VIVEKANANDA COLLEGE
THAKURPUKUR
KOLKATA-700063

NAAC ACCREDITED 'A' GRADE

Topic:	Surface Tension
Course Title:	General Physical Chemistry
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Unit:	Biophysical Properties
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Name of the Teacher:	**Dr. Subharthi Banerjee**
Name of the Department:	Biochemistry

Surface Tension:

- When a small quantity of water is poured on a clean glass plate, it spreads in all directions in the form of a thin film.

But, when a drop of Hg is poured on a glass plate, it takes the form of a spherical drop. Similarly, a small quantity of water poured on a greasy plate takes the form of small globules.

→ Thus behavior of liquids is controlled not only by gravitational force (weight), but also by the nature of surfaces in contact with it.

→ For liquids of negligible weight, their shape is perfectly spherical eg. soap bubble (sphere → min. area)

→ Liquid surfaces always tend to contract to a minimum possible area due to tensions on its surface.

Let an imaginary line AB be drawn on a liquid surface. The surface on either side of this line exerts a pulling force on the surface on the other side. This force lies on the plane of the surface and is ⊥r to the line AB.

The magnitude of this force (F) per unit length of AB (l) is surface tension (T) or (γ)

$$T = F/l$$

If $l = 1$, then $T = F$.

Thus, surface tension of a liquid is defined as the force per unit length in the plane of the liquid surface, acting at right angles on either side of an imaginary line drawn in that surface.

Unit: SI → Nm^{-1}

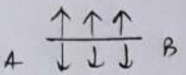
CGS → dyne cm^{-1}

Dimension: $\frac{[F]}{[l]} = \frac{MLT^{-2}}{L} = MT^{-2}$

T depends on temp, nature of liquid & the nature of the surfaces on its either side.

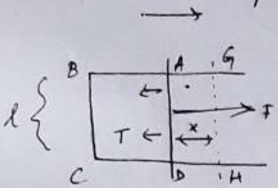
- A liquid surface acts a stretched membrane and a tension acts tangentially on its surface.

The tension in a stretched membrane increases with increase in stretching, whereas the surface tension of a liquid surface remains constant.



A small line AB on a liquid surface is in equilibrium due to equal & opposite forces acting on each side of it.

- Surface energy:



A thin wire is bent at right angles twice to form a framework GBCH. Another wire AD is slid perpendicularly between the arms BG & CH, such that AD can slide on either side without friction.

The framework is dipped on a soap solution & taken out. A thin film will from in the space ABCD. Due to surface tension, forces will act on AD wire ⊥r to its length ~~& the f~~ on the thin film surface (above & below) to pull AD towards BC. To keep AD fixed in its position, an equal & opp. force (F) must be applied ⊥r to its length, to balance out the surface tension (T).

Force acting on AD towards BC = Surface tension × length of AD×2

(∵ there are 2 surfaces)

$$= T.\,2l$$

∴ opposing force $F = 2Tl$.

If F moves the wire AD by a distance x towards GH,

Work done $= F \times x = 2lTx$.

Total increase in surface area $= 2lx$ [upper & lower increases by lx]

$$\therefore \boxed{W = \gamma\, \Delta A} \Rightarrow \boxed{\gamma = \frac{W}{\Delta A}}$$

Work done to increase surface area by $2lx = 2lTx$.

" " " " " " " unity $= \frac{2lTx}{2lx}$

$= T$.

Similarly,

work obtained (stored as p.e. of the film) if the surface contracts by unity $= T$.

Thus, surface tension is numerically equal to surface energy / unit area.

- Surface energy is defined as the amount of work done in increasing the area of a surface film by unity under isothermal conditions.

  Unit : $J m^{-2}$ / $ergs\ cm^{-2}$

- Note : If surface area is increased rapidly adiabatically,

  → the film cools down & T changes.

  If the expansion is performed isothermally, heat flows into the surface from the surroundings to keep steady temp.

  → The sum total of the mechanical energy & heat energy involved for unit area expansion is called surface energy.

i.e. $E = T + Q$

$Q = -\theta \frac{dT}{d\theta}$ θ = temp. in absolute scale

$\frac{dT}{d\theta}$ = rate of increase of T with temp (θ).

$\therefore E = T - \theta \frac{dT}{d\theta}$

When $\theta = 0$ or $\frac{dT}{d\theta} = 0$, $E = T$.

Now, T decreases with θ. $\therefore \frac{dT}{d\theta}$ is $\ominus$ve.

$\therefore$ for liquids, $E = T - \theta\left(-\frac{dT}{d\theta}\right) = T + \theta\frac{dT}{d\theta}$

i.e. Surface energy of liquids always greater than surface tension.

• Molecular Theory of surface tension :

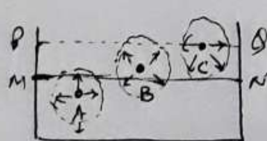
→ Force of adhesion → attractive forces between different molecules
→ " " cohesion → " " " similar "

[∵ these forces die out if distance > 1 nm]

→ These forces are different from gravitational forces and do not obey inverse square law.

→ Force of cohesion greatest in solids, less in liquids & least in gases.

→ The greatest distance at which molecules can attract each other by cohesion/adhesion is called their <u>molecular range</u> [~ 10^{-9} m]



Let us consider 3 molecules A, B & C of a liquid. A is inside the liquid mass, B is just below the free surface & C is on the free surface.

A → no resultant cohesion as all forces balance out

B → the sphere of influence is partly outside & mostly inside the liquid. The no. of molecule exerting cohesive forces on B are less on its upper side than on its lower side. Thus B experiences a net downward pull.

C → Downward pull is maximum as the upper surface has no molecules to exert upward cohesive force.

PQ → free liquid surface
MN → liquid surface || to PQ at a distance equal to the molecular range.

Surface film → Liquid surface between PQ & MN.

→ All molecules on the surface film experience a net downward cohesive attraction, the magnitude of which increases as the free surface PQ is approached.

→ Downward cohesive forces prevent molecules from escaping from the free surface.

→ To bring a molecule from the bulk to the surface, work has to be done against this downward cohesive force, which is stored as P.E. in the surface molecules. Thus molecules on the surface have a greater P.E.

→ A mechanical system tries to attain minimum PE for stability. Hence the surface is under tension & tends to occupy the least surface area to decrease the no of molecules on its surface.

- Factors affecting T:

i) Contamination: $T \downarrow$ with impurities on the surface, as the no. of molecules on the surface decreases.

eg oil in water surface decreases its T.

ii) Presence of dissolved impurities:

$T \uparrow$ if inorganic substances are present.
$T \downarrow$ " organic " " "

$T_{H_2O} \rightarrow 0.072\ Nm^{-1}$
$T_{H_2O-NaCl} \rightarrow 0.083\ Nm^{-1}$
$T_{H_2O-soap} \rightarrow 0.03\ Nm^{-1}$

iii) Temperature: $T \downarrow$ with θ (temp.)

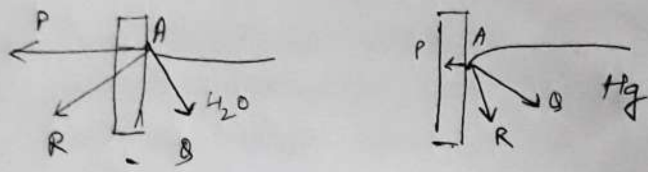
$$T = T_0(1 - \alpha t)$$

T = S.T. at t°C
T_0 = " " 0°C
α = temp. coeff. of S.T.

$T \sim 0$ at T_c.

iv) Medium (above & below liquid) affects its S.T.

• Shape of liquid meniscus in glass tube:

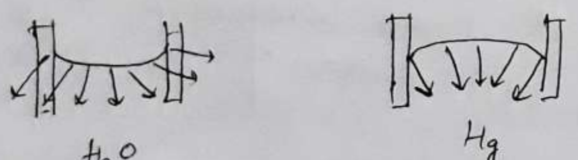


P → adhesive force between H_2O/Hg molecules & glass

Q → cohesive " " " " "

R → Resultant

If liquid is water, P > Q, & thus R acts outwards towards the glass surface. For molecules farther & farther away from the glass surface, P decreases & R is almost vertical. In the middle, $P \sim 0$, & R is vertical.



• Liquid surface is always ⊥r to R at each and every point.

Thus for water, surface is concave. (θ is acute)

" Hg, " " convex. (θ is obtuse)

→ Obviously for maintaining the shapes of these surfaces, the pressure difference between either sides is non-zero. This excess pressure inside balances out the surface tension & maintains the surface shape.