BSc 1st year Physical Chemistry

1. Mathematical Concept and Computer
2. Gaseous State
3. Liquid State and Colloidal State
4. Solid State
5. Chemical Kinetics

LIQUID STATE

Liquid state is simply defined as the material that takes the shape of the container in which it is taken.

Intermolecular forces

The forces which exist b/w molecules

Let F is the intermolecular force b/w the 2 molecules which is related to the P.E as ~~provide~~ following

$$F = -\frac{dE_P}{dr}$$

E_P = potential energy
r = distance b/w the molecules.

Origin of intermolecular forces
OR
Types of Intermolecular forces

① Dipole - Dipole interaction
or Orientation Effect
or Keeson forces

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

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ϕ = avg Energy of interaction b/w two dipoles
μ_1, μ_2 = dipole moment of molecules
$4\pi\varepsilon_0$ = permeability factor
r = distance b/w both dipoles
K = Boltzman constant
T = Temp^r (In K)

② Dipole Induced Dipole

It depend upon 2 factor
① How much is dipole moment of a polar molecule
② polarizibility of a neutral molecule

$$\phi = \frac{-\mu_1^2 \alpha_2}{(4\pi\varepsilon_0)^2 r^6}$$

μ_1 = dipole moment of polar molecule
α_2 = polarizibility of neutral molecule

③ Instantaneous Dipole

$$\phi = -\left\{\frac{3}{2}\frac{\varepsilon_1\varepsilon_2}{(\varepsilon_1+\varepsilon_2)}\right\}\left\{\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^2 r^6}\right\}$$

E_1 & E_2 = ionisation energies

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④ Ion - Dipole force

$U = \frac{-eu}{r^2}$ e = charge on ion

u = dipole moment of polar molecule
r = distance b/w ion and dipole

⑤ Ion induced dipole

$U = \frac{-1}{2} \frac{\alpha e^2}{r^4}$

α = polarisiblity of neutral molecule
e = charge on ion.

⑥ Repulsive force

When molecules comes to close each other than this is repulsion b/w $e^- - e^-$ and nucleus - nucleus of both atoms

$U = \frac{B}{r^n}$ $n = 9$ to 12

$U = ?$

$r = ?^0$

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2) Structural Differences b/w Solid liquid and Gases

① Intermolecular forces and interatomic distances

ⓐ Gas →
In gaseous state molecules are far away to each other hence inter molecular forces are very less. That's why gaseous molecule can show translatory, vibratory and rotatory motion.

ⓑ Solids →
In solids constituent particles are very closely spaced hence inter molecular forces are greater. That's why solid particle can vibrate around their mean posⁿ.

ⓒ Liquid →
In liquid molecules are far away in comparison of solid and are closely spaced in comparison of Gaseous molecules. That's why liquid ~~Gaseous~~ particle show rotatory or vibratory motion.

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② Shape and Volume

ⓐ Solid
Shape → Definite
Volume → Definite

ⓑ Liquid
Volume → Definite
Shape → Indefinite

ⓒ Gases
Shape → Indefinite
Volume → Indefinite

③ Compressiblity

ⓐ Gases → Highly compressible
ⓑ Solid → No compressiblity
ⓒ Liquid → Very less compressiblity

compressiblity coefficient →
Compressiblity coefficient of a substance is the change in volume, per unit volume, per unit change in pressure at const. temp^r.

$$K \text{ (Kappa)} = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$K = \frac{V_0 - V_P}{V_0 (P - 1)}$$

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V_0 = volume of liquid at 0°C and 1atm pressure

V_p = volume of liquid at 0°C and p atm pressure.

④ Diffusion

ⓐ Solid → No diffusion
ⓑ Liquid → Less diffusion
ⓒ Gas → More diffusion.

Solid cannot diffuse due to highly closed packing.

Liquid can diffuse due to loose packing.

Gases diffuse easily due to free movement of gaseous particle.

⑤ Viscosity as property of flowing

ⓐ Solid → Solid have no viscosity
ⓑ Liquid → Liquid have tendency to flow (from high to low)
ⓒ Gases → Gases can flow in all direction.

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⑥ Effect of Heat

ⓐ Solid → Solids convert into liquid on heating.

ⓑ Liquid → Liquid convert into vapour on heating

ⓒ Gases → Gases become hot on heating

⑦ Surface Tension

ⓐ Solid → No surface tension.

ⓑ Liquid → They have S.T on surface

ⓒ Gases → Gaseous particles exert equal pressure on the walls of container.

⑧ Anisotropy and Isotropy

ⓐ Solid → Crystalline solid are anisotropic except cubic crystal.

ⓑ Liquid → isotropic

ⓒ Gases → isotropic

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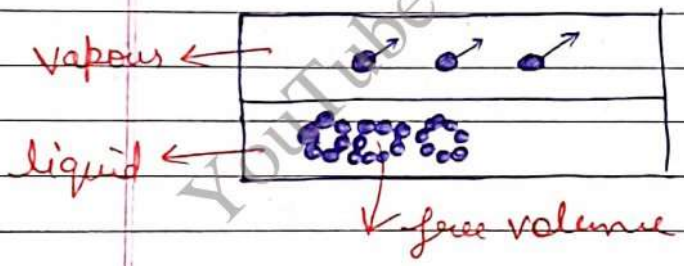
Structure of Liquid

① Eyring Theory

When any solid is converted into liq. by heating then its volume Inc by 10 % But intermolecular space is Incr by 3 %. Hence liquid have some vacant space which are not occupied by molecules such space is known as free volume.

Any liquid have only 3 % free volume of its total volume; At normal temp^{r} and pressure. these vacant spaces are molecular sized and randomly distributed in liquid.



model of liquid A/c to Eyring

Acc to this theory the molecules surrounding a given hole can jump into it Hence they behave like gas molecule. While other molecules behave as solid

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if V_l and V_s are respective volume of liquid and solid

Fraction of molecules near hole $= \frac{V_l - V_s}{V_l}$ (and this frac^n behave like gas molecule)

Frac^n of other molecules $= \frac{V_s}{V_l}$ (this frac^n behave like solid molecule)

On ↑ing temp^r conc^n of molecules ↑ea in vapour phase while conc^n of holes ↑eas in liquid phase. Hence density of vapour ↑eas bt density of liquid ↓eas.

And at critical Temp^r density of both becomes constant.

Law of rectilinear diameter

Acc to this law at eq^m avg density of liquid and vapours must ~~be~~ constant Bt in really it ~~is~~ nearly ↓eas with temp^r

$$\rho_{av} = \rho_0 - aT$$

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ρ_{av} = Average density
ρ_0, a = constant
T = temp^r (in K)

Acc to Eyring and Ree heat capacity of any liquid can be calculated acc to following formula

$$C_v = \left(\frac{V_s}{V_e}\right) 6 + \left(\frac{V_e - V_s}{V_i}\right) 3$$

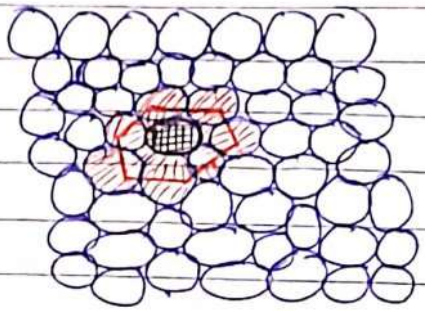
Values of C_v calculated by this formula matched with their experimental values

② Bernal and Scott theory

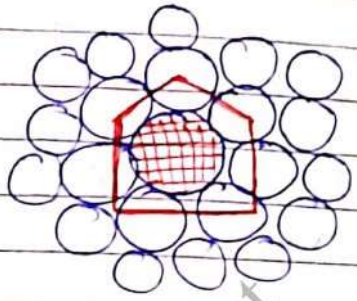
This theory is based on random packing of liquid molecules. Acc to them liquid is randomly packed str in which molecules are randomly arranged bt relatively closed.

Acc to this model molecules of liquid form irregular polyhedron shape which have 13 plane and shape of plane is pentagonal.
Such type of str shows close packing But it is loose packing.

In liquid ~~state~~ str C.N vary from 4 to 11



Solid



Liquid

★ Liquid Crystal

~~When~~ The intermediate phase (turbid liquid) lying b/w solid and liquid phase is K/n as mesomorphic ~~state~~.

This mesomorphic state shows an-isotropy ~~shows~~ which is characteristic property of crystalline solid that's why it is also K/n as liquid crystal.

Solid $\underset{\leftarrow}{\overset{\Delta}{\rightarrow}}$ turbid liquid (mesomorphic state)

Δ

gas $\underset{\leftarrow}{\overset{\Delta}{\rightarrow}}$ pure liquid

Transition Temp^r →
The temp^r at which solid converts into turbid liquid (mesomorphic state) is K/as trans^n temp^r.

Melting point →
The temp^r at which solids converts into clear liquid is K/as M.P.

Solid $\underset{\text{trans}^n \text{ temp}}{\rightleftharpoons}$ turbid liquid (liquid crystal)

Solid $\underset{\text{M.P.}}{\rightleftharpoons}$ Clear liquid

The comp^{n}ds which exibit mesomorphic state are all organic comp^{n}ds with long chain and terminating active grp such as $-OR$ (Ether), $-COOR$ (Esters) and mild active grp such as $-C=C-$, $-C=N-$, $-N=NO-$ in the middle of the molecule.

p-cholestryl Benzoate (solid) $\underset{}{\overset{145^\circ C}{\rightleftharpoons}}$ p-cholestryl Benzoate (turbid liquid)

$(C_6H_5COOC_{27}H_{45})$

$\Big\downarrow\Big\uparrow$ 178°C

p-cholestryl Benzoate (pure liquid)

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differences b/w solid, liquid crystal and liquid

Property	Solid	Liquid crystal	liquid
1. Mobility	Do not show	Show	Show
2. Viscosity	Do not show	Show	Show
3. Fluidity	Do not show	Show	Show
4. Surface Tension	Do not posses	posses	posses
5. Anisotropic nature	Aniso-tropic	Aniso-tropic	isotropic in all direction
6. Double Refraction	Show	Show	Do not Show
7. Interference pattern	form	form	Do not form

It is obvious that some property of liquid crystal matched with liquids and some property matched with crystalline solid Hence they are known as crystalline liquids, anisotropic liquid and liquid crystals.

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But appropriate word is mesomorphic state which means intermediate form of solids and liquids.

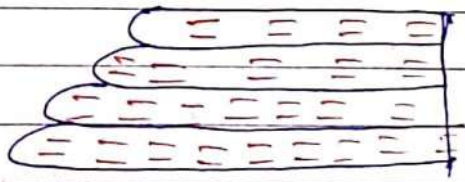
Classification of liquid crystal

① Smectic liquid crystal

* Str→ In the smectic liquid crystal molecules are arranged parallely in the form of layers but it's not necessary that molecule of one layer are ∥ to molecules of other layer.

Different layers are at a regular distance from each other and these layers can be slide on each other easily.

Smectic means soap like which is the property of these liquid crystal.



The presence of layers, suggest a crystalline str for liquid crystal.

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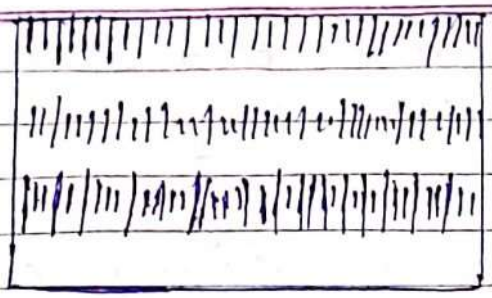

characteristic of smectic liquid crystal

① They does not flow like normal liquid. They flow in the form of layers.

② There is no newtonian flow in smectic liquid crystal i.e they does not follow Viscosity rule of newton.

③ They form X-ray diffraction pattern like normal crystals

④ In smectic liquid crystals molecules are uniaxial and non-affected by magnetic field.

⑤ These liquid crystals disperse light and by changing the temp^{r} wavelength of dispersed light changes. Hence they show different colors at diff temp^{r}.

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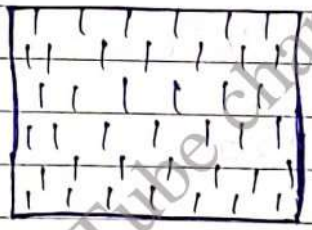
	Transⁿ temp^{r} T.T	M.P
Ethyl p-azoxy cinnamate	140°C	249°C
Ethyl p-azoxy Benzoate	114°C	121°C

② Nematic liquid crystal

Str→ In nematic liquid crystal molecules are arranged in parallel order But there are no layers and molecules are ~~in~~ looks like thread

The arrangement of molecules is irregular



Characteristic of nimatic liquid crystal

① They flow like normal liquid.

② There is neutonian flow in nimatic liquid crystal i.e they follow rules of viscosity of neutons. But there viscosity is lower then the normal liquid.

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③ They form X-ray diffraction pattern like normal crystal.

④ In nematic liquid crystal molecules are uniaxial but they are affected by magnetic field.

When turbid liquid is seen in the direc^n of magnetic line of force, it looks clear but when the magnetic field is removed it again seems turbid

⑤ They do not disperse light.

	T.T	M.P
eg → para Azoxy Anisole	116°C	135°C
para Azoxy Phenitole	137°C	167°C

③ Cholestric liquid crystal

The liquid crystals which posses characteristic of nimetic as well as smectic liquid crystal are known as cholestric liquid crystals.

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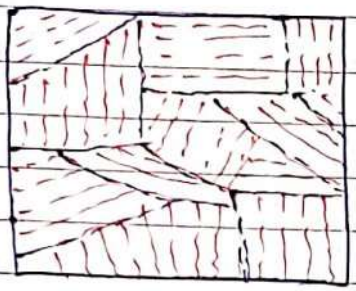
There are thin liquid like nimetic but they show color in polarised light Hence there str is layer type like smectic these layers form an angle with each other which gets change.



Eg → p-cholestryl Benzoate (Solid) $\underset{}{\overset{145°C}{\rightleftharpoons}}$ p-chlestryl Benzoaate (liquid crystal) ‖ 178°C p-cholestryl Benzoate (liquid)

④ Mixed liquid Crystal

Some comp'd shows both smectic and nimetic phase.

Cholestryl myristate (Solid) $\underset{}{\overset{72°C}{\rightleftharpoons}}$ cholestryl myristate (smectic phase) $\underset{}{\overset{78°C}{\rightleftharpoons}}$ cholestryl myristate (Nematic phase)

Cholestryl myristate (liquid) $\overset{83°}{\rightleftharpoons}$

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Some mixed liquid crystal have 2 smectic & one nematic phase.

Eg → Ethyl. Anisole p- amino cinnamate (EAPAC)

EAPAC (Solid) $\overset{83^\circ}{\rightleftharpoons}$ EAPAC (Smectic-I) $\overset{91^\circ C}{\rightleftharpoons}$ EAPAC (Smectic-II)

EAPAC (liquid) $\overset{133^\circ C}{\rightleftharpoons}$ EAPAC (nematic) $\overset{118^\circ C}{\rightleftharpoons}$ EAPAC (Smectic-II)

Application of liquid crystal

① Numbers Display

If a thin layer of nematic liquid crystal is placed b/w a electrode and electric field is applied then their regular str is distributed & liquid becomes non-transparent.

When Electric field is removed the liquid again becomes transparent. This property is used in digital watches, electronic calculator to display the numbers.

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② Thermography

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This is the technique of moniteriig of body temp ~~like~~ ~~is~~
Eg → Solid crystal, liquid crystal, refract light

Cholestric liquid crystal show color chays with change in temp^{r}. This property is used for knowig body temp^{r} and K/as Thermography.

Thermography is wed in detctig the pos^{n} and size of a tumour in any part of human body.

In this method a small amnt of cholestric liquid crystal is injected in the affectig part of the body that part is irradiate with high energy radiation.

The temp^{r} of tumour affected part is diff from the other part of the body as wavelength & color of the reflecting radiation will be different.

A photo of the affected part can be developed on the photographic plate or computer screen.

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⑤ Seven Segment Cell

These cells are used in pr meters, meters of petrol & diesel, digital watches, calculators etc to form the numerals from 0 to 9.

These cells are made up of nematic liquid crystals & have 7 segment 'a to g'.

Digits are converted into electrical signals and then sent to the cell which make liquid crystal non-transparent and visible in the proper segment.

When the electrical sig are removed the liquid crystal in cell again ——— becomes transparent and digits are invisible.

⑥ As a lubricant

The str of smectic liquid crystal is layered & these layers can slide on each other making it a good lubricant.

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