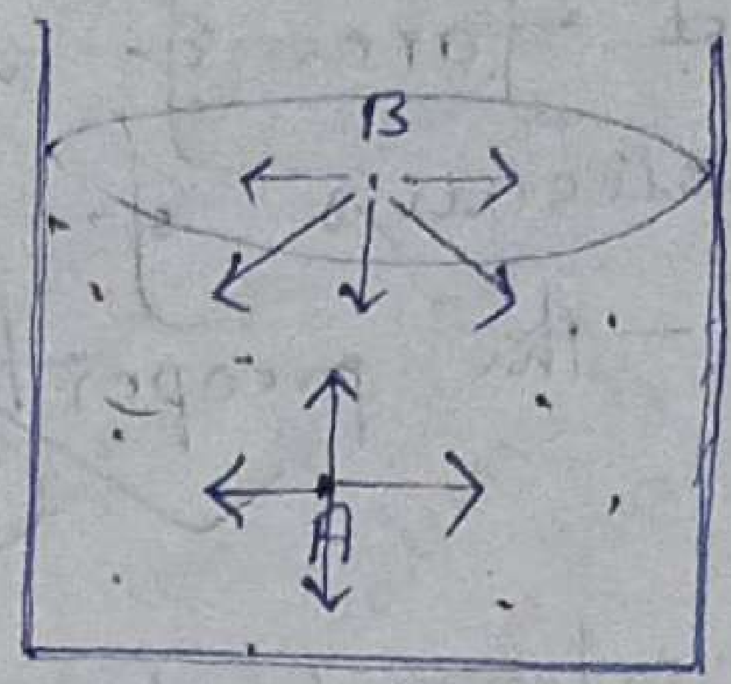
Surface Tension and . Surface energy.

①



Ⓐ — in the bulk of the liquid.
— uniformly surrounded by other molecules.
— resultant force on it becomes nil.

Ⓑ — on the surface of the liquid.
— Partially surrounded by other molecules.
— resultant force inward side.

ⓐ — The molecules on the surface try to leave the surface and enter into the bulk of the liquid.

ⓑ — The surfaces is thus under tension
→ minimum surface area.

②

This unbalanced force of attraction on the surface molecules of a liquid is the origin of the property.

→ Higher the intermolecular attraction force, greater is the magnitude of the surface tension of the liquid.

Consequences of the property :

1) 1 liquid ⟶ shape ⟨Sphere⟩ (minimum surface area) $\gamma \propto S$

↓

Droplets, when falls freely. ⟨Sphere⟩ ✓

the max^m no. of molecules to remain in the bulk rather than on the surface.

ii) Formation of bubbles of gas in liquid.

iii) Rise and fall in capilary.... etc.

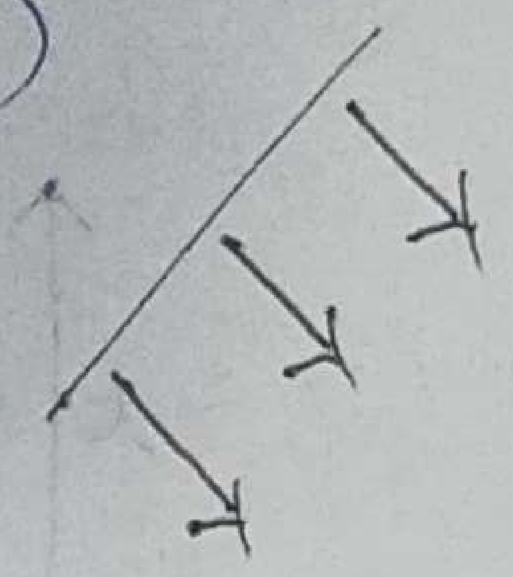
③

Since surface tension is under tension, any attempt to make a penetration along any line on the surface will require an application of force to hold the separate portions of the surface together. This force is called surface tension.

This is expressed in force / length.

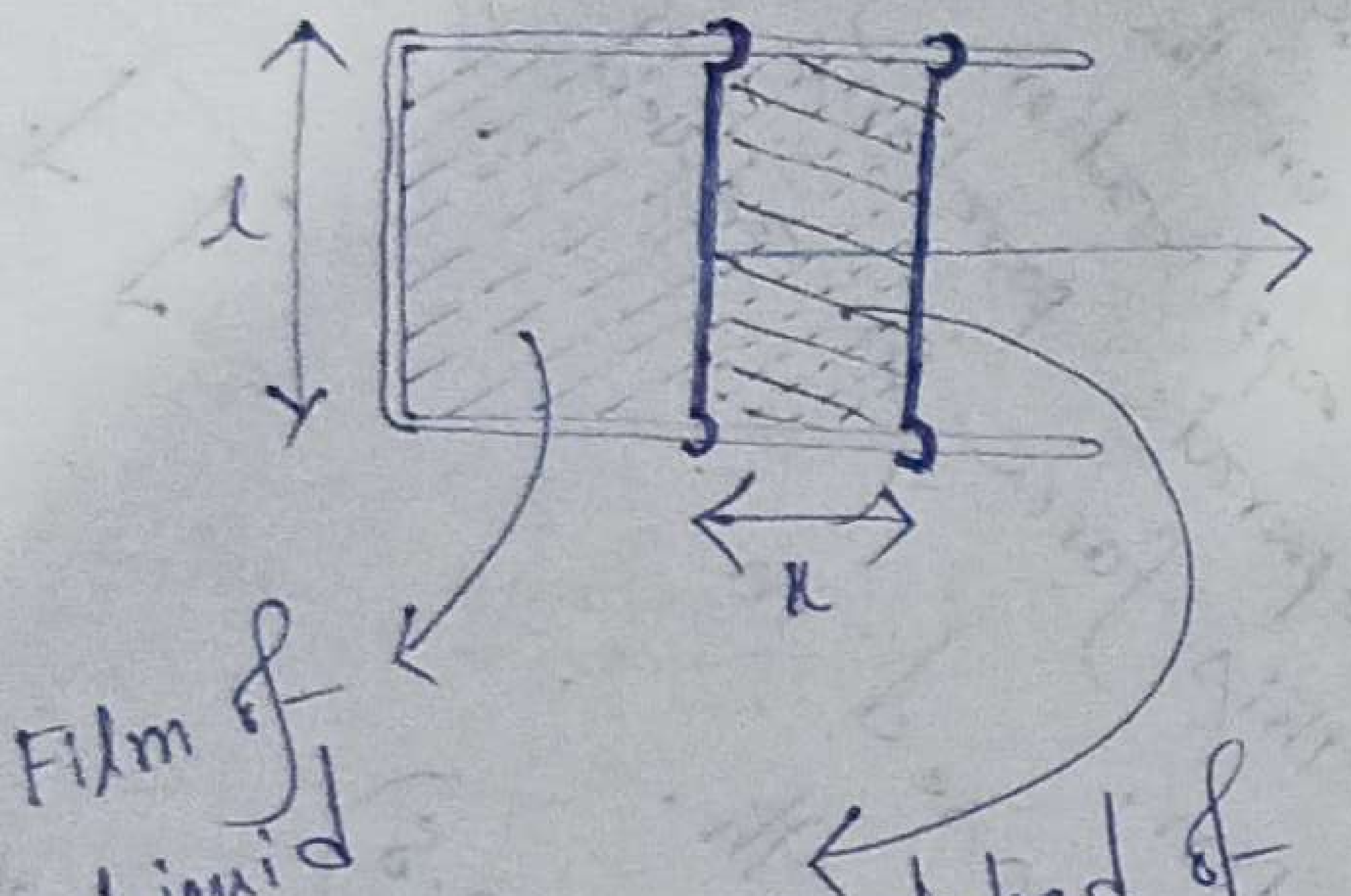
dyne/cm (c.g.s) and Newton/metre (MKS)

$\frac{MLT^{-2}}{L}$ MT^{-2}



⟹ Thus surface tension is the force per unit length on the surface that opposes the explansion of the surface area.

Relation between surface-tension and surface energy.



stretched of Liquid-film area = $(l \times x)$ ✓

The opposing force against the stretching is due to the surface-tension $\approx (\gamma \times 2l)$

l = Length of the film in contact with wire.

W = opposing force × displacement

$= (\gamma \times 2l) \times x$

$= \gamma \times 2 \times (l \times x)$

$W = \gamma \cdot \Delta A$

ΔA = increase of surface area of the film on both side

w = surface energy associated with the surface area (ΔA)

$$\gamma = \frac{w}{\Delta A}$$

⇒ Defination of surface-tension

⇒ γ is the amount of work (w) required to increase the surface area of the liquid by unit.

$\Delta A = 1$

⇒ surface energy / unit area

⇒ unit of surface energy per unit area = erg/cm^2

Thermodynamics of the property in the presence of a single component system with variable surface area,

$$dG = -SdT + Vdp + \gamma . ds$$

ds = change in surface area of the liquid.

at const T, P

$$dG_{T,P} = \gamma . ds$$

For any system $dG \rightarrow$ smaller

so, $ds \rightarrow$ small or less.

$dG < 0$

⑥

At const T and P, for spontaneity of the system, $dG < 0$ and $ds < 0$

That means the surface area have natural tendency to contract.

Wetting and non-wetting liquids

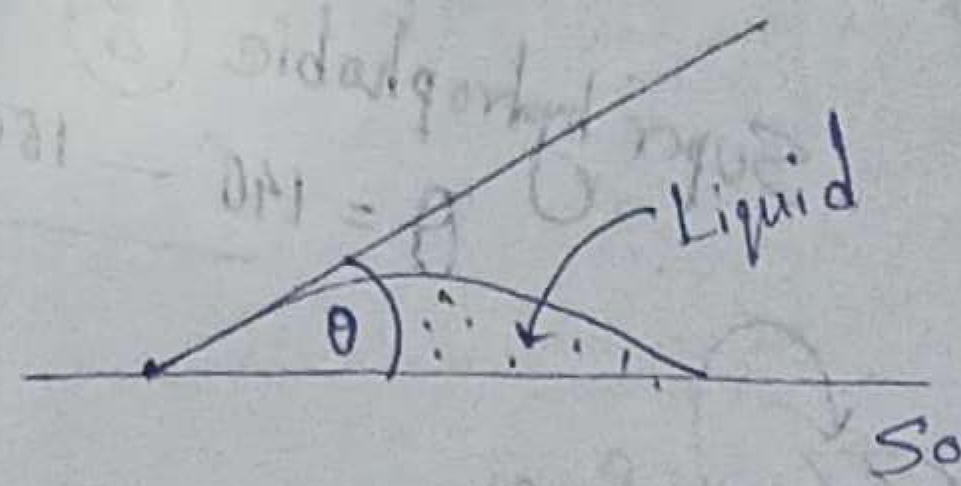
Liquids can be classified into two types depending on their ability to wet the solid surface.

↓

Angles of contact (θ)

It is defined as the angle between the tangent to the liquid surface at the point of contact and the solid surface inside the liquid.

⑦



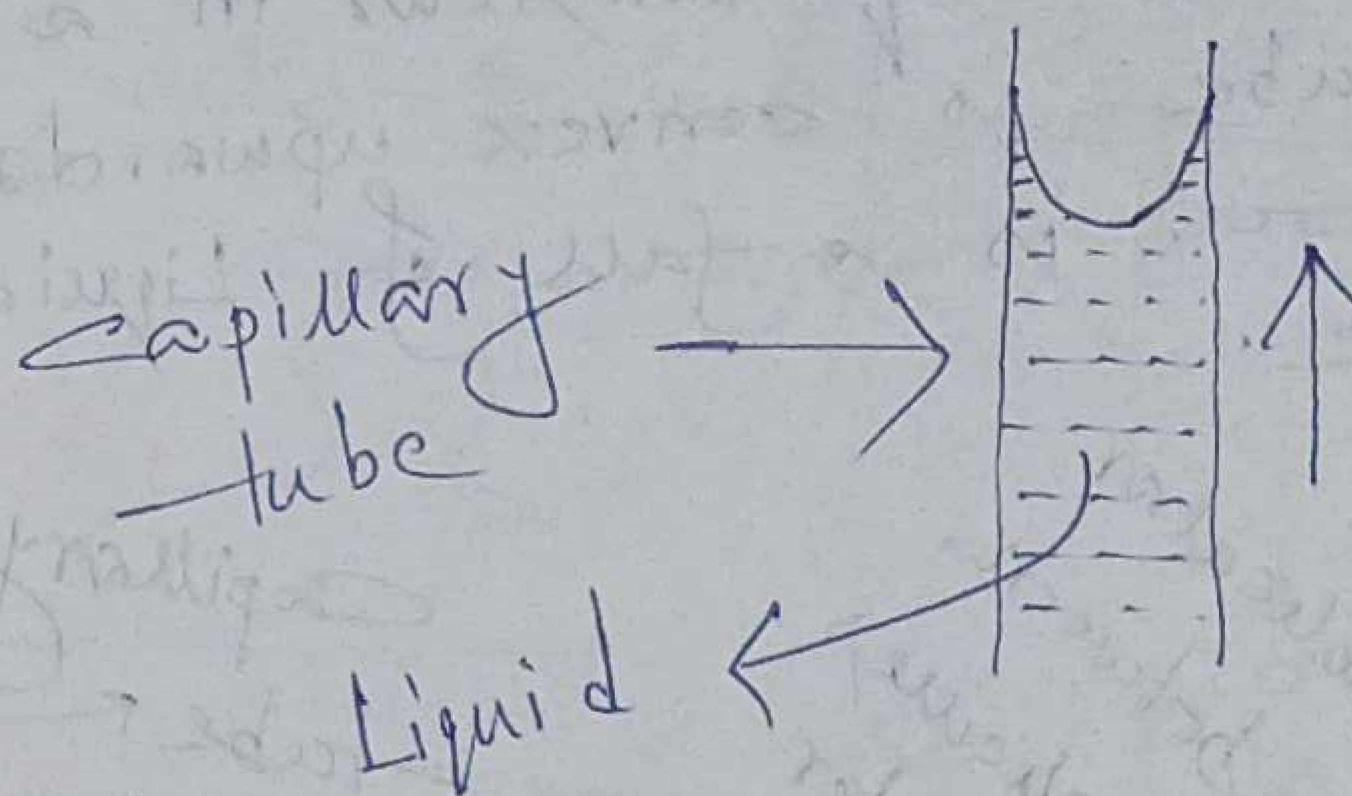
$\theta = 5^\circ$ = super hydrophilic

Example → Water on glass $\theta = 18^\circ$

Wetting Liquid ($\theta < 90^\circ$)

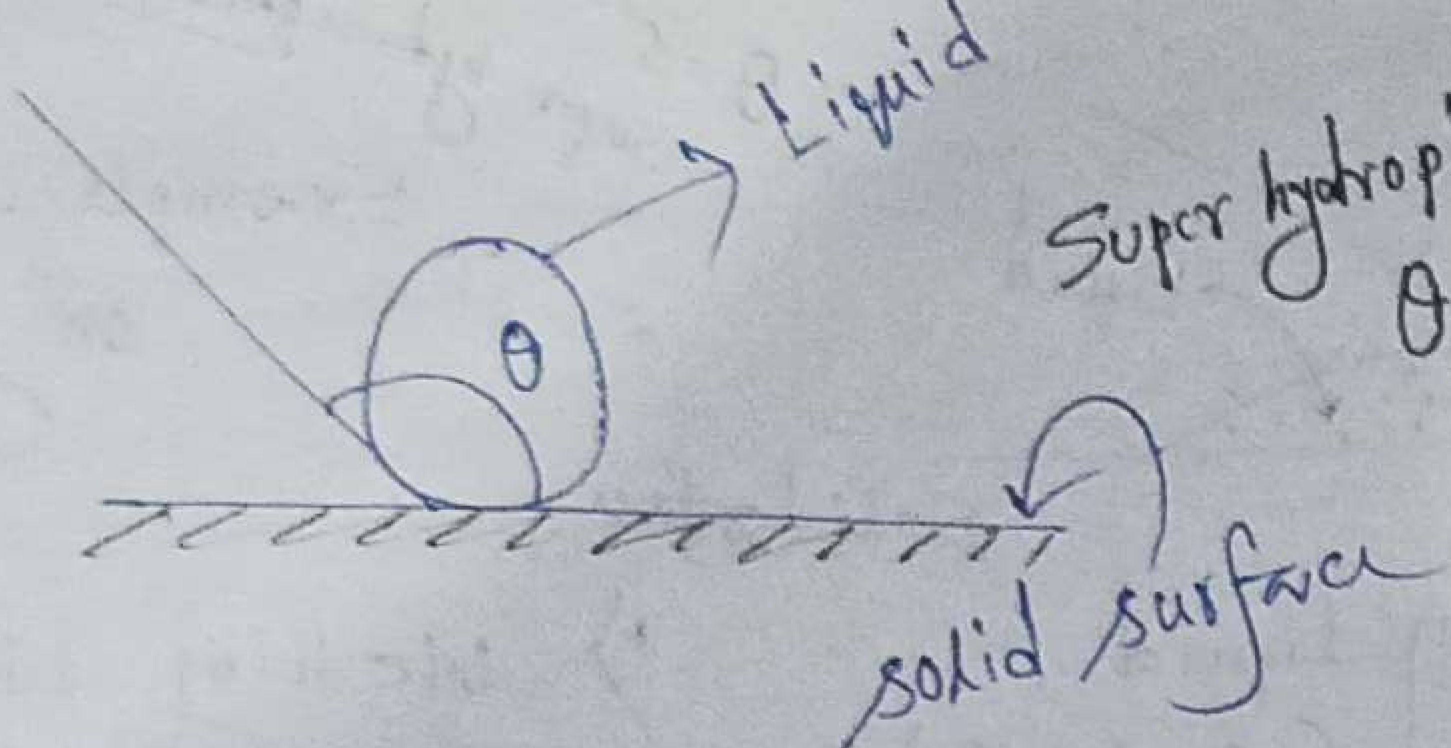
i) Wetting Liquid has tendency to spread on the surface

ii) The Liq meniscus in a capillary tube is concave upwards and so there is a rise of Liquid in the tube.



iii) Inter molecular attraction (cohesion) between the liquid molecules is less than that liquid molecules and solid molecules (adhesion)

?



Super hydrophobic
θ = 140° – 150°

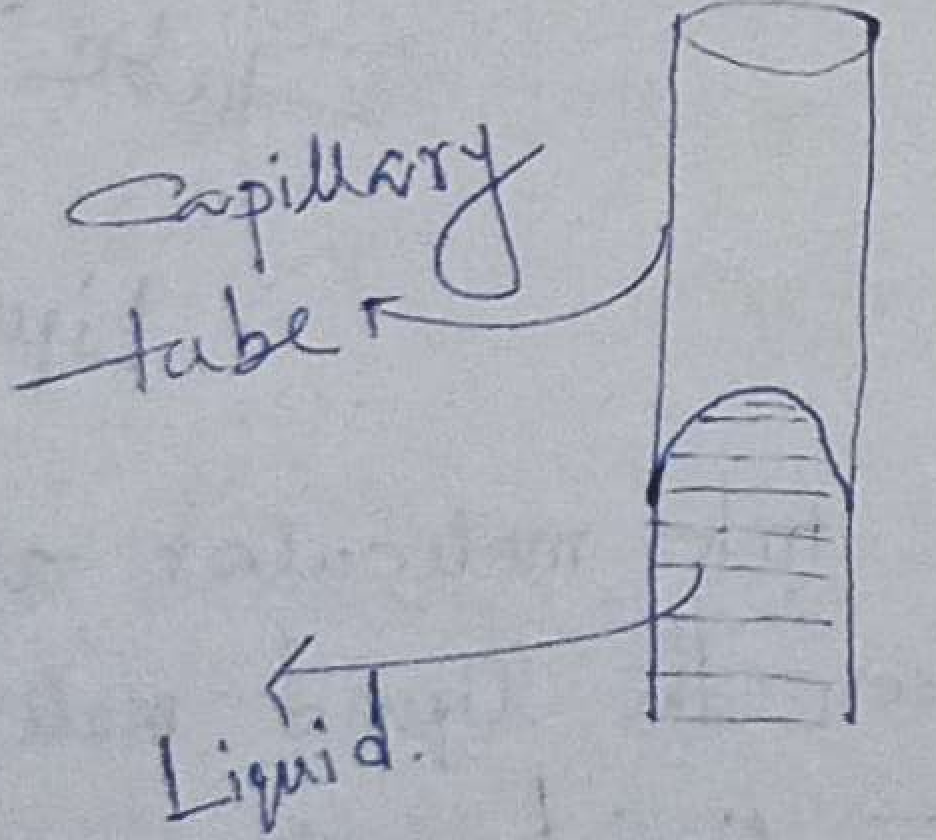
Non-wetting Liquid $(\theta > 90^\circ)$

Mercury on glass, $\theta = 140^\circ$

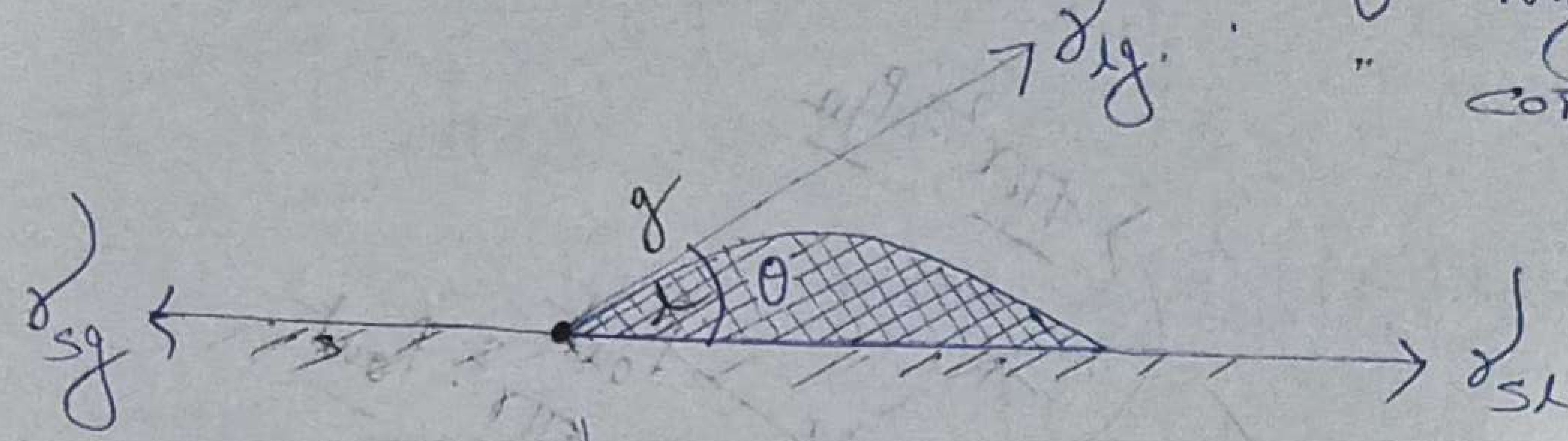
i) Non-wetting liquid has a tendency to detach the solid surface.

ii) The liq. meniscus in a capillary tube is convex upwards and so there is a fall of Liquid in the tube.

iii) Inter molecular attraction between the liquid molecules (co-hesion) is greater than that between the liquid molecules and solid molecules (adhesion).



condition of wettability :-



θ = angle of contact.

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cdot \cos\theta$$

or,

$$\boxed{\cos\theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}}$$

i) Liquid wets the solid surface, $\theta < 90^\circ$, $\cos\theta = (+)\text{ve}$, $\therefore$

$$\gamma_{sg} > \gamma_{sl}$$

→ The liquid spreads.

ii) When the Liquid does not wet the surface, $\theta > 90^\circ$, $\cos\theta = (-)\text{ve}$ and

$$\gamma_{sg} < \gamma_{sl}$$

The liquid does not spread. inside

$$\boxed{P = \frac{2\gamma}{r}}$$ — This simple relation is called Laplace equation.

When $r = \infty$

= infinity radius of curvature of curved surface.

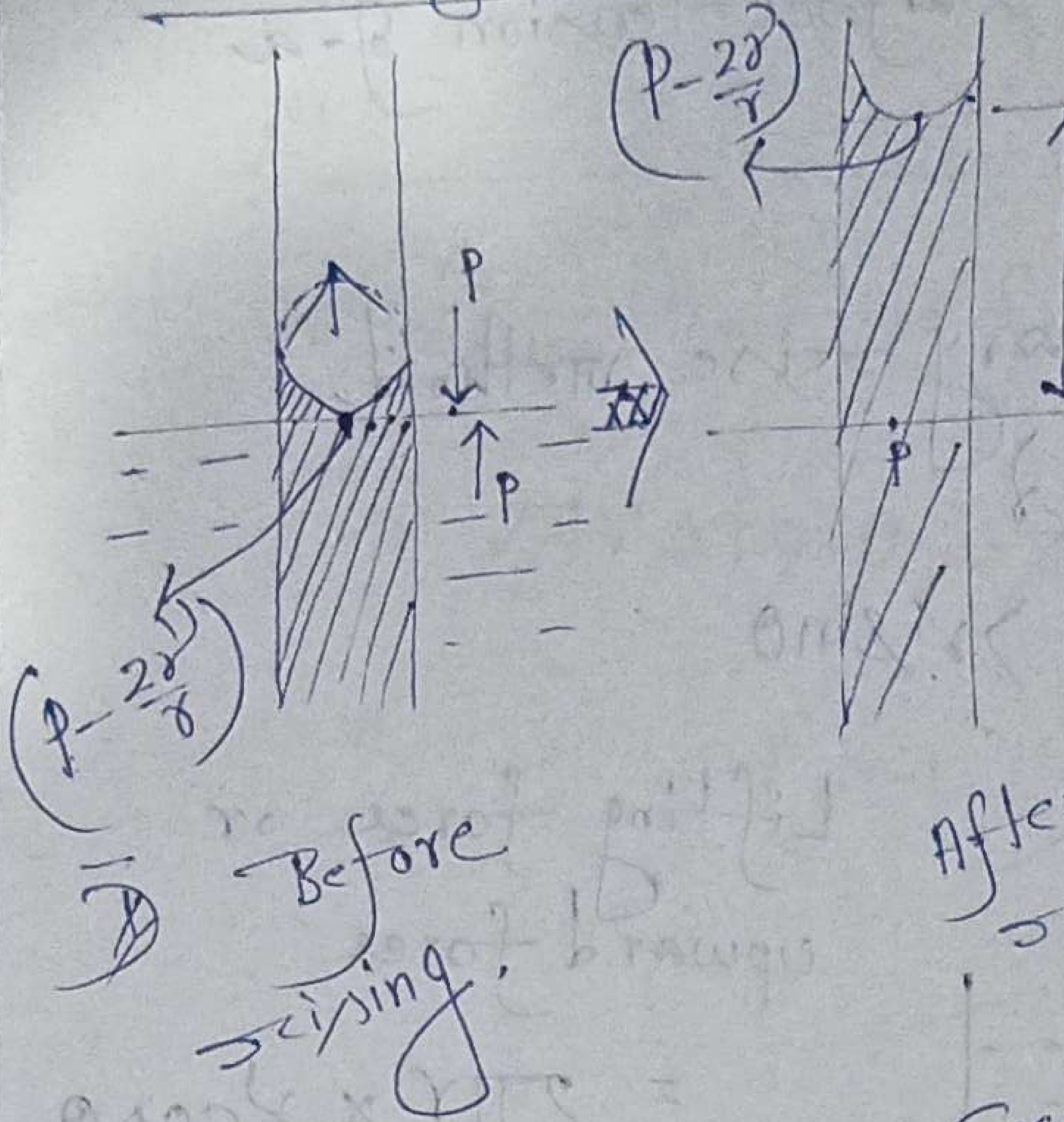
= ie — the surface is flat.

— the pressure difference becomes Zero.

$$P \propto \frac{1}{r}$$

It means, — the smaller bubble requires higher pressure for its formation and maintanance.

Capillary - rise phenomena



$$P = \left(P - \frac{2\gamma}{r}\right) + h\rho g$$

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

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

Excess pressure

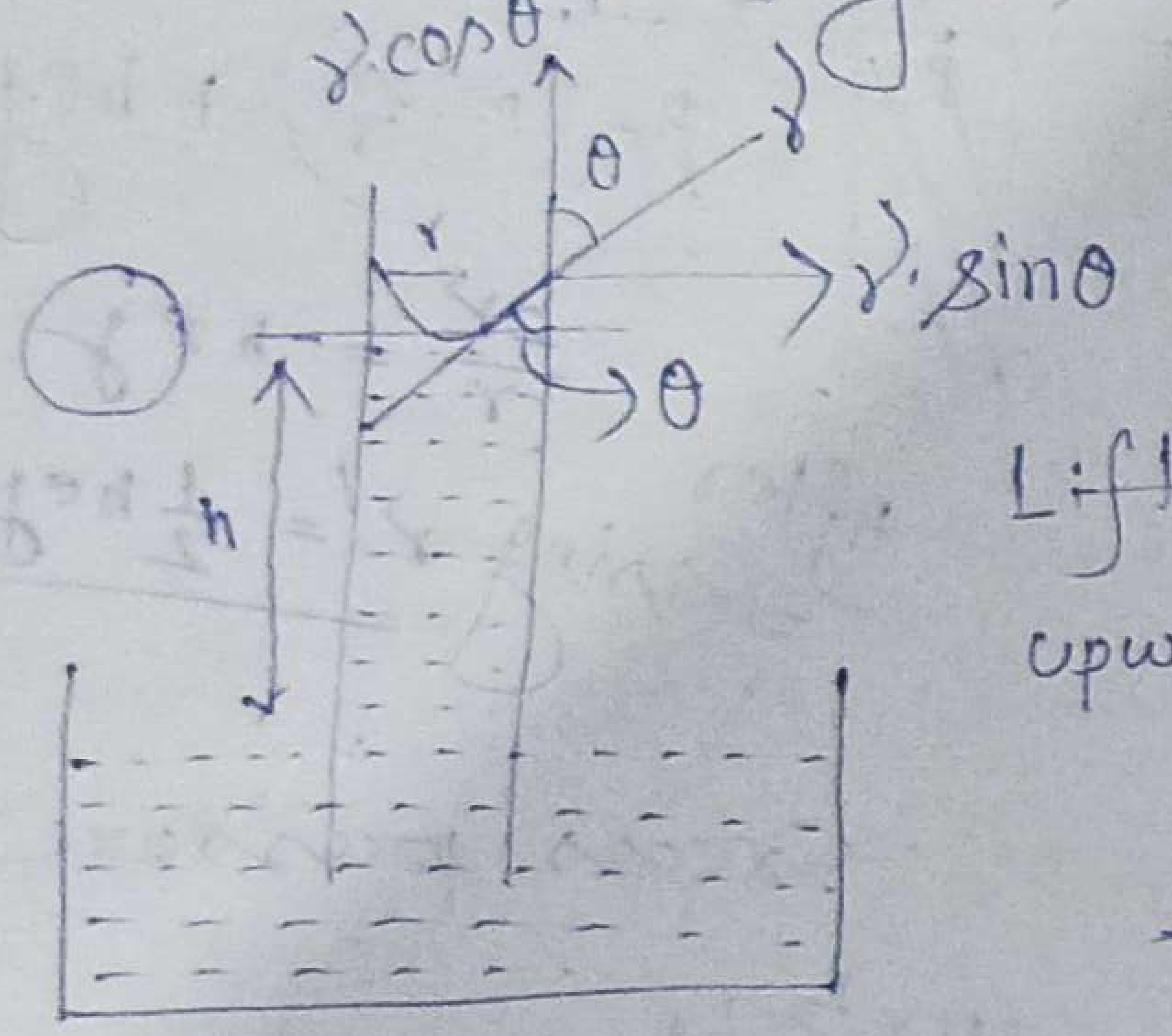
$$\frac{\pi r^2 \rho h g}{\pi r^2} = \frac{2\gamma}{r}$$

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

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

Determination of surface-tension of a liquid.

ⓐ capillary rise method.



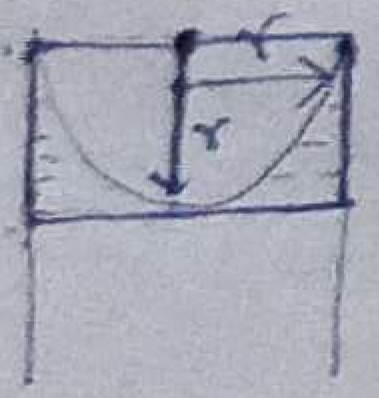
Lifting force or upward force

$= 2\pi r \times \gamma\cos\theta$

r = radius of capillary tube or radius of meniscus.

The weight of liquid or downward force $= \pi r^2 h\rho\cdot g + v\cdot\rho g$.

v = volume of the liquid in the meniscus itself.



$= \pi r^2\cdot r - \frac{1}{2}\cdot\frac{4}{3}\pi r^3$

$= \frac{1}{3}\cdot\pi r^3$

so, Down-ward force

$= \pi r^2\cdot h\cdot\rho\cdot g + \frac{1}{3}\pi r^3\cdot\rho\cdot g$

Downward force $= \pi r^2\cdot(h + \frac{1}{3}r)\cdot\rho\cdot g$

At equil^m, the two forces are equal

so, $2\cancel{\pi} r\cdot\gamma\cos\theta = \cancel{\pi} r^2 (h+\frac{1}{3}r)\cdot\rho\cdot g$

$$\gamma = \frac{(h+\frac{r}{3})\cdot\rho\cdot g\cdot r}{2\cdot\cos\theta}$$

For most liquids (wetting), $\cos\theta = 1$

and $r \ll h$

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

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16

Relative surface tension of a liquid with ref. to water can be easily determined by using the same capillary tube

$$\gamma_l = \frac{1}{2} \cdot h_l \cdot \rho_l \cdot g \cdot r$$

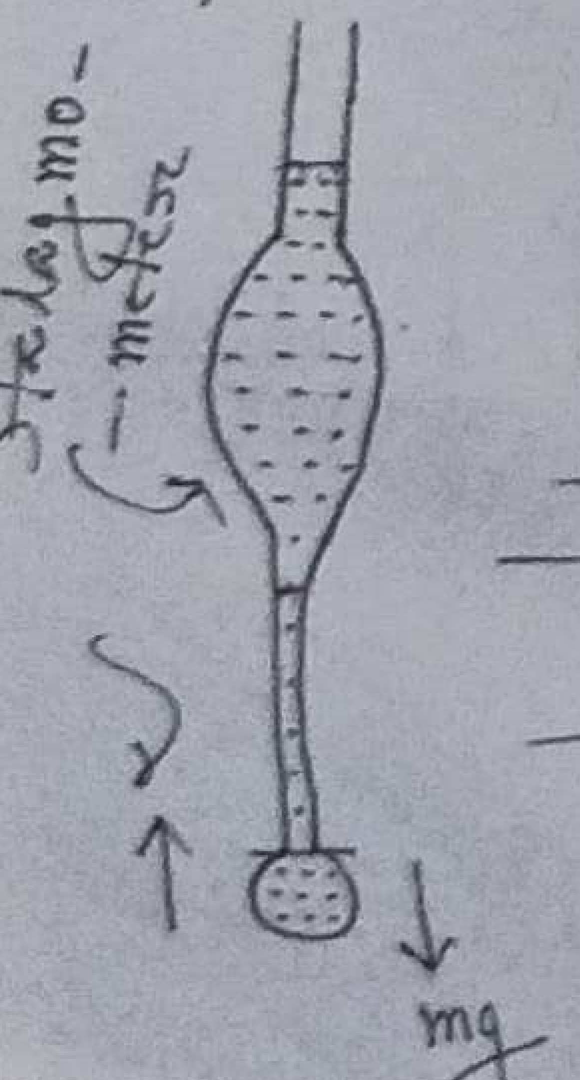
$$\gamma_w = \frac{1}{2} \cdot h_w \cdot \rho_w \cdot g \cdot r$$

Now, $$\frac{\gamma_l}{\gamma_w} = \frac{\rho_l}{\rho_w} \times \frac{h_l}{h_w}$$

$$\therefore \gamma_l = \gamma_w \times \left(\frac{\rho_l}{\rho_w}\right) \times \left(\frac{h_l}{h_w}\right)$$

This is obtained from std. table. (T).

b) Drop - weight or drop No. method



Surface tension is the force, when this force is balanced by the mass of the lower portion, a drop breaks off.

ie $2\pi r\gamma = mg$

17.

$$\gamma = \frac{mg}{2\pi r}$$

Where m = mass of the drop.

$$\Rightarrow \gamma_l = \frac{m_l \cdot g}{2\pi r} \text{ and } \gamma_w = \frac{m_w \cdot g}{2\pi r}$$

Relative method $$\frac{\gamma_l}{\gamma_w} = \frac{m_l}{m_w}$$

$$\therefore \gamma_l = \gamma_w \times \left(\frac{m_l}{m_w}\right)$$

$$= \gamma_w \times \left[\frac{\rho_l \times \frac{V}{n_l}}{\rho_w \times \frac{V}{n_w}}\right]$$

$\rho = \frac{\text{mass}}{\text{vol}}$

$$\gamma_l = \gamma_w \times \left(\frac{\rho_l}{\rho_w}\right) \times \left(\frac{n_l}{n_w}\right)$$

V = volume of liquid or water, same.

n_l and n_w → Drop No. of liquid and water

i) The liquid is allowed to drop slowly. and

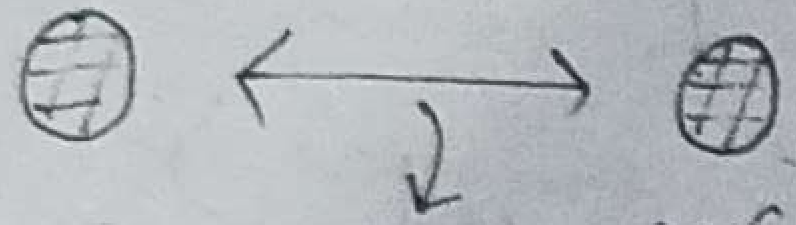
ii) stalagmometer must be cleaned

iii) During falling of the liquid, air current or disturbance is avoided to get accurate result.

∴ $EtOH/H_2O$ = ~~20 ml/20 ml~~

H_2O

Effect of tempr on surface tension



inter molecular attraction (γ)

Tempr ↑ (increase)

intermolecular attraction ↓ (decrease)

↓

so the value of γ ↓ (decreases) with T ↑ (increase)

so at critical tempr $\gamma = 0$.

R. von. Eotvos found that molar surface energy $[K' \cdot (mv)^{2/3} \cdot \gamma]$ varies linearly with tempr in deg centigrade ($t°c$) ie

$K' (mv)^{2/3} \gamma = a - bt$ v = sp. volume of the liquid

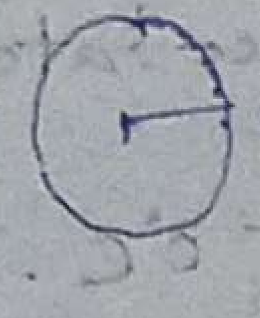
or, $(mv)^{2/3} \gamma = K_1'' - K'' t$

But at $t = t_c$, $\gamma = 0$

so, $0 = K_1'' - K'' t_c$ or, $K_1'' = K'' t_c$

$(mv)^{2/3} \gamma = K \cdot [t_c - t]$

Molar volume $= M \cdot v$ v = sp. volume of the liquid



$V = \frac{4}{3}\pi R^3 = M \cdot v$

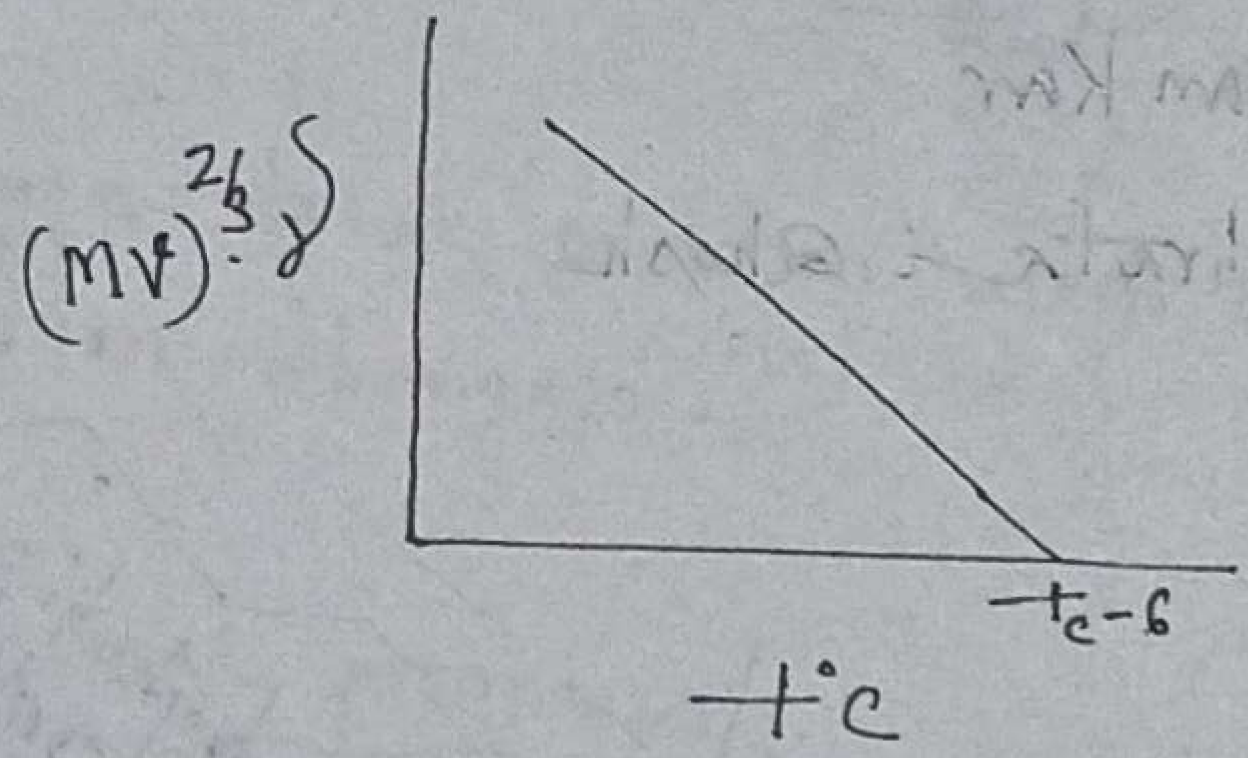
∴ $R = \left[\frac{3}{4\pi}(Mv)\right]^{1/3}$

The surface area, $A = 4\pi R^2$

$= 4\pi \times \left[\frac{3}{4\pi} \cdot (Mv)\right]^{2/3}$

= ~~4π~~ $A \propto (Mv)^{2/3}$

Molar surface energy $= K' \cdot (Mv)^{2/3} \cdot \gamma$



W. Ramsay and J. shields made a study of Eotvos equation and found that, the expl result could be better expressed by the relation,

$$(Mv)^{2/3} \cdot \gamma = K(t_c - t - 6)$$

ie γ becomes zero at 6°c below the critical tempr (t_c).

The surface tension of ethyl acetate ($T_c = 523°K$) is 25 dynes/cm at 0°C. Estimate its value at 50°C.

$(MV)^2$

14/6/2021

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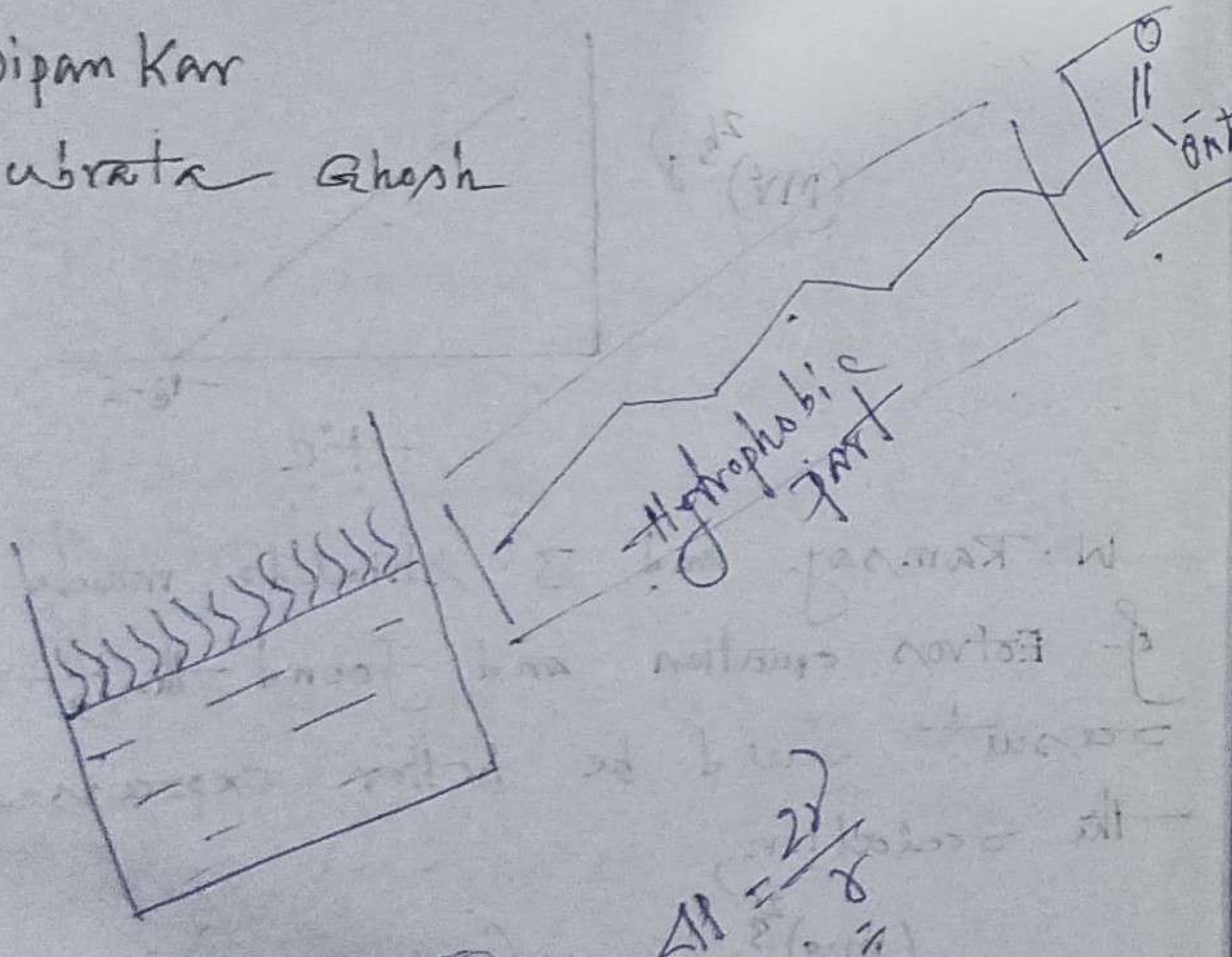

$$\Delta P = \frac{2\gamma}{r}$$