GENESIS TUTORIALS

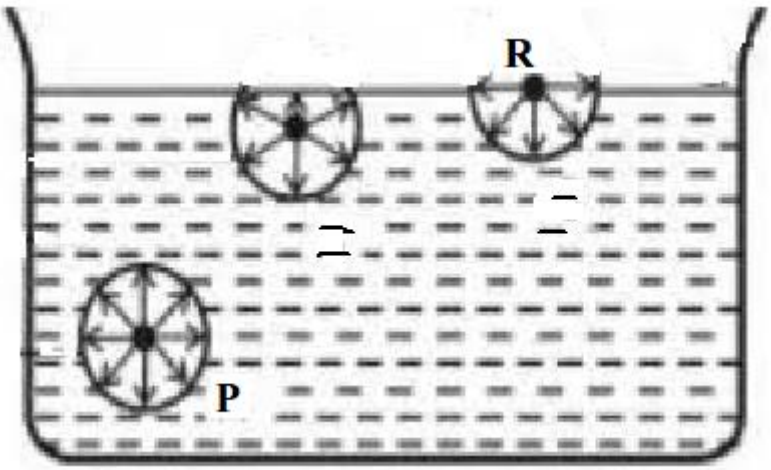
Institute for CSIR-UGC-NET/JRF, GATE & IIT-JAM

Assignment- Surface chemistry

Surface Tension

→ Surface tension is a characteristic of surface of liquids due to which it try to decrease its area. For this purpose, a force of attraction is applied betweem the molecules of liquids on the surface. For this reason, surface of a liquid behave like a stretched membrane.

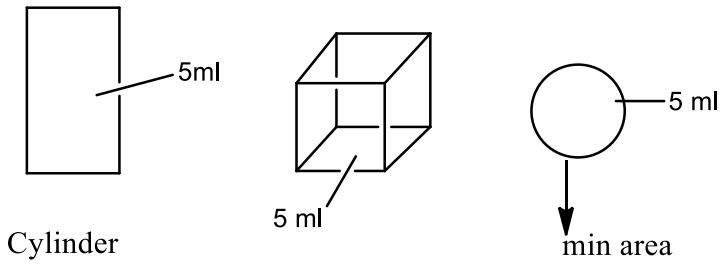
→ Consider a molecule P some where in the body of the liquid. This is attracted equally in all dieactions by other molecules which surround it as shown in figure and therefore cancel the effect of one another.



→ Consider, next, a molecule R at the surface of the liquid. The downward attractive force are greater than the upward forces because there are more molecules of liquid below than that in air above the surface. These unbalanced atttractive forces acting downward tend to draw the surface mlecules into the body of the liquild and therefore, tend to reduce the surface to a minimum.

→ It is well known that force of attraction tend to decrease the energy of a system. The molecules at the surface possess greater energy than those in the bulk. The molecules tend to move from a state of higher energy to a state of lower enegy. As a result, the number of molecules at the surface becomes less than that in bulk.

→ The surface molecules tend to move closer to one another in order to acquire a normal distance between them. It is the reason that drops of a liquid or bubbles of a gas are spherical in shape. A sphere has minimum surface for a gives volume.



→ A a result of the tendency to contract, surface of a liquid behave as if it were in a state of tension. The force that tends to contract the surface of a liquid is called as surface tension.

→ Mathematically, surface tension may be defined as the force acting at right angle to the surface along unit length of the surface.

It is generally represented by the symbol γ and

$\gamma = \frac{Force}{length}$ unit of γ → dyne cm^{-1}

S.I unit is Newtons per meter

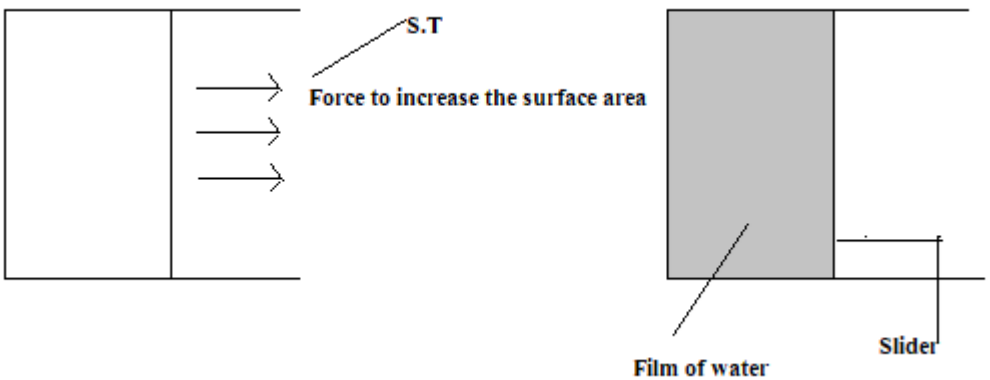
Nm^{-1} 1N= 10^5 dynes

1 dyne cm^{-1} = 10^{-3} N-m^{-1}

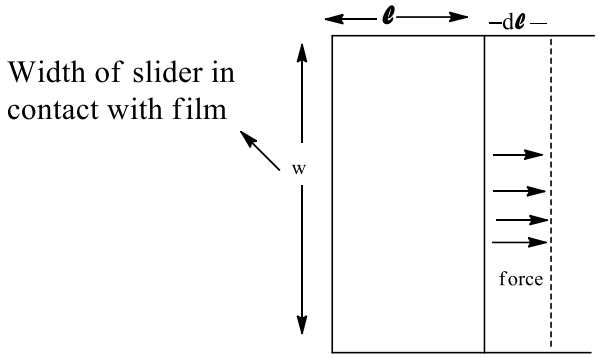
Surface tension of water, nitrobenzene, benzens, acetic acid, ethyl alcohol and ethyl ether are 72.8 dyne cm^{-1} (0.0728 Nm^{-1}), 41.8 dyne cm^{-1} 28.9 dyne cm^{-1}, 27.6 dyne cm^{-1}, 22.3 dyne cm^{-1} and 17.0 dyne cm^{-1} respectively.

For most liquids. surface tension at room temperature varies between 27 and 42 dyne cm^{-1}. For water, r is 72.8 dyne cm^{-1}. This high value is due to strong initermolecular forces which exist in water as a result of extensive hydrogen bonding.

Surface energy



If we want to increase the area of the surface of a liquid, we have to work against the force of surface tension. The work that is required to be done in order to extend the area of the surface of a liquid by one m^2 is called surface energy of the liquid



Force = $\gamma \times w$

work done = $F \times d\ell$

$dW = \gamma \times w \times d\ell$

$dW = \gamma.dA$

$W = \gamma.A$

$\gamma = \frac{W}{A}$ This work done is converted to surface energy

$\gamma = \frac{surface\ energy}{A}$

Surface energy = $\gamma.A$

The term surface tension implies that a state of tension exist between the surface molecules where as the term surface energy implies that work is required to bring molecules from the bulk to the surface of the liquid

The unit of surface energy is work (energy) per unit area

Generally, the unit of surface energy is erg cm^{-2}

1 erg cm^{-2} = 1. dyne-cm. cm^{-2} (1 erg = 1 dyne-cm)

= dyne-cm^{-1} → unit of surface tension

→ Basically surface tension denotes force of unit length but numerically it is equal to energy of unit area.

→ Thus surface tension is equal to surface energy per unit area numerically as well as dimensionally.

Effect of temperature on surface tension

→ The rise in temperature is accompanied by increase in energy of the molecules.

→ Surface tension arises due to intermolecular forces of attraction. The intermolecular force of attraction decreases with rise in temperature. Hence surface tension of a liquid decreases with rise in temperature.

→ At critical temperature, since the distiction between liquid and vapour phase disappears molecules are far apart. There is no forces of attraction between them, the surface tension falls to zero.

Eotvos found that surface tension varies linearly with temperature. He suggested the following expression for the variation of surface tension with temperature.

$\gamma\left(\frac{M}{\rho}\right)^{2/3}$ = a-K.T---------- (1)

M→ Molar mass

ρ → density

γ→ surface tension at temperature T

a and K are constant

At the critical temperature (when $T = T_C$), the $\gamma = 0$

$0 = a - K.T_C$

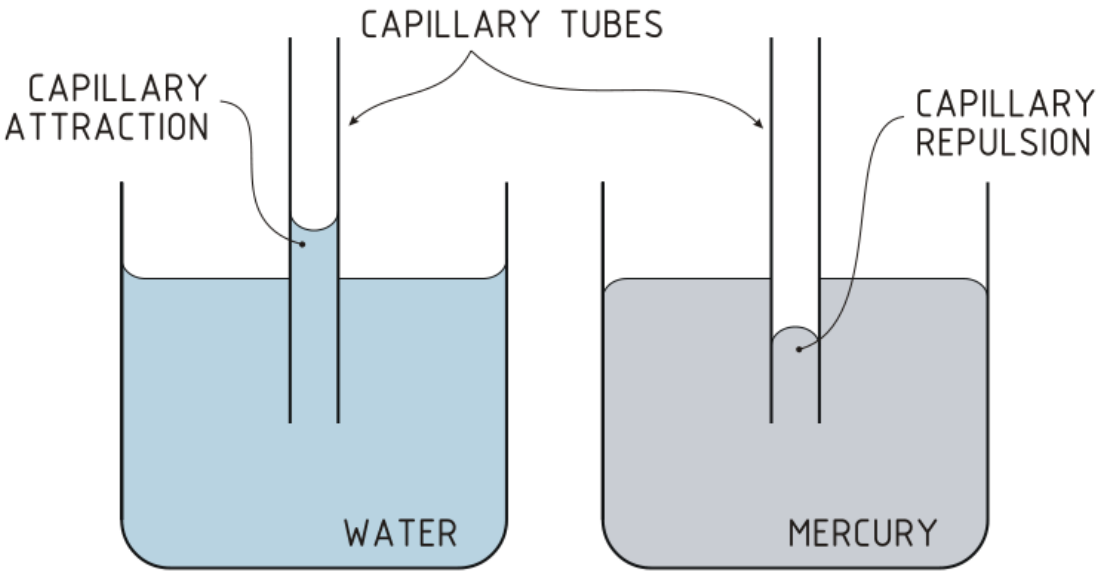
substituting the value of a in equation (1)

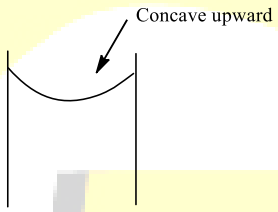
$\gamma\left(\frac{M}{\rho}\right)^{2/3} = K.T_C - K.T$

$\gamma\left(\frac{M}{\rho}\right)^{2/3} = K(T_C - T)$

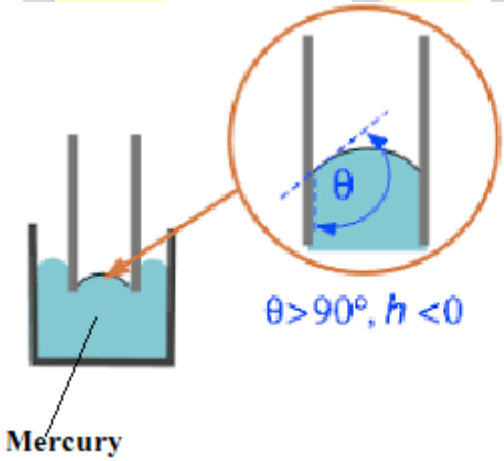
CAPILLARY ACTIONS

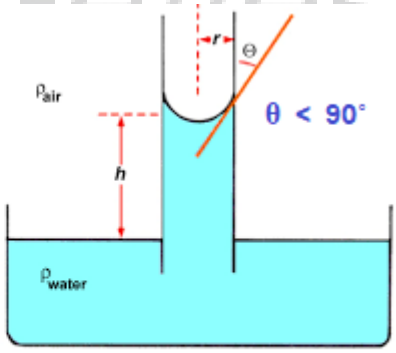
Capillary tube is a tube of very small bore. When a capilary tube is dipped in a liquid, there occurs either a rise or a fall of liquids in tube. This phenomenon is called capillary action and is basically due to surface tension of the liquid. If the forces of attraction between the molecules of a liquid and those of the solid surface of the tube (adhesion) are greater than those existing amongst the molecules of the liquid(cohesion), then the liquid has a tendency to spread on the solid surface and its meniscus in the tube is concave upwards such type of liquid are known as wetting liquids and they rise in the capillary tube





→The angle of contact, which is measured within the liquid from the side of the tube to the tangent drawn at the meniscus touchiing the surface of the tube, is less than 90˚





→ If the cohesive force in the liquid are greater than solid-liquid attraction forces (adhesive) or if there occurs repulsion between the molecules of the liquid and those of the solid surface, the liquid detaches from the surface of the solid. The meniscus of such a liquid in the tube is convex upwards and its level falls withini the tube. The angle of contact is greater than 90˚.

→ The rise and fall of a liquid in a capillary tube is due to surface tension. For example. Take the case of wetting liquid. The surface tension forces act all arround the capillary tube in the direction shown in the fig.

The liquid rises in the tube because of these upward forces. It continues to rise till the vertical component of the lifting force becomes equal to the weight of the liquid in the capillary tube

Lifting Force = $(\gamma\cos\theta)\ (2\pi r_c)$

$r_c \rightarrow$ radius of capillary tube

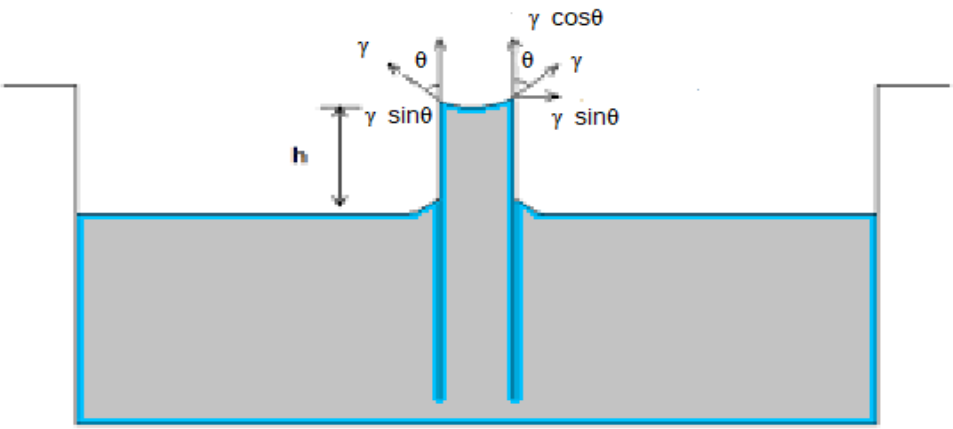
$2\pi r_c \rightarrow$ circumference of capillary tube

weight of the liquid in the capillary tube = $\{(\pi r_c^2)h\}\ \rho.g$

At equilibrium, lifting force is equal to the downward force due to the weight of the liquid in the capillary tube. Therefore-

$(\gamma\cos\theta)\ (2\pi r_c) = \pi r_c^2 h.\rho.g$

$\gamma = \frac{h\rho.g}{2} \cdot \frac{r_c}{\cos\theta}$ or $h = \frac{2\gamma\cos\theta}{r_c\rho.g}$



For most of the wetting liquids, θ is very very small and thus cosθ≃. Therefore, the value of r for such liquid is –

$\gamma = \frac{1}{2}.h\rho g r_c$ $\qquad$ r_c = radius of capillary tube

γ = surface tension

or

$h = \frac{2\gamma}{r_c\rho.g}$ for Hg → θ > 90°

cosθ → -ve

so h → -ve

Capillary of insufficient height

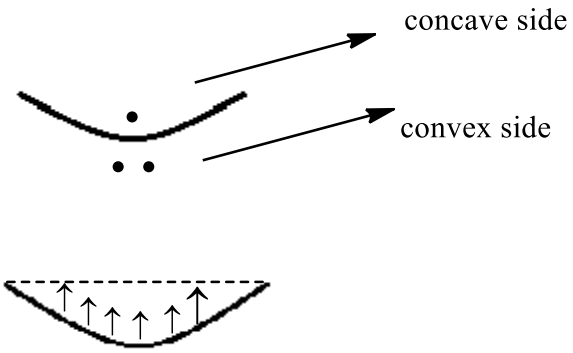
→ For insufficient height of capilliary , the liquid will rise upto top, then, the shape of meniscus will change in such a way that the present length of the capillary h' is given by the

$$h^1 = \frac{2\gamma\cos\alpha}{r_c\rho.g}$$

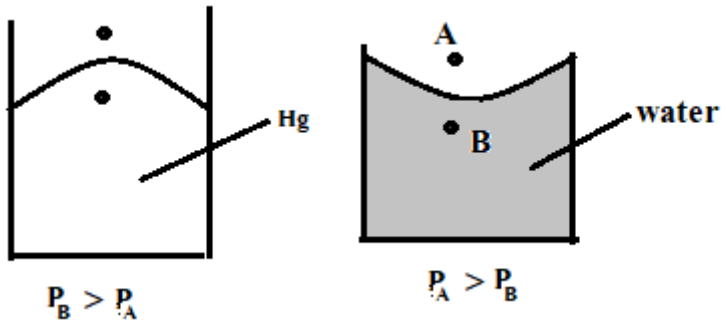
where α is now new angle of contact

Curved surface

→ The minimization of the surface area of a liquid may result in the formation of a curved surface

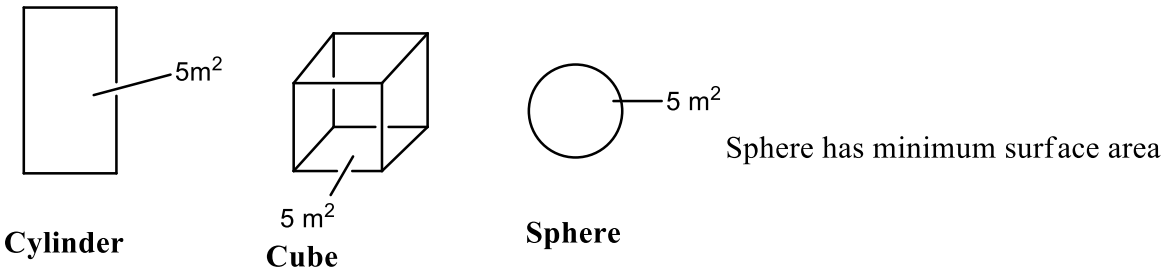


→ Across a curved surface, pressure is more on concave side compared to pressure on convex side



→ A water drop has more pressure inside as compare to outside

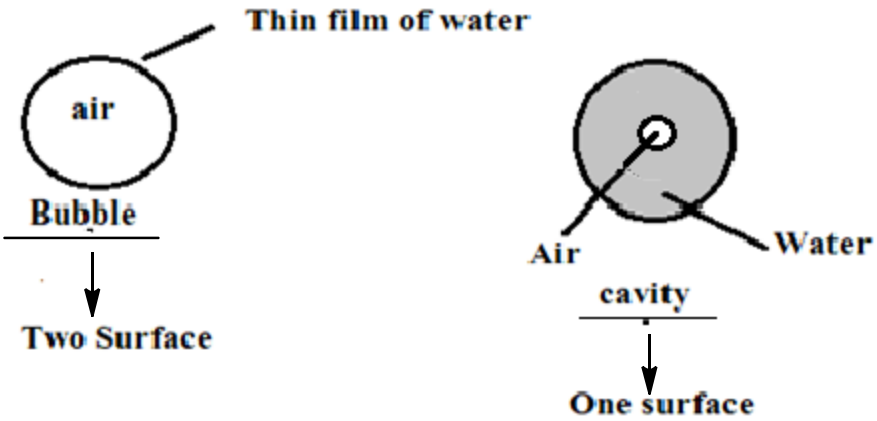
→ A drop acquire a spherical shape because sphere has minimum surface area



The natural shape of a liquid of very small quantity is spherical beacuse for any given volume the minimum surface area is of a sphere

→ A bubble is a region in which air (or gas) is trapped by a thin film, a cavity is a gas filled hole in a liquid

→ Bubble in liquid are cavities



→ True bubbles have two surface (one on each side of the film) while the cavities have only one.

→ The treatment of both are similar but a factor of 2 is required for bubble to take into account the doubled surface area.

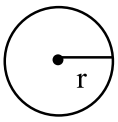
→ A droplet is a small volume of liquid at equilibrium surrounded by its vapour (gennally air).

→ A surface of a drop try to reduce its area and therefore press the surface inwards. Due to this reason, there is excess pressure within the drop.

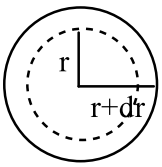
The presure on the convave side of an interface, P_{in}, is always greater than the pressure on the convex side, P_{out}. This relation is expressed by the **Laplace equation** which is given by the expression.

$P_{in} = P_{out} + \Delta P$ ---------- (1)

→ There is a drop of radius r of a liquid having surface tension γ. The excess pressure inside is ΔP



→ Let's increase the radius by dr



so,

work done (dW) = γ. dA $\qquad$ $dA = 4\pi(r+dr)^2 - 4\pi r^2$

$dA = 4\pi[r^2+dr^2+2r.dr]-4\pi r^2$ (dr^2 can be neglected) because dr is small & square of a smaller quantity is very small

$dW = 8\pi\gamma.r.dr$ -------(2) $dA = 4\pi r^2+8\pi r.dr-4\pi r^2 = 8\pi r.dr$

we know that $P = \frac{F}{A}$

$F = P.A$ A for sphere $= 4\pi r^2$

so the force which is required to increase the size of the drop-

Force $= \Delta P.\ 4\pi r^2$

So work done for small displacement (dr)

dW = Force × displacement

$dW = \Delta P.\ 4\pi r^2.dr$ ———————— (3)

compare the equation (2) & (3)

$\Delta P.\ 4\pi r^2.dr = 8\pi\gamma.r.dr$

$\Delta P = \frac{2\gamma}{r}$ ΔP = excess pressure

Hence equation (1) becomes

$P_{in} = P_{out} + \frac{2\gamma}{r}$ This equation is called the **laplace equation** The laplace equation shows that the difference in pressure decrease to zero as the radius of curvature becomes infinite. Small cavities have small radii of curvature. So the pressure difference across their surface is quite large.

Condensation

The vapour pressure of a liquid depends on the pressure applied to the liquid. because curving a surface gives rise to a pressure difference of $\frac{2\gamma}{r}$, we can expect the vapour pressure above a curved surface to be different from that above a flat surface.

The quantitative realtion between the vapour pressure, P, when a pressure ΔP is applied and the vapour pressure, P of the liquid in the absence of an additional pressure is__

$$P = P^* e^{\frac{V_{m(l)}.\Delta\rho}{RT}}$$

The equation shows how the vapour pressure increases when the pressure acting on the condensed phase is increased.

Substituting the value of $\Delta P = \frac{2\gamma}{r}$ we obtain the **Kelvin equation** for the vapour presure of a liquid when it is dispersed as droplets of radius r.

$$P = P^* e^{\frac{2\gamma V_m}{rRT}}$$

$$\frac{P}{P*} = e^{\frac{2\gamma V_m}{rRT}}$$

Taking logarithms-

$$ln\frac{P}{P*} = \frac{2\gamma V_m}{rRT}$$

Molar volume $V_m = \frac{Molarmass(M)}{\rho\ (density)}$

$$V_m = \frac{M}{\rho}$$

The above equation becomes

$$\ln\frac{P}{P*} = \frac{2\gamma M}{r\rho RT}$$

This is the kelvin equation of a liquid

Gibbs Adsorption Isotherm for Adsorption from Solution

The concentration of a solute at the surface of a solution may be different from that present in the bulk. while discussing the surface tension of a liquid, we have seen that the surface tends to decrease its surface area in order to obtain a minimum value of surface free energy. The latter arises because of the unbalanced molecular force experienced by the molecules at the surface.It was also seen that the surface tension is numerically equal to the surface energy per unit area of the surface.

→ Now if the added solute has a surface tension lower than that of a liquid, then it has a tendency to accumulate more at the surface of the liquid. In this way the surface tension of the liquid (or surface free energy per unit area of the surface) is decreased.

→ A quantitative expression which relates the excessive concentration of the solute at the surface (or the extent of adsorption) and the change in surface tension of the liquid (solvent) due to addition of solute was derived by Gibbs and is thus called '**Gibbs-adsortion equation'** or **Gibbs-adsorpion isotherm**

It can be dervied as follows—

following the additivity rule, the free energy of a system consisting of two component is given by—

$G = n_1\mu_1 + n_2\mu_2$_____ (1)

n_1 → solvent molecules

n_2 → solute molecules

n_1 and n_2 are amounts and μ_1 and μ_2 are the chemical potentials of the components respectively.

Since in the present case, we are dealing with the change in surface free energy. We must also add a factor corresponding to surface energy in equation (1). If γ is the surface tension (or surface free energy per unit area) and A is the surface area then the surface energy is equal to γA the above equation (1) modifies to–

$G = n_1\mu_1 + n_2\mu_2 + \gamma A$ _____ (2)

The complete differential of the equation is given by $dG = n_1\, d\mu_1 + \mu_1\, dn_1 + n_2\, d\mu_2 + \mu_2\, d\mu_2 + \gamma dA + A d\gamma$ -------- (3)

The function G will now depend on five independent variables, namely T, P, n_1, n_2 and A

$G = f(T, P, n_1, n_2, A)$ -------- (4)

The total differential of G will be given by__

$$dG = \left(\frac{dG}{dT}\right)_{p,n,n2,A} . dT + \left(\frac{dG}{dP}\right)_{T,n_1 n_2,A} . dP + \left(\frac{dG}{dn_1}\right)_{T,P,n_2,A} . dn_1 + \left(\frac{dG}{dn_2}\right)_{T,P,n_1,A} . dn_2 + + \left(\frac{dG}{dA}\right)_{T,P,n_2,n_1} . dA \quad \text{---(5)}$$

equation (5) becomes

$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \gamma . d . A$ ------- (6)

At constant temp and pressure, equation (6) becomes__

$dG = \mu_1 dn_1 + \mu_2 dn_2 + \gamma dA$ ------- (7) →

Comparing the equation (3) & (7)

$n_1 d\mu_1 + \cancel{\mu_1 dn_1} + n_2 d\mu_2 + \cancel{\mu_2 dn_2} + \cancel{\gamma dA} + A d\gamma = \cancel{\mu_1 dn_1} + \cancel{\mu_2 dn_2} + \cancel{\gamma dA}$

$n_1 d\mu_1 + n_2 d\mu_2 + A d\gamma = 0$ ____ (8)

The corresponding expression for the bulk phase of the liquid is—(in bulk phase, no surface tension is present)

$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0$ ----------(9)

where n_1^0 and n_2^0 are repective amounts (number of moles) of liquid and solute in the bulk phase.

→ When the system is at equilibrium the chemical potential of each of the components in both phases (surface and bulk) must be identical. When the system is slightly disturbed and it attains the new equlibrium, then the changes in chemical potentials must be identicals $d\mu_1$ are related to each other according to **Gibbs Duhem equation–**

$$d\mu_1 = -\left(\frac{n_2^0}{n_1^0}\right) . d\mu_2$$

substituting the value of $d\mu_1$ in equation (8)

$$n_1 \left[-\left(\frac{n_2^0}{n_1^0}\right) . d\mu_2\right] + n_2\, d\mu_2 + A.d\gamma = 0$$

$$-\frac{n_1 n_2^0}{n_1^0} . d\mu_2] + n_2\, d\mu_2 + A.d\gamma = 0$$

$$\left(n_2 - \frac{n_1 n_2^0}{n_1^0}\right) d\mu_2 + A.d\gamma = 0$$

$-A.d\gamma = (n_2 - (\frac{n_1 n_2^0}{n_1^0}))d\mu_2$

$$\frac{-d\gamma}{d\mu_2} = \frac{n2-(\frac{n_1 n_2^0}{n_1^0})}{A} \text{ \_\_\_\_\_ (10)}$$

The term on R.H.S. within bracket of equation (10) gives the amount n_2^0 of solute 2 associated with the amount n_1 of liquid 1 in the bulk phase. On the other hand, n_2 is the amount of the liquid at the surface. Thus the numerator on the right handside of equation (10) gives the excess amount of the solute present in the surface of the liquid. The right hand side of equation (10) give the excess concontration of the solute per unit area of the surface, desingnated as Γ_2

$$\frac{n2-(\frac{n_1 n_2^0}{n_1^0})}{A} = \Gamma_2$$

$$\Gamma_2 = -\frac{d\gamma}{d\mu_2} \text{ -------- (11)}$$

The chemical potential of solute 2 is given by $\mu_2 = \mu_2^*(l) + RT \ln a_2$-------- (12)

Where $\mu_2^*(l)$ is the chemical potential of the pure solute in the liquid phase.

Differentiating the equation (12) w.r to $\ln a_2$

$$\frac{d\mu_2}{dlna_2} = \frac{d\mu_2^*(l)}{dlna_2} + RT\frac{dlna_2}{dlna_2} \qquad \frac{d}{da_2}\ln a_2 = \frac{1}{a_2}\frac{da_2}{da_2}$$

$$\frac{d\mu_2}{dlna_2} = 0 + RT \qquad d\ln a_2 = \frac{da_2}{a_2}$$

$d\mu_2 = RT\, d\ln a_2$---------(13)

The equation (13) becomes

$$d\mu_2 = \frac{RT}{a_2}.da_2$$

Substituting the value of $d\mu_2$ in equation (11)

$$\Gamma_2 = -\frac{a_2}{RT}\left(\frac{d\gamma}{da_2}\right)_T \qquad \text{(Temp is constant)}$$

When the solution is very dilute, it behave ideally so that the activity a_2 of the solute can be replaced by its concentration c_2. Thus

$$\Gamma_2 = -\frac{c_2}{RT}\left(\frac{d\gamma}{dc_2}\right)_T \text{ \_\_\_\_\_ (14)}$$

$\Gamma_2 \rightarrow$ unit Mole m^{-2} The unit of Γ_2 is mole m^{-2}

The equation (14) is called the Gibbs adsorption isotherm.

→ For a solute that lowers the surface tension, the surface excess concentration Γ_2 is positive and for a solute that raises the surface tension, Γ_2 is negative.

→ The surface tension of water is quite high i.e. 0.0728 Nm^{-1} (72.8 dyne cm^{-1}) at the room temperature and most of the solutes are positively adsorbed from aqueous solution by adsorbents such as charcoal and silica gel. The surface tension of ethanol (0.0223 Nm^{-1} or 22.3 dyne cm^{-1}) is

considerably lower than that of water. Hence most of the solutes decrease the surface tension of ethanol to a much smaller magnitude than they do in the case of water.

→ It is concluded that a given solute would be more readily adsorbed from aqueous solution than from alcoholic solution.

Question-The surface tension of dilute solution of a solute varies linearly with the solute concentration c_2 as $\gamma = \gamma_0 - ac_2$, where γ_0 is the surface tension of the solvent and a is a constant. Show that

$$\Gamma_2 = \frac{(r_0 - r)}{RT}$$

Solution $\gamma = \gamma_0 - ac_2$, (Given)

Differentiating w.r. to c_2 at constant T

$$\left(\frac{d\gamma}{dc_2}\right)_T = 0 - a\left(\frac{dc_2}{dc_2}\right)_T$$

$$\left(\frac{d\gamma}{dc_2}\right)_T = -a$$

Hence $\Gamma_2 = -\frac{c_2}{RT}(-a)$

$$\Gamma_2 = \frac{ac_2}{RT}$$

It is given that

$\gamma = \gamma_0 - ac_2$

$ac_2 = \gamma_0 - \gamma$

Hence

$$\Gamma_2 = \frac{\gamma_0 - \gamma}{RT}$$

Question For a 1.0×10^{-4}M aqueous solution of n-butanaic acid $\frac{d\gamma}{dc}$ = -0.080 $Nm^2\ mol^{-1}$, at 25°C. Using the Gibbs adsorption equation determine the surface excess concentration of butanoic acid and also calculate the average surface area available to each molecule.

$$\Gamma_2 = -\frac{C}{RT}\frac{d\gamma}{dc}$$

$$\frac{\overset{\text{mol m}^{-3}}{1.0 \times 10^{-4} \times 10^3}}{\underset{\text{J k}^{-1}\text{ mol}^{-1}}{8.341 \times 298\text{ K}}} \cdot \overset{\text{N-m}^2\text{mol}^{-1}}{(-0.080)} \qquad \frac{\text{N m}^{-1}}{\text{N-m mol}^{-1}} = \text{Mol m}^{-2}$$

$C = 1.0 \times 10^{-4}$mol dm^{-3}

$= 1.0 \times 10^{-4}\ \frac{\text{mol}}{dm^3} = 1.0 \times 10^{-4} \times 10^3$ mol m^3

$dm^3 \rightarrow 10^{-3} m^3$

1m = 10dm

$1m^3 = (10^3)dm^3$

$1dm^3 = 10^{-3}m^3$

$$\Gamma_2 = \frac{1 \times 10^{-1} \times 0.08}{8.314 \times 298} = \frac{80 \times 10^{-4}}{8.314 \times 298}$$

$$\Gamma_2 = \frac{8000 \times 10^{-6}}{8.314 \times 298} = 3.22 \times 10^{-6}\ \text{mole-m}^{-2}$$

it means

3.22×10^{-6} mole molecules are present in area = $1m^2$

1 mole ——— $\frac{1}{3.22 \times 10^{-6}}\ m^2$

|||

$NA = 6.023 \times 10^{23}$

6.023×10^{23} molecules

1 molecule ——— $\frac{1\ m^2}{3.22 \times 10^{-6} \times 6.023 \times 10^{23}}$

$= 5.15 \times 10^{-19}\ m^2$

BET (BRUNAUER, EMMETT & TELLER) Equation:-

→ The adsorption of gases on the surface of an adsorbent is no more monolayer at high pressure and low temperature.

At high pressure, the number of molecules striking per unit area of the surface per unit time is quite high

On the other hand, at low temperature, the thermal energy of molecules is not sufficiently large to overcome the force of attraction (Vander Waals forces of attraction) between adsorbed molecule and nearby unabsorbed molecules. This result into the multilayer adsorption.

The most widely used isotherm dealing with multilayer adsorption was derived by Brunauer, Emmet and Teller and is called the BET isotherm.

$$\frac{V_{ads}}{V_{mono}} = \frac{CZ}{(1.Z)[1+(c-1)Z]}$$

Where, $Z = \frac{P}{P^0} = x.p$

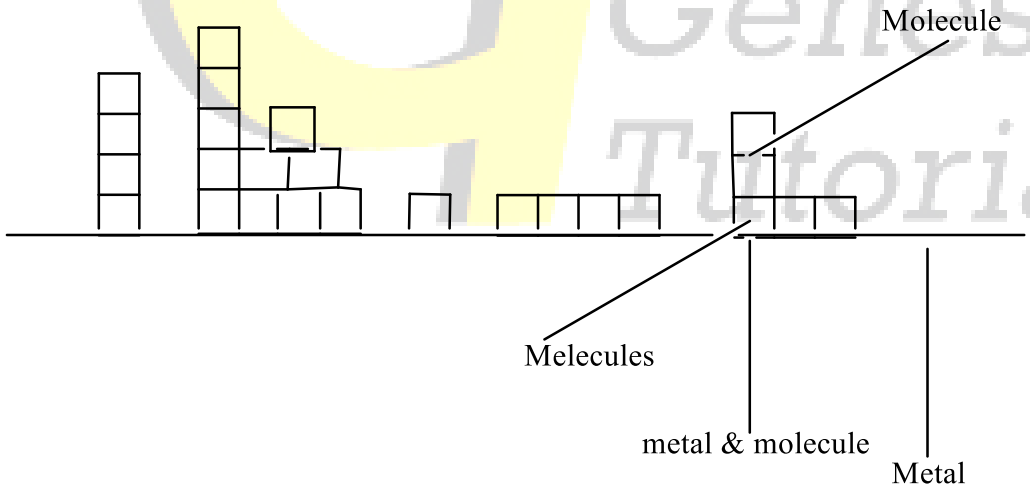
P → Pressure of gas

P^o → Saturated vapour pressure of the gas

In the above expression, c is a constant

The value of C is large when enthalpy of desorption is larger than the enthalpy of vaporization

$$c = e^{\frac{(\Delta H_{des} - \Delta H_{vap})}{RT}}$$



(1) first layer formation

$$M(s) + A(g) \underset{K_d}{\overset{K_a}{\rightleftharpoons}} MA(s)$$

$$K = \frac{K_a}{K_d}$$

(2) 2nd layer formation

$$MA(s) + A(g) \underset{Kd^1}{\overset{Ka^1}{\rightleftharpoons}} MA(s)$$

$$K' = \frac{ka^1}{Kd^1}$$

(3) 3rd- layer formation

$$MA_2(s) + A(g) \underset{Kd''}{\overset{Ka''}{\rightleftharpoons}} MA_3(s)$$

$$K'' = \frac{Ka''}{Kd''}$$

→ Both K' & K″ are approximately equal to each other

$$\text{Saturated vapour} \underset{Kd''}{\overset{Ka''}{\rightleftharpoons}} \text{liquid}$$

$$K^1 = \frac{Ka^1}{Kd^1} = \frac{\{liquid\}}{\{Vapour\}} = \frac{1}{P^0}$$

$K^1 = \frac{1}{P^0}$ $\qquad$ $K = CK' = C \times \frac{1}{P^0}$

→ From BET isotherm expression

$$\frac{V_{ads}}{V_m} = \frac{CZ}{(1.Z)[1+(c-1)Z]}$$

$$\frac{V_{ads}}{V_m} = \frac{C\left(\frac{P}{P^0}\right)}{\left(\frac{1}{1}-\frac{P}{P^0}\right)[\left(1+(c-1)\frac{P}{P^0}\right)]} \qquad [Z = \frac{P}{P^0}]$$

$$\frac{V_{ads}}{V_m} = \frac{\frac{c.p}{\cancel{p^0}}}{\frac{P^0-P}{\cancel{p^0}}\left(1+(c-1)\frac{P}{P^0}\right)}$$

If $V_{ads} = V$

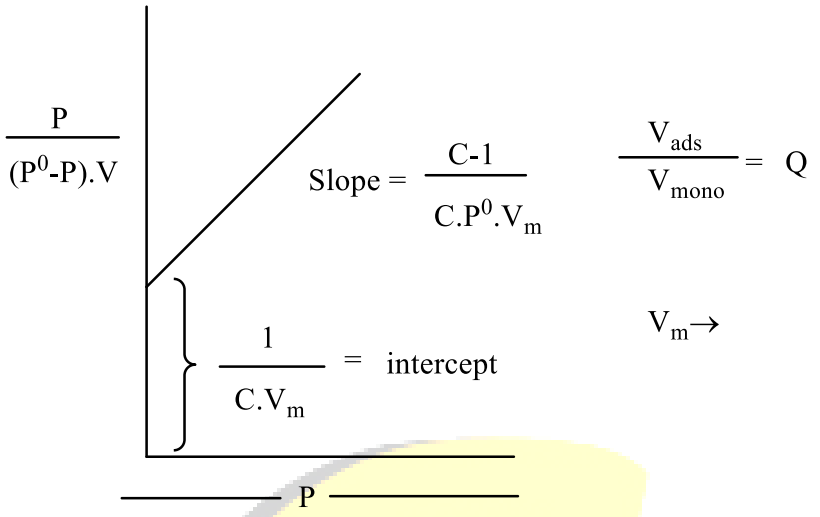
$$\frac{V}{V_m} = \frac{c.p}{(p^0-p)\left(1+(c-1)\frac{P}{P^0}\right)}$$

$$\frac{1+(c-1)\frac{p}{p^0}}{V_m} = \frac{c.p}{(p^0-p).V}$$

$$\frac{1}{V_m} + \frac{(c-1)p}{p^0.V_m} = \frac{c.p}{(p^0-p).V}$$

$$\frac{1}{c.V_m} + \frac{(c-1)p}{c.p^0.V_m} = \frac{p}{(p^0-p).V}$$

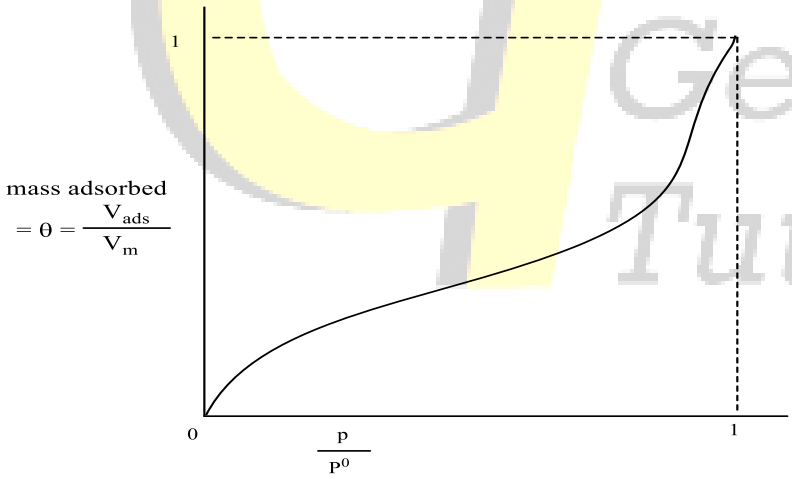
This is the well-known BET equation on plotting $\frac{P}{(p^o-p).V}$ Vs p , we get intercept = $\frac{1}{C.V_m}$ and slope = $\frac{(c-1)}{C.P^0V_m}$



With the help of graph we can calculate the value of V_m

Graph between $\frac{V_{ads}}{V_m}$ Vs P

Mass adsorbed = θ = $\frac{V_{ads}}{V_m}$ Vs P



Condition for conversion BET to Langmuir isotherm

C > > 1

P^0 > > P

K = C.K^1

K = C.$\frac{1}{P^0}$ → C = K.P^0

If C is very large C-1 ≃ C

From BET equation →

$$\frac{1}{C.V_m} + \frac{c-1}{C.V_m P^0}\frac{P}{} = \frac{P}{(P^0-P).V}$$

If $P^0 >> P$ $\quad P^0 - P \simeq P^0$

$$\frac{1}{C.V_m} + \frac{\cancel{c}.P}{\cancel{C}.V_m P^0} = \frac{P}{p^0.V}$$

$$\frac{1}{C.V_m} + \frac{C.P}{C.V_m.P^0} = \frac{p}{p^0.V} \qquad C = K.P^0$$

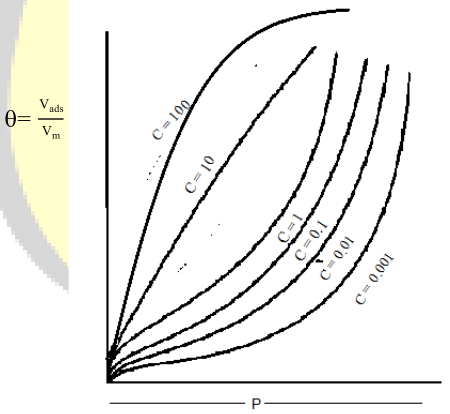
$$\frac{1}{K.P^0 V_m} + \frac{P}{V_m \cancel{P^0}} = \frac{P}{\cancel{P^0}.V}$$

$$\frac{1}{k.V_m} + \frac{P}{V_m} = \frac{P}{V}$$

Divided by P on both sides

$$\frac{1}{k.V_m P} + \frac{1}{V_m} = \frac{1}{V}$$

This is the equation for langmuir adsorption isotherm



So we can say that on increasing the value of C, the BET isotherm is converted to Langmuir isotherm for monolayer

At $C \simeq 100$, BET is converted to Langmuir because $\Delta_{dis}H$ is then significantly greater than $\Delta_{vap}H$

<u>Determination of the surface area of the adsorbent</u>: The area of cross section 'a' of the molecule can be determined from the density of the adsorbate. Thus if ρ is the density and M is the molar mass of the adsorbate then the volume υ occupied by a single molecule, assuming the adsorbate to be closely packed with no void volume, is obtained as follows

$$\rho = \frac{M}{V_m} = \frac{M}{N_A.V}$$

$$v = \frac{M}{N_A.\rho}$$

Assuming the molecule to be spherical with radius r, we have

$v = \frac{4}{3}\pi r^3 = \frac{M}{N_A.\rho}$

$r = \left[\frac{3M}{4\pi N_A.\rho}\right]^{\frac{1}{3}}$

Hence area, $a = \pi r^2 = \pi\left[\frac{3M}{4\pi N_A.\rho}\right]^{\frac{2}{3}}$

The above expression is used for calculating the area of cross-section (surface area) of a molecule since it does not take into the account the nature of packing at the surface of the adsorbent. The presence of void volume in the crystal lattice has been ignored.

Insoluble surface films on liquid

→ The long-chain, water-insoluble compounds like stearic acid, $CH_3(CH_2)_{16}$ COOH, lauryl alcohol, $CH_3(CH_2)_{11}$ OH and ethyl palmitate $CH_3(CH_2)_{14}$ $COOC_2H_5$ spread spontaneously on the water surface giving rise to surface films. These films are found to be one molecule thick and are called spread monolayers

→ Both solids and liquids can form spread monolayers but the rate of spreading of liquid is more than that of solids. These surface films can be studied by a surface balance in which a floating barrier (float) separetes a clean water surface from a water surface containing the monolayer. The force on the float is measured by a torsion wire attached to it. This is the princile of the langmuir film balance.

The lowering of the surface tension of solvent by the surface can be expressed in terms of the surface film pressure,**π**, which is the negative of the change in surface tension

$\pi = -\Delta\gamma = \gamma_0 - \gamma$ _____ (1)

where γ_0 → surface tension of water

γ → surface tension of the solution cantaining long compoun

We know that at low concertrations, the surface tension of a binary solution becomes a linear function of concentration and is given by__

$\gamma = \gamma_0 - bc_2$ ___ (2)

Differentiating with respect to c_2

$$\frac{d\gamma}{dc_2} = \frac{d\gamma_0}{c_2} - b\frac{dc_2}{dc_2}$$

$$\frac{d\gamma}{dc_2} = -b$$

substituting this realtion in gibbs-adsorption isotherm

$$\Gamma_2 = -\frac{c_2}{RT}\left(\frac{d\gamma}{dc_2}\right)_T$$

from the equation $\gamma = \gamma_0 - bc_2$ $\qquad -b = \frac{\gamma - \gamma_0}{c_2}$

$-\frac{\gamma-\gamma_0}{c_2} = -b$

$\frac{d\gamma}{dc_2} = -b = \frac{\gamma-\gamma_0}{c_2}$ $\quad \frac{d\gamma}{dc_2} = \frac{\gamma-\gamma_0}{c_2}$

$$\frac{-d\gamma}{dc_2} = \frac{\gamma_0-\gamma}{c_2} = \frac{\pi}{c_2}$$

Hence

excess cmc^n $\Gamma_2 = -\frac{c_2}{RT}\frac{\gamma_0-\gamma}{C_2}$ $\quad (\gamma_0 - \gamma = \boldsymbol{\pi})$

$\Gamma_2 = \frac{\pi}{RT}$

$\boldsymbol{\pi} = \Gamma_2 . RT$ _____ (3)

The surface excess concentration Γ_2 may also be written as __

$\Gamma_2 = \frac{N}{N_A.A}$

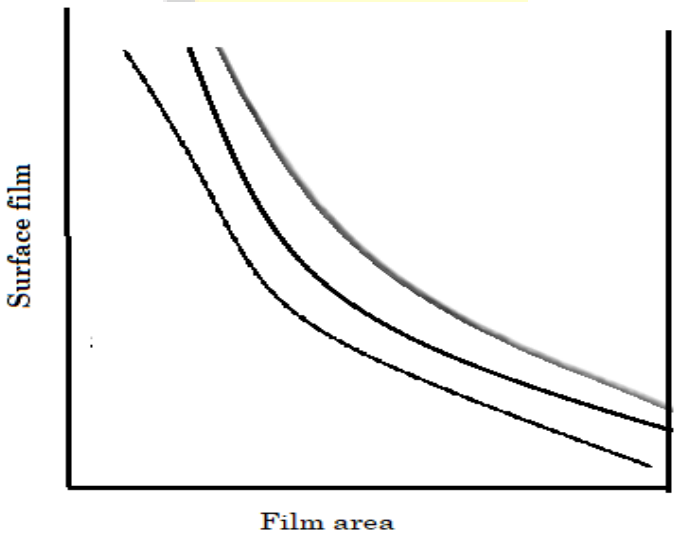
N → number of molecules contained in a film area now equation (3) can be written as __

$\boldsymbol{\pi} = \frac{N}{N_A.A} . RT$ $\qquad \frac{R}{N_A} = k_B$

$\boldsymbol{\pi}.A = \frac{N}{N_A} . RT$

$\boldsymbol{\pi}.A = N . K_B.T$ ____ (4)

The equation (4) shows the variation of the surface film pressure with area. On plotting the graph **π** Versus A, it shows the variation of **π** with area for different bulk concentration



Question It was found experimentally that 0.106mg of stearic acid covered 500 cm^2 of water surface Estimate the cross-esctional area of the strearic acid molecule and thickness of the stearic acid molecule and thickness of the stearic acid film on water. The molar mass of stearic acid is 284 g mol^{-1} and its density is 0.85 g cm^{-3}

Solution Number of molecules of stearic acid = $\frac{0.106\times10^{-3}g}{284\ gmol^{-1}} \times 6.022 \times 10^{23}$ molecules

1 mole = 6.022×10^{23} *molecules*

suppose a is the surface area of a molecule then area of water surface covered = $\frac{0.106\times6.022\times10^{20}\times a}{284}$ = 500cm^2 (given)

a = $\frac{500\times284}{0.106\times6.022\times10^{20}}$ = $2.224\times 10^{-15} cm^2$molecule^{-1}

a = 2.224 × 10^{-15}cm^2 per molecule

If t is the thinkness of the surface film then volume = area × thinkness = $\frac{\text{mass}}{\text{density}}$

$$= 500\text{cm}^2 \times t = \frac{0.106\times10^{-3} g}{0.85\ g\ cm^{-3}}$$

$$t = \frac{0.106\times10^{-3}\ cm}{500\times0.85} = 2.49 \times 10^{-7}\text{cm}$$

$$= 24.9 \times 10^{-8}\text{cm}$$

$$\simeq 25 \times 10^{-10}\text{m}$$

t ≃ 25 Å

Question An organic fatty acid forms a surface film on water that obey two-dimensional ideal gas law. If the surface tension lowering is 10 mN m^{-1} at 25˚C, calculate the surface excess concentration and the surface area per adsorbed molecule.

Solution **π** = 10×10^{-3}Nm^{-1} T = 25˚C = 298K

$\Gamma_2 = \frac{N}{N_{AV}.A}$ surface area per molecules means $\frac{A}{N}$

$$\frac{A}{N} = \frac{1}{\Gamma_2.N_{av}} = \frac{1}{4.036\times10^{-6}\cancel{mol}m^{-2}\times6.022\times10^{23}molecule\cancel{mol}^{-1}}$$

$$\frac{A}{N} = \frac{1}{4.036\times6.022\times10^{17}}\text{m}^2\text{molecule}^{-1}$$

$$= \frac{100\times10^{-19}}{4.036\times6.022} = 4.11\times10^{-19}\text{m}^2\ \text{molecule}^{-1}$$

Area of 1 molecule = 4.11×10^{-19} m^2

$$= 0.411\times10^{-20}\text{m}^2 = 41.1 \times 10^{-18}\ \text{m}^2$$

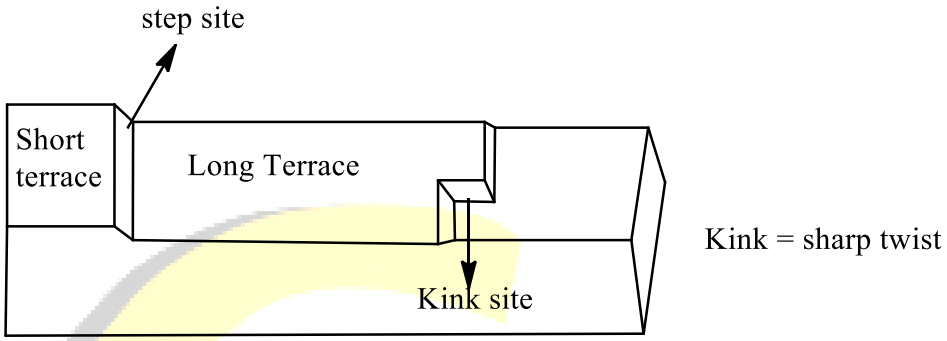
$$= 41.1(\text{nm})^2$$

Catalytic activity at surfaces

→ Catalytic activity of a surface depends on its structure as well as its composition. The cleavage of C-H and H-H bonds apperars to depend on the presence of steps and kinks and a tarrace

→ terrace often has only minimal catalytic activity.

→ The terrace sites are inactive but one molecule in ten reacts when it stikes a step



Slug→A strip of type of metal used for spacing

→ Although the step itself might be the important frature, it may be that the presence of the step merely exposes a more reactive crystal face. The dehydrogenation of hexane to hexene depends strongly on the kink density and it appears that kinks are needed to cleave the C-H bonds. These observation suggest a reason why even small amouts of impurities may poison a catalyst. They are likely to attach to step and kink sites and so impair the activity of the catalyst.

→A constructive out come is that the extent of dehydrogenation may be controlled relative to other types of reactions by seeking impurities that adsorb at kinks and acts as specific poisons.

→Molecular beam studies can also be used to invertigate the details of the reaction process, particularly by using **Pulsed beams** in which the beams is chopped into short slugs.(= intereption).

→The activity of a catalyst depends on the strength of chemisorption. To be active, the catalyst should be extensively covered by adsorbate molecules which is case of chemisorption is strong.

→On the other hand, if the strength of the substrate-adsorbate bond becomes too great, the activity declines either because the other reactant molecules can not react with the adsorbate or because the adsorbate molecules are immobilized on the surface. This pattern of behaviour suggests that the activity of a catalyst should initially increase with strength of adsorption and then decline.

→ The most active metals are those that lie close to the middle of the d-block

Many metals are suitable for adsorbing gases like O_2, C_2H_2, CO, H_2, CO_2 N_2. Elements from d-block such as Iron, vanadium(V), chromium (Cr) show a srong activity towards all these gases but Mn and Cu are unable to adsorb N_2 and CO_2. Metals towards the lift of the perodic table (eg Mg, Li) can adsorb only most activite gas (O_2)

* least active gas = N_2

Least active gas (N_2) can adsorb only most active metals like V, Cr, Mo,Fe.