHg so it is distilled at this pressure. Similarly H_2SO_4 decomposes at its normal boiling point (330°C) so its vacuum distillation is carried out.
- To Avoid Burning of Liquid:** Some liquids are inflammable near their normal boiling point. e.g. Acetic acid is inflammable near its normal boiling point (118°C) so its vacuum distillation to prevent it from catching fire.
- To Save Fuel:** Some liquids have high boiling points. e.g. mobile oil has high boiling point so it is obtained by vacuum distillation of petroleum. It is boiled at lower temperature by reducing pressure to save energy (fuel).



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- (d) To facilitate Distillation: Lower temperatures are easy to achieve so vacuum distillation is carried out at lower temperatures by reducing pressure.

Energetic of Phase Changes:

Whenever, matter undergoes a physical change, it is always accompanied by an energy change. Energetic of physical changes is measure of strength of intermolecular forces.

Heat of fusion (ΔH_f):

It is defined as “The amount of heat required for conversion of one mole of solid into liquid at its melting point”.



Heat of vaporization (ΔH_v):

It is defined as “The amount of heat required for conversion of one mole of liquid into vapours (gas) at its boiling point”.



Heat of sublimation (ΔH_s):

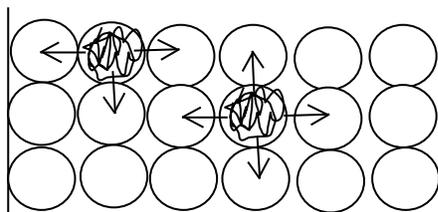
It is defined as “The amount of heat required for sublimation of one mole of solid to give vapours at a particular temperature and one atmospheric pressure”.



Surface Tension:

Consider a molecule in the interior of liquid present in a container, it is attracted from all sides by other molecules so no net force is on it.

Now consider a molecule on the surface of liquid. It is attracted from all sides except upper side so it experience a net downward force due to which liquid surface stretches. This is surface tension.



Liquid in container

It is defined as

“Stretching of liquid surface due to net downward force”

OR

“The force acting perpendicularly downward at right angle to unit length of liquid surface”

OR

“The work done in increasing unit area of liquid surface”

Factors affecting Surface Tension:

1. Intermolecular forces:

Stronger are the intermolecular forces high will be the surface tension and vice versa. e.g. Surface tension order for water, alcohol (spirit), mercury & ether is



Ether has London forces; mercury has metallic bonding while other two have Hydrogen bonding. London forces are weaker so ether has low surface tension. Water and alcohol have hydrogen bonding so their surface tension is higher than ether. Hydrogen bonding of water is stronger than that of alcohol so the surface tension of water is higher than alcohol. Mercury has metallic bondings which are stronger than hydrogen bonding so surface tension of mercury is still higher.

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2. Temperature:

Higher is the temperature weak will be the forces and thus low will be the surface tension. e.g. surface tension of hot water is lower than that of cold water.

3. Soap or detergent:

Presence of soap or detergent decreases the surface tension of water because forces among water molecules become weaker.

4. Salt:

Presence of salt increases the surface tension of water because salt ions attract water molecules with greater force. e.g. surface tension of sea water is higher than that of fresh water.

- Razor blade can float on water surface, mosquito can walk over water surface, cleaning action of water all these are explained by surface tension.

Measurement of Surface Tension:

Units: S.I. Units → N/m , J/m²
 CGS System → dyne/cm, erg/cm²

Method for measurement of surface tension:

There are three method of measurement of surface tension

1. Torsion balance method

2. Capillary rise method

3. Drop method using Stalagmometer:

In this method relative surface tension is measured. For this purpose number of drops of reference and test liquid are counted for volume of liquids present between two marks **a & b** on stalagmometer (See figure-I).

$$\gamma_T = \frac{n_R d_T}{n_T d_R} \times \gamma_R$$

Where γ_R = surface tension of ref. liquid

n_R = number of drops of ref. liquid

d_R = density of ref. liquid

γ_T = surface tension of test liquid

Water is usually chosen as reference liquid.

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Its surface tension at 293K is 7.275×10^{-2} N/m or
72.75 dyne/cm

n_T = number of drops of test liquid

d_T = density of test liquid

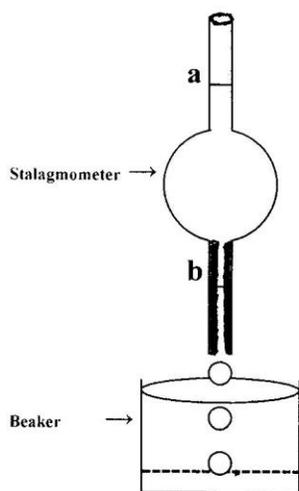


Figure-I

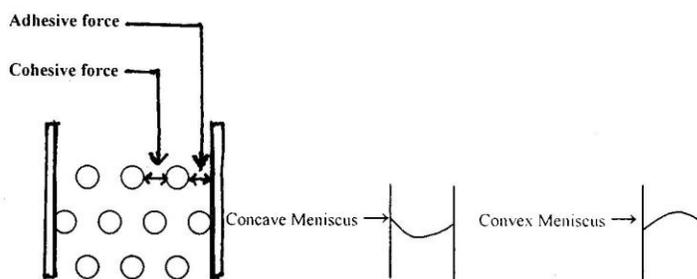


Figure-II

Figure-III

Figure-IV

Cohesive and Adhesive Forces:

The forces of attraction among liquid molecules themselves are called cohesive forces (See Figure-II). The forces of attraction between liquid molecules and wall of container are called adhesive forces (See Figure-II).

The liquids that have adhesive forces stronger than cohesive forces, form concave meniscus and they are wetting liquids e.g. water (See Figure-III).

The liquids that have cohesive forces stronger than adhesive forces, form convex meniscus and they are non-wetting liquids e.g. mercury (See Figure-IV).

Shape of liquid surface is called meniscus.

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Capillary Action:

The rise of liquid in a capillary tube is called capillary action.

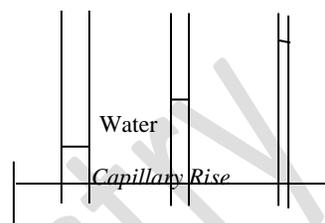
It is due to strong adhesive forces between liquid and wall of capillary. e.g. spreading ink or water on blotting paper, absorption of water by cotton,

water absorbed by roots from soil is supplied to leaves

through xylem, supply of oil to flame by wicks, all these are

due to capillary action. These materials are porous and their

pores act as capillaries.



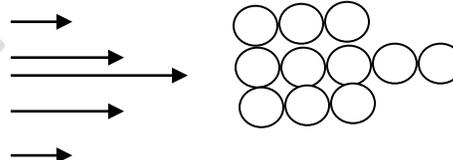
The tubes of narrower bores show more height. Actually same volume of liquid rises through capillary tubes, so less is area of cross section of the tube more will be the height gained by liquid as $\text{Volume} = \text{Area} \times \text{Height}$.

Viscosity:

Water flowing in river runs fast in the middle but slow along the bank. It means liquid flows in the form of layers. Liquid's molecules layers slide one past the other and they offer resistance to each other. This internal resistance

which one layer offer to flow of other layer is

called viscosity.



Factors affecting Viscosity:

1. Intermolecular forces:

Stronger are intermolecular forces among molecules of liquid higher will be the viscosity and vice versa e.g. viscosity of glycerin is higher than water because hydrogen bonding in glycerin is stronger than water.

2. Temperature:

Higher is the temperature low will be the viscosity and vice versa e.g. it is easy to pour honey from a bottle placed out side as compared to a bottle placed in refrigerator. In refrigerator due to low temperature viscosity of honey was high.

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3. Molecular Size and Mass:

Molecules having bigger size or more molecular mass offer more resistance to each other's flow, so more will be the viscosity e.g. mobile oil, grease etc have high viscosity, they consist of larger hydrocarbon molecules.

4. Density:

Higher is the density high will be the viscosity and vice versa e.g. viscosity of sulphuric acid is higher than water due to higher density of sulphuric acid.

5. Molecular Shape:

Irregular shaped molecules offer more resistance for each other's flow as compared to regular shaped molecules e.g. viscosity of liquid Sulphur is higher at 190°C than that at 140°C. Sulphur molecules are ring shaped at 140°C and offer less resistance to each other's flow while the molecules at 190°C are tangled and offer more resistance for flow.

Measurement of Viscosity:

Viscosity is measured in terms of coefficient of viscosity (η). Coefficient of viscosity is defined as the force required to maintain a difference of velocity of 1m/s between two parallel layers of liquid one metre apart.

Units:

S.I Unit is $\text{Kg.m}^{-1}.\text{s}^{-1}$

Other units are poise and centi poise

$$1 \text{ poise} = 10^{-1} \text{ Kg.m}^{-1}.\text{s}^{-1}$$

$$\text{Or } 1 \text{ Kg.m}^{-1}.\text{s}^{-1} = 10 \text{ poise}$$

$$1 \text{ poise} = 100 \text{ centi poise}$$

Viscosity is usually measured by Oswald viscometer (See Figure given below).

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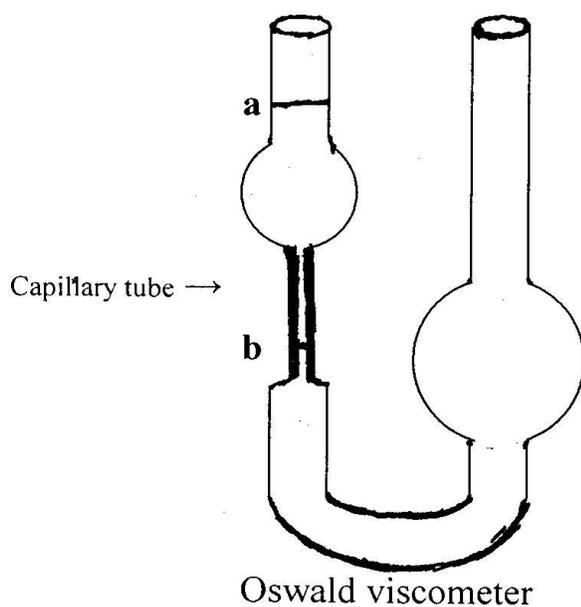
In this method relative viscosity is measured. For this purpose time for the flow of reference and test liquid between two marks **a** & **b** made on viscometer is noted. And viscosity is calculated by using formula:

$$\eta_T = \frac{d_T t_T}{d_R t_R} \times \eta_R$$

Where $\eta_{R, R}$, $t_{R, R}$ and $d_{R, R}$ are viscosity, time of flow and density of reference liquid

Where $\eta_{T, T}$, $t_{T, T}$ and $d_{T, T}$ are viscosity, time of flow and density of test liquid

Water is usually chosen as reference liquid. Viscosity of water is taken as 1 centi poise at 25°C.



Liquid Crystals:

“The phase which is intermediate of solid and liquid (semi solid) which has properties in between true crystalline solid and true liquid (clear liquid) is called liquid crystal”.

There are many crystalline solids, which first melt to a turbid liquid phase and then to a clear liquid. W. Heintz, for example, reported in 1850 that stearin melted from solid to a turbid liquid at 52°C, changed at 58°C to an opaque and at 62.5°C to a clear liquid. The turbid liquid phases have properties of liquids e.g. surface tension, viscosity etc, but they also have properties of crystalline solids e.g. optical activities etc. These turbid liquids are called liquid crystals. This state exists between two temperatures i.e. melting temperature and clearing temperature.



Characteristics:

- They are semi solids.
- They have little order among particles like solid.
- They have fluidity like liquids.
- They have surface tension, viscosity etc like liquids.
- They have optical properties like crystalline solids.
- They have properties in between crystalline solids and liquids.
- They are always isotropic.

Uses of Liquid Crystals:

Some of important uses of liquid crystals are

- (i) They diffract light. When some wavelength of visible light is reflected, from a liquid crystal it appears coloured. As temperature changes, the distance between layers of molecules of liquid crystals changes and thus colour of the reflected light changes accordingly. So liquid crystals can be used as temperature sensors.
- (ii) Liquid crystals are used to find the point of potential failure in electrical circuits.

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- (iii) They are used in room thermometers, different temperatures are shown in different colours.
- (iv) Liquid crystals are used to locate blockage in veins & arteries, infections and tumors. The reason is that these parts of the body are warmer than surrounding tissues. e.g. when a layer of liquid crystal is applied on the surface of breast, it turns blue where tumor is, as this part is warmer.
- (v) Liquid crystals are used in the display of electrical devices such as digital watches, calculators, computers, LCD (liquid crystal display) etc
- (vi) Liquid crystals are used as solvents in chromatography.
- (vii) Oscillographic and T.V display also use liquid crystal screens.
- (viii) Liquid crystals change colour with change in temperature.