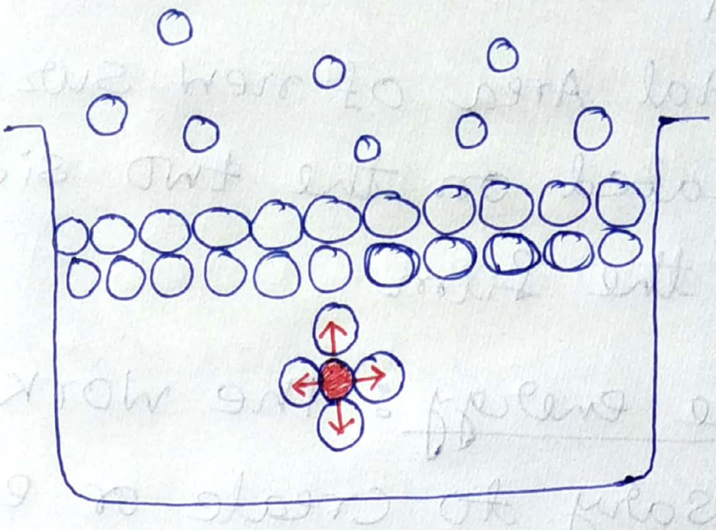
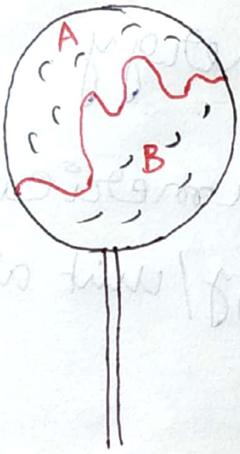
Name of the Teacher: DR. SUBHANKAR SARDAR
Class: Semester-6
Paper: C-14T (Physical Chemistry)
Topic: Surface Tension and Adsorption

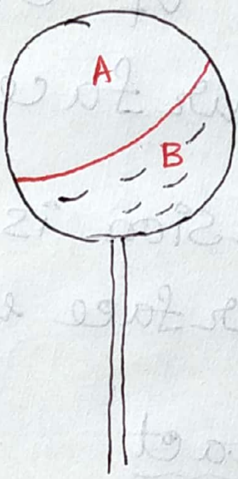
Comments: Read as much as you can. The highlighted and the quoted portions are must read.

Reference:
Physical Chemistry: P.C. Rakshit
Physical Chemistry (Vol, 5) K.L.Kapoor

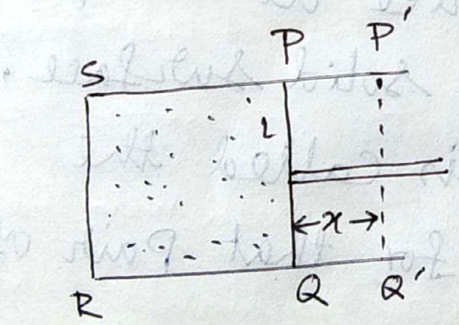
Surface Tension







Surface Tension (γ)



$\gamma \to$ surface tension acting / cm.

The force acting towards the film is $\gamma . 2L$

Work done in stretching the film,

$$W = \gamma . 2L \times x = \gamma . 2xL = \gamma . (xL + xL)$$

$$= \gamma . \Delta A = \gamma \times \text{change in Area}$$

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

$\Delta A \rightarrow$ Total Area of new surfaces created on the two sides of the film

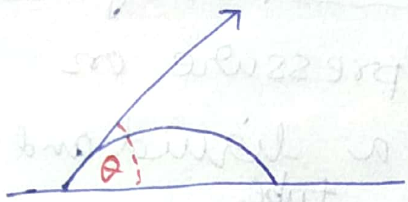
Surface energy: The work (ergs) necessary to create or extend on squ. cm of surface area is called surface energy.

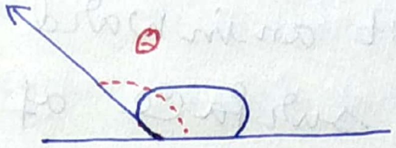
* surface tension is numerically same as surface energy/unit area.

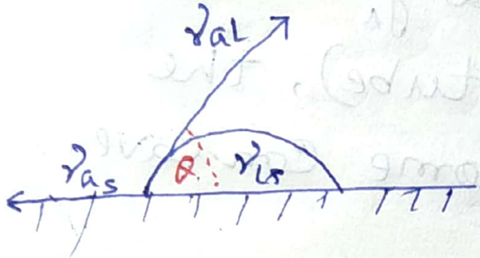
Angle of Contact

The angle between the tangent to the liquid surface at the point of contact and the solid surface, inside the liquid, is called the angle of contact for that pair of liquid and solid.

Angle of Contact $\propto$ nature of liquid & solid







γ_{aL} → surface tension for air, liquid

γ_{Ls} → " " " liquid - solid

γ_{as} → " " " air - solid

At equilibrium,

$$\gamma_{as} = \gamma_{Ls} + \gamma_{aL} \cos\theta$$

if, $\gamma_{as} > \gamma_{Ls} + \gamma_{aL} \cos\theta$ (no equilibrium)

⇒ liquid will spread over solid.

কেরোসিন, Alcohol.

$$\cos\theta = \frac{\gamma_{as} - \gamma_{Ls}}{\gamma_{aL}}$$

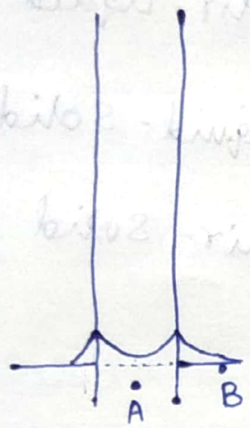
if,

$\gamma_{as} > \gamma_{Ls}$, $\cos\theta = +ve$, $\theta < 90°$ {water on glass

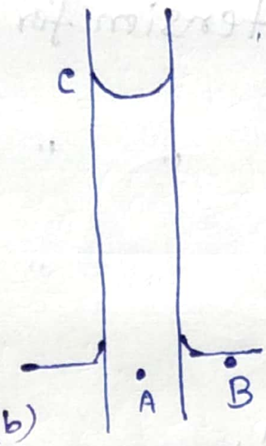
$\gamma_{Ls} > \gamma_{as}$, $\cos\theta = -ve$, $\theta > 90°$ {Hg on glass

• Rise of a liquid in a capillary tube

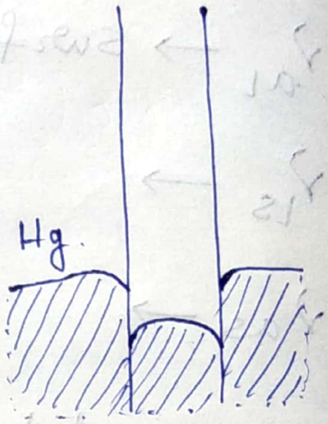
There exist an inward pressure on the free surface of a liquid and thus when a capillary tube is immersed in liquid. (inside the tube), the shape of liquid become concave.



(a)



(b)



resultant pressure $(P) = \frac{2\gamma}{r}$

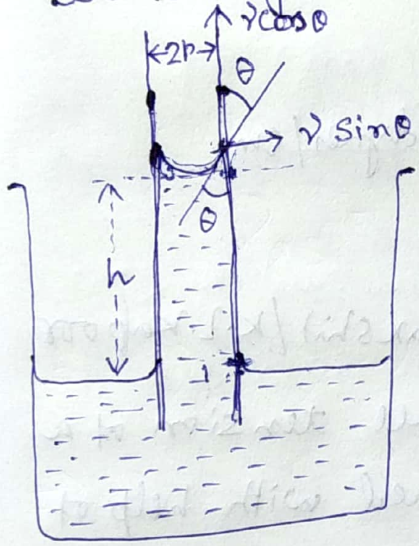
The pressure on the concave side is higher than the convex side. The resultant pressure $(P) = \frac{2\gamma}{r}$ of the curved surface is then generated. r → radius of curvature

If a capillary tube is immersed vertically in a liquid, which wets the surface, the maniscus of liquid within the tube will be concave upwards [See Fig. (a)]. At point A (Just below the surface at Fig(a)], the pressure is less than vapour side above by amount $2\gamma/a$, a → radius of curvature of maniscus.

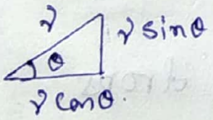
whereas at B, there is no unbalanced pressure on two sides of surface. But the pressure on the vapour side both in the tube and out side are same. Hence, The liquid at B pused inward to push/raise the liquid through capillary until the level reaches at C. Now the pressure of A & B points is equal & thus equilibrium is attained.

• Measurement of Surface tension

Ⓐ Capillary Rise method:



A throughly cleaned capillary glass tube is immersed in liquid & placed vertical. The liquid rises to attain a particular height. The h (the liquid height from surface to bulk) is measured by travelling microscope. r is radius of capillary tube. θ is angle of contact.



The vertical component of surface tension is $\gamma \cos\theta$. The contact line of meniscus is $2\pi r$. Hence, Net upward pull is $2\pi r \gamma \cos\theta$.

This force is balanced by the weight of liquid, which has been drawn up.

The weight of liquid column is $(\pi r^2 h + v)\rho g$

$v \rightarrow$ vol. of liquid in curved mariscus.

$\rho \rightarrow$ density of liquid

At equilibrium,

$$2\pi r \gamma \cos\theta = (\pi r^2 h + v)\rho g$$

The radius of curvature of concave meniscus is same as radius of the capillary tube.

So, $v = \pi r^3 - \frac{2}{3}\pi r^3 = \frac{1}{3}\pi r^3$

Substituting,

$$2\pi r \gamma \cos\theta = \left(\pi r^2 h + \frac{1}{3}\pi r^3\right)\rho g$$

$$\Rightarrow \gamma = \frac{r\rho g\left(h + \frac{1}{3}r\right)}{2\cos\theta}$$

if $\theta \rightarrow 0$, $\cos\theta = 1$.

$$\gamma = \frac{r\rho g\left(h + \frac{1}{3}r\right)}{2}$$ dynes/cm.

B. Drop-weight method :

For details see P.C. Rakshit / K.L. Kapoor

* By this method, the surface tension of a unknown liquid is measured with help of γ of a known liquid.

$$\frac{\gamma}{\gamma'} = \frac{n'\rho}{n\rho'}$$

$n \rightarrow$ Number of drops.

$\rho \rightarrow$ density

Surface tension and Temperature :

The γ of a liquid decreases with rise in temperature. A relation is given by Eötvös.

$M \rightarrow$ Molecular weight,
$v \rightarrow$ specific volume of liquid

Molar surface of a liquid assuming it to be a spherical mass $\propto (Mv)^{2/3}$

$\Rightarrow$ Molar surface energy $= k_1 (Mv)^{2/3} \gamma$
↳ some const.

He suggested, $k_1 (Mv)^{2/3} \gamma \propto t$

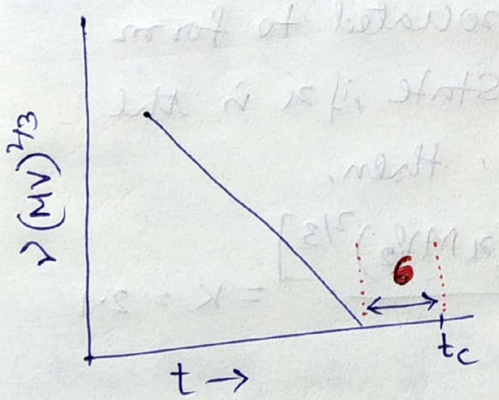
$$\Rightarrow k_1 (Mv)^{2/3} \gamma = -k_2 t + C_1 \text{ (const.)}$$

$$(Mv)^{2/3} \gamma = -kt + c$$

As at critical temp (t_c), γ is zero.

$$c = k t_c$$

$$\Rightarrow (Mv)^{2/3} \gamma = -kt + kt_c$$
$$= k(t_c - t)$$



if we plot $\gamma (Mv)^{2/3}$ vs. t, the line meet the x axis at t_c. But Ramsay & shields showed for many liquids the line actually cuts the temp. axis 6° below the t_c. Thus the relation modified to,

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

↳ Eotvos-Ramsay-shields relation

K → Eotvos-Ramsay-Shields const. & it has same magnitude, 2.1.

The K evaluated by measuring γ & specific volume (from density) at two temp.s.

~~K~~ For, liquid 1,

$$(M v_1)^{2/3} \gamma_1 = K(t_c - t_1 - 6) \quad \text{——} \text{(i)}$$

$$(M v_2)^{2/3} \gamma_2 = K(t_c - t_2 - 6) \quad \text{——} \text{(ii)}$$

(i) − (ii), $\gamma_1 (M v_1)^{2/3} - \gamma_2 (M v_2)^{2/3}$

$$= K(\cancel{t_c} - t_1 - \cancel{6} - \cancel{t_c} + t_2 + \cancel{6})$$

$$= K(t_2 - t_1)$$

$$K = -\frac{\left[\gamma_1 (M v_1)^{2/3} - \gamma_2 (M v_2)^{2/3}\right]}{t_1 - t_2}$$

for water, alcohol, carboxylic acid K < 2.1 & it rises with temp. For associated liquids K < 2.1.

if x molecules be associated to form each unit in liquid state, if x is the degree of association, then,

$$-\frac{\left[\gamma_1 (x M v_1)^{2/3} - \gamma_2 (x M v_2)^{2/3}\right]}{t_1 - t_2} = K = 2.1$$

Adhesion & Cohesion

Both the words based on the root word 'hesion', which means stick. Adhesion refers to the clingling (आसंजन) of unlike molecules & cohesion refers to the clinging of like molecules.

Adhesion: Adhesion is the mutual attraction between unlike molecules that causes them to cling to one another. e.g. glues and tapes. The adhesion of water molecules to the plastic beaker causes them to cling at a higher level around the edges.

Cohesion: Cohesion is mutual attraction between like molecules them to stick together.

Adhesion is responsible for a meniscus when water is observed in glass or plastic, because water clings to the glass around edges.

Cohesion is responsible for surface tension, such as droplets of water beading together on waxed paper.

IV.9. Surface Teniosn and Vapour Pressure

Surface tension is connected with the attraction between the molecules. The process of evaporation in which the molecules escape from the surface also depends upon the intermolecular attraction. A relation therefore must exist between the vapour pressure and the surface tension. We may proceed to find*out the relation in the following way.

A capillary tube is dipped into a liquid and the capillary rise AB is h, when $\gamma = \frac{1}{2}h\rho gr$, where r is the radius of the tube and ρ is the density of the *liquid*. Further imagine the system is enclosed in a chamber and is in equilibrium (Fig. IV.11). There is a vapour pressure difference at A and B. If p be the vapour pressure at B, then the vapour pressure at A is $p-hdg$, where d is the density of the vapour. This must be the maximum vapour pressure in contact with the curved surface at A. If it were not so, then there would have been condensation or evaporation at A, and a circulation would set up without any supply of energy. This is contrary to our experience. The difference of vapour pressure,

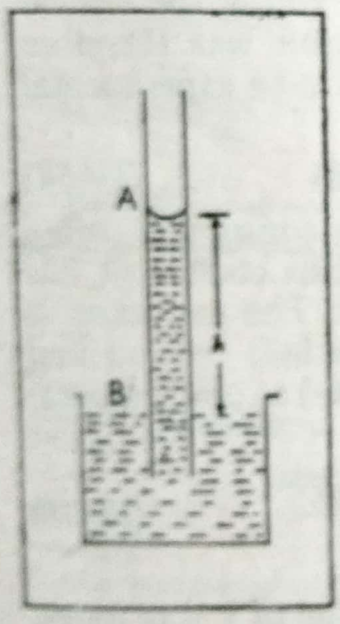


Fig. IV.11

$$dp = hdg$$

But we know,
$$h = \frac{2\gamma}{\rho gr}$$

$$\therefore \quad dp = \frac{2\gamma dg}{\rho gr} = \frac{2\gamma d}{\rho r}$$

Assuming ideal gas laws for the vapour, $d = \frac{Mp}{RT},$

we have,

$$dp = \frac{2\gamma pM}{\rho RTr}, \quad i.e. \ \frac{dp}{p} = \frac{2\gamma M}{\rho RTr} \qquad \ldots(\text{IV.13})$$

This is the relation between the surface tension and the vapour pressure.

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* J. Am. Chem. Soc. 1930, 52, 1756.

1

Adsorption

1.1 INTRODUCTION

The term adsorption implies the presence of excess concentration of any particular component at the surface of liquid or solid phase as compared to that present in the bulk of the material. This phenomenon of adsorption is basically due to the presence of residual forces at the surface of the body. These residual forces, in case of liquids, arise from the nonuniform distribution of molecules around the molecules at the surface. In solids, these residual forces are due to the presence of unsatisfied valence forces of atoms at the surface. The latter are created when some of the inter-atomic bonds are broken as a result of cleavage of a bigger crystal into the smaller units as shown by the dotted line in Fig. 1.1.1.

It is because of these residual forces that the substances stick to the surface and thus create an excessive concentration at the surface. The phenomenon of adsorption is a spontaneous process and hence, like any other spontaneous process, is attained by a decrease in free energy of the system, i.e. ΔG of the adsorption process has a negative value. Since $\Delta G = \Delta H - T\Delta S$ and that the entropy change ΔS for adsorption is necessarily a negative quantity (since the molecules at the surface are in more ordered state than in the solution), it may be concluded that the enthalpy change of the adsorption process must have a negative value and must satisfy the relation

$$|\Delta H| > |T\Delta S|$$

Hence, the process of adsorption is an exothermic process. This also follows directly from the fact that the adsorption process involves the forces of attraction between the adsorbate (the substance which is being adsorbed) and the adsorbent (the substance which adsorbed the absorbate) and hence on adsorption, there must be a release of energy.

The term adsorption must clearly be distinguished from the term absorption. The latter implies the presence of more or less uniform concentration throughout the substance.

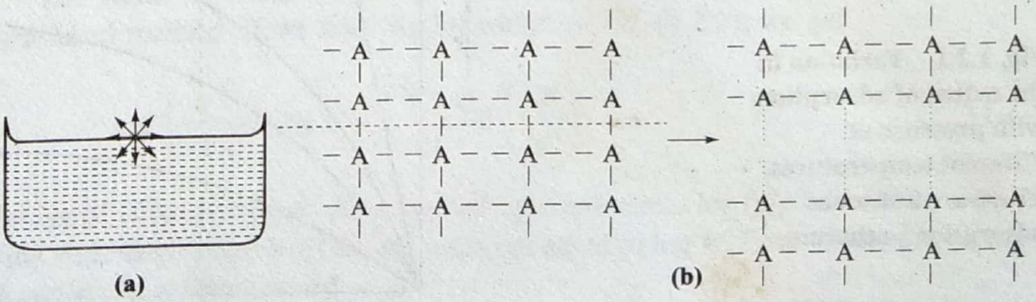


Fig. 1.1.1 Residual forces at (a) the liquid surface, and (b) the solid surface

1.2 ADSORPTION OF GASES BY SOLIDS

Preliminary Discussions

Adsorption of gases by solids is very common. The amount of a gas adsorbed, besides depending upon the nature of the gas and the surface involved, is highly dependent upon the surface area for a given mass of the adsorbent. The total surface area available in a given mass of the adsorbent depends upon its size. Take, for example, a cube of edge-length equal to 1 cm. It has a surface area of 6 cm^2. If this cube is divided into very small cublets of edge-length say of 10^{-3} cm, then the total surface area becomes equal to 6×10^3 cm^2. More and more of residual forces are created when a substance of bigger size is divided into the smaller units and hence causes more of adsorption. It is because of this reason, most of the adsorbents are available in the finely divided form. One of the extensively used adsorbents is the activated charcoal. The process of activation involves the heating of charcoal to a high temperature (ranging between 300 °C to 1000 °C) in vacuum or in the presence of an inert gas. This process removes the already adsorbed gases such as hydrocarbons and other impurities.

Effect of Temperature

As stated above, the process of adsorption is an exothermic process and thus, according to the Le-Chatelier's principle, a decrease in temperature of the system would result in an increase in adsorption. In fact, it is found to be so, as shown by the broken vertical line in Fig. 1.2.1. Qualitatively, the above effect of temperature can be understood on the basis of two parameters, namely, the thermal energy of gaseous molecules and the residual forces of the surface. These two parameters act in the opposite directions. If the temperature of the system is large, then because of the larger thermal energy, lesser number of molecules are held to the surface of the solid by the residual forces and hence lesser is the adsorption. At lower temperatures, the thermal energy is less and thus more number of molecules remain stick to the surface and hence larger is the adsorption.

Effect of Pressure

At a constant temperature, the extent of adsorption of gases increases with increase in pressure. This fact is in agreement with the Le-Chatelier principle. According to the latter, the system would move in a direction of lesser number of molecules with increase in external pressure. Since the process of adsorption decreases the

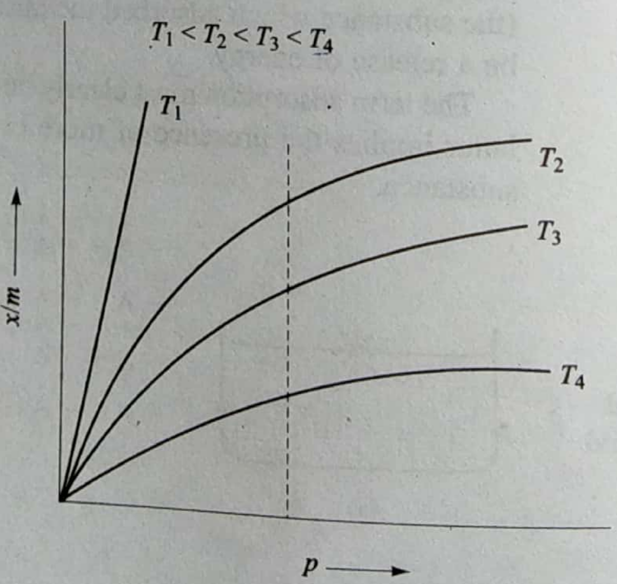


Fig. 1.2.1 Variation in the extent of adsorption with pressure at different temperatures. These are known as adsorption isotherms

number of molecules in the gaseous phase, it is expected that the extent of adsorption would increase with the increase in external pressure as it would result in the decrease of number of molecules in the gaseous phase.

Figure 1.2.1 displays qualitatively the variation in the extent of adsorption with pressure at different temperatures. The adsorption isotherm shown in Fig. 1.2.1 can be easily understood on the basis of a fixed number of adsorption sites at the surface of adsorbent where only gaseous molecules can be adsorbed. Initially as pressure is increased, the number of molecules which strike the unit area of the surface increases in proportion to the increase in pressure and hence adsorption increases almost linearly with pressure. Since a fixed number of adsorption sites are available, eventually at some high pressure a stage would be reached where all the sites are occupied and hence further increase in pressure would not cause any further increase in adsorption, i.e. the extent of adsorption becomes independent of pressure. In the intermediate range of pressure, the increase in adsorption is not as fast as the increase in pressure.

Explanation of Fig. 1.2.1

The facts shown in Fig. 1.2.1 can be explained on the basis of reversible nature of adsorption where adsorption and desorption processes proceed simultaneously. At equilibrium, both these processes proceed with equal speeds. This equilibrium process may be represented as follows:

$$\mathrm{G} + \mathrm{S} \underset{\text{desorption}}{\overset{\text{adsorption}}{\rightleftharpoons}} \mathrm{GS} \qquad (1.2.1)$$

where G, S and GS represent, respectively, the unadsorbed gaseous molecule, adsorption site at the surface of the solid and the adsorbed gaseous molecule. Though the adsorption process increases in proportion to pressure but because of the reverse reaction (i.e. desorption), the increase in adsorption is not as fast as the increase in pressure.

Freundlich Adsorption Equation

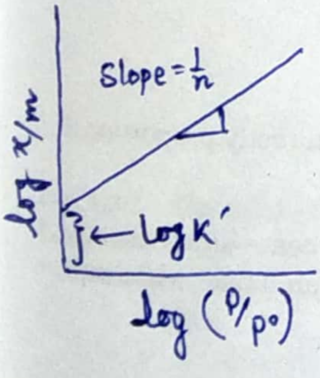
An empirical expression representing the isothermal variation in the extent of adsorption with pressure as suggested by Freundlich is

$$\left(\frac{x}{m}\right) = kp^{1/n} \qquad (1.2.2)$$

where x is the mass of gas adsorbed by the mass m of adsorbent at the pressure p, and k and n are constants for a given pair of adsorbent and adsorbate. The value of n is generally greater than one and thus its reciprocal is less than one. This accounts the fact that the increase in adsorption is not as fast as the increase in pressure.

The values of k and n for a given system can be determined by following the graphical method. If we take the logarithm of Eq. (1.2.2), we get

$$\log\left(\frac{x}{m}\right) = \log k' + \left(\frac{1}{n}\right)\log\left(\frac{p}{p^\circ}\right) \qquad (1.2.3)$$



where p° is the unit pressure. A plot of log (x/m) versus log (p/p°) would be a straight line with slope equal to $(1/n)$ and intercept equal to log k'. From these, the values of k and n can be determined.

Langmuir Adsorption Equation

Langmuir derived an expression for the variation in the extent of adsorption with pressure on the basis of following approximations.

- The surface of solid consists of a fixed number of adsorption sites where only adsorption of gaseous molecules can take place.
- Each site can hold only one gaseous molecule and involves a constant heat of adsorption. The latter is identical for all adsorption sites.
- The adsorption is monolayer, i.e. only one layer of adsorption of gaseous molecules is formed.
- The gaseous molecules adsorbed at different sites do not interact with each other.
- The phenomenon of adsorption involves a dynamic equilibrium and can be represented as

$$G + S \rightleftharpoons GS$$

where G, S, and GS represent, respectively the unadsorbed gaseous molecule, the vacant site on the surface of adsorbent and the adsorbed gaseous molecule.

Equilibrium Constant involving Adsorption

The above equilibrium process implies that the forward reaction (adsorption) and backward reaction (desorption) can take place simultaneously. At equilibrium, the rates of these two processes are identical. On equating these two rates, we get the equilibrium constant characterizing the given equilibrium reaction.

According to the law of mass action, we can write

$$\text{Rate of forward reaction} = k_f\,[G]\,[S]$$

$$\text{Rate of backward reaction} = k_b\,[GS]$$

Therefore, at equilibrium,

$$\text{Rate of adsorption} = \text{Rate of desorption}$$

i.e. $$k_f\,[G]\,[S] = k_b\,[GS]$$

or $$K = \frac{k_f}{k_b} = \frac{[GS]}{[G][S]} \qquad (1.2.4)$$

The constant K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase.

Derivation of Langmuir Equation

The concentration of adsorbed molecules GS depends only on one factor, namely, the number of occupied adsorption sites. The latter will be directly proportional to the fraction θ of the surface that is covered with gaseous molecules. Thus, we can write,

$$\text{Rate of desorption} \propto \theta$$

i.e. $$\text{Rate of desorption} = k_d\theta$$

The concentration of unadsorbed gaseous molecules G will be directly proportional to the pressure of the gas.

The concentration of vacant sites on the surface of an adsorbent will be directly proportional to the fraction of the surface that remains uncovered and hence will be directly proportional to the factor $(1 - \theta)$. Thus we can write,

$$\text{Rate of adsorption} \propto p(1 - \theta)$$

i.e.

$$\text{Rate of adsorption} = k_a\, p(1 - \theta)$$

Now since at equilibrium

$$\text{Rate of adsorption} = \text{rate of desorption},$$

it follows that

$$k_a\,(1 - \theta)p = k_d\theta$$

i.e.

$$\theta = \frac{k_a p}{k_d + k_a p} = \frac{(k_a/k_d)}{1 + (k_a/k_d)p} = \frac{K_1 p}{1 + K_1 p} \tag{1.2.5}$$

Equation (1.2.5) is known as *Langmuir adsorption equation*. The form of Langmuir isotherm for several values of K_1 is shown in Fig. 1.2.2. The surface coverage increases with pressure, and approaches unity only at very high pressures. Since the value of K_1 depends only on temperature, Fig. 1.2.2 also represents the form of Langmuir isotherm at various temperatures.

Physical Significance of the Constant K_1

The constant K_1, which is equal to k_a/k_d, is known as distribution coefficient. The constant K_1 is, in fact, an equilibrium constant for the distribution of adsorbate between the surface and the gas phase and is given by

$$K_1 = \frac{k_a}{k_d} = \frac{\theta}{1 - \theta}\,\frac{1}{p} \tag{1.2.6}$$

The equilibrium constant K_1, like any other equilibrium constant, depends only on the temperature of the system. Thus, for a given pressure p, different values of K_1 are obtained at different temperatures. The fraction θ of the area covered with gases is expected to increase with decrease in temperature. Thus, from Eq. (1.2.6) it follows that a given pressure, the equilibrium constant K_1 will increase with decrease in temperature, i.e. the equilibrium constant K_1 and temperature will have inverse relation with each other.

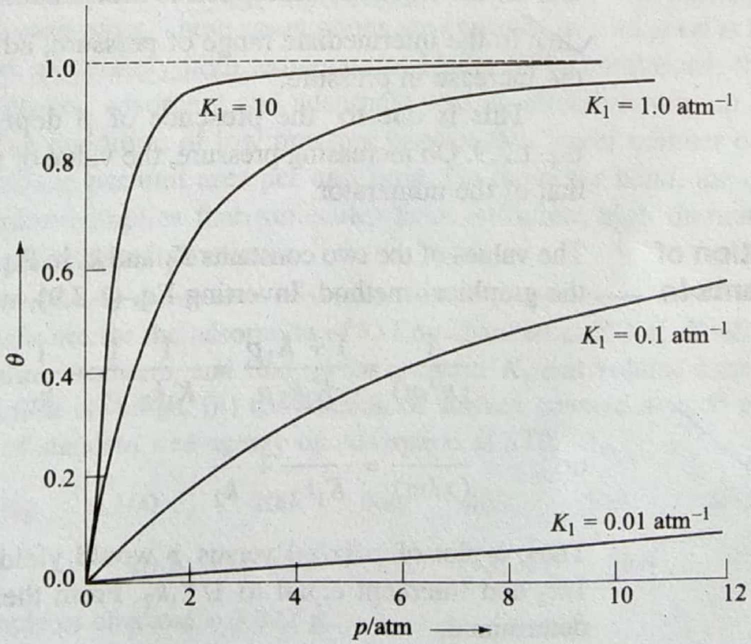


Fig. 1.2.2 The form of Langmuir isotherm at various values of K_1

The equilibrium constant K_1° can be utilized for calculating the change in standard free energy on adsorption by the relation

$$\Delta G^\circ = -RT \ln K_1^\circ \tag{1.2.7}$$

Explanation of Adsorption Isotherms of Fig. 1.2.1

Since the formation of a single layer of adsorbed gaseous molecules is assumed, it is obvious that the mass of gas adsorbed by the unit mass of adsorbent, will be directly proportional to the factor θ that is,

$$\left(\frac{x}{m}\right) \propto \theta \qquad \text{i.e.} \qquad \left(\frac{x}{m}\right) = k_2\theta \tag{1.2.8}$$

Substituting Eq. (1.2.8) in Eq. (1.2.5), we get

$$\left(\frac{x}{m}\right) = \frac{K_1k_2p}{1 + K_1p} \tag{1.2.9}$$

Equation (1.2.9) can be used to correlate the following experimental facts regarding the adsorption of gases as shown in Fig. 1.2.1.

(i) At low pressure, the extent of adsorption is proportional to pressure. At low pressure, the factor K_1p in Eq. (1.2.9) is much smaller than 1 and hence can be ignored. Thus, we have

$1 >> K_1P$

$$\left(\frac{x}{m}\right) \simeq K_1k_2p \qquad \text{or} \qquad \left(\frac{x}{m}\right) \propto p$$

that is, the extent of adsorption is directly proportional to the pressure of the gas.

(ii) At high pressure, the extent of adsorption is independent of pressure. Here K_1p will be much greater than 1 and hence the factor one can be ignored in comparison to K_1p. Thus, we have

$$\left(\frac{x}{m}\right) = \frac{K_1k_2p}{K_1p} = k_2$$

that is, the extent of adsorption is independent of pressure.

(iii) In the intermediate range of pressure, adsorption does not increase as fast as the increase in pressure.

This is due to the presence of p dependent term in the denominator of Eq. 1.2.9. On increasing pressure, the value of the denominator increases faster than that of the numerator.

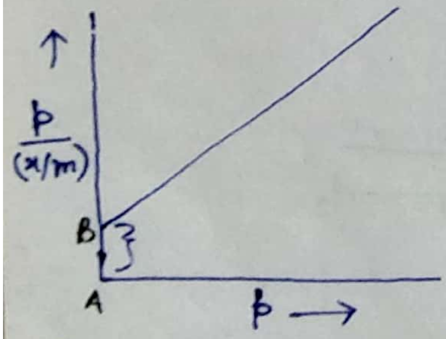
Determination of the Constants in Eq. (1.2.9)

The values of the two constants K_1 and k_2 in Eq. (1.2.9) can be obtained by following the graphical method. Inverting Eq. (1.2.9), we get

$$\frac{1}{(x/m)} = \frac{1 + K_1p}{K_1k_2p} = \frac{1}{K_1k_2}\frac{1}{p} + \frac{1}{k_2}$$

$$\text{or} \qquad \frac{p}{(x/m)} = \frac{1}{K_1k_2} + \frac{p}{k_2} \tag{1.2.10}$$

Thus, a plot of $p/(x/m)$ versus p would yield a straight line with slope equal to $1/k_2$ and intercept equal to $1/K_1k_2$. From these, the values of K_1 and k_2 can be determined.



$p \rightarrow$ known, Slope = $\frac{1}{K_2}$

Alternative Form of Langmuir Equation

Equation (1.2.5) can be written in an alternate form involving the volume of the adsorbed gas. Since θ is the fraction of the surface covered, it will be given by

$$\theta = \frac{\upsilon}{\upsilon_{\text{mono}}}$$

where υ is the volume of gas adsorbed at the given conditions of pressure and temperature and υ_{mono} is that adsorbed at sufficiently high gas pressure so as to give a complete coverage of the surface with a single layer of gaseous molecules. These volumes are reduced to STP conditions and then substituted in Eq. (1.2.5). Thus, we have

$$\frac{\upsilon}{\upsilon_{\text{mono}}} = \frac{K_1 p}{1 + K_1 p} \tag{1.2.11}$$

Equation (1.2.11) can be written in a more suitable form by taking its reciprocal, i.e.

$$\frac{\upsilon_{\text{mono}}}{\upsilon} = \frac{1 + K_1 p}{K_1 p} \quad \text{or} \quad \frac{\upsilon_{\text{mono}}}{\upsilon} = \frac{1}{K_1}\frac{1}{p} + 1$$

$$\text{or} \quad \frac{p}{\upsilon} = \frac{1}{K_1 \upsilon_{\text{mono}}} + \frac{p}{\upsilon_{\text{mono}}} \tag{1.2.12}$$

Now, if a plot is made between p/υ and p, one would get a linear plot with slope equal to $1/\upsilon_{\text{mono}}$ and intercept $1/K_1\,\upsilon_{\text{mono}}$. From these, the values of υ_{mono} and K_1 can be determined.

Conditions for the Applicability of Langmuir Equation

It is worth pointing out the temperature and pressure conditions over which the Langmuir adsorption isotherm is expected to be applicable. While deriving the Langmuir adsorption isotherm, two important assumptions have been made. These are: (i) formation of monolayer adsorption, and (ii) adsorbed molecules do not interact with each other. These assumptions are expected to hold good at low gaseous pressure and moderately high temperature. Under these conditions, the forces of attraction between adsorbent and adsorbate will be effective only up to the short distances. The condition of low pressure implies that lesser number of molecules strike the surface per unit area per unit time. On the other hand, the condition of high temperature implies that molecules have sufficient high thermal energy to prevent the multilayer formation.

✓ Multilayer Adsorption

The adsorption of gases on the surface of an adsorbent is no more monolayer at high pressures and low temperatures. 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 forces of attraction (van der Waals forces of attraction) between the adsorbed molecule and nearby unadsorbed molecule. This results into the multilayer adsorption, i.e. more than one layer of molecules is adsorbed at the surface. The formation of multilayer is very much enhanced as the pressure of the gas reaches near to the saturation vapour pressure of the liquefied adsorbent at the given experimental temperature. Consequently, the shape of adsorption isotherm is no more identical with that given in Fig. 1.2.1. In fact, four different types of isotherms are observed. These are shown in Fig. 1.2.4 along with the monolayer adsorption isotherm.

✗ Derivation of BET Equation

(Out of syllabus)

The adsorption isotherms shown in Fig 1.2.4 have been interpreted by Brunauer, Emmett and Teller on the basis of formation of multilayer. They derived a theoretical expression, known as BET adsorption isotherm, on the lines very similar to those adopted by Langmuir. While deriving the expression, it was again assumed that interactions amongst the adsorbed molecules in the adsorption layer along the adsorbent surface are neglected.

The formation of multilayer may be represented by the following equilibria.

$$\left.\begin{array}{l} G + S \rightleftharpoons GS \\ G + GS \rightleftharpoons G_2S \\ G + G_2S \rightleftharpoons G_3S \\ \dots\dots\dots\dots\dots\dots\dots\dots \\ G + G_{n-1}S \rightleftharpoons G_nS \end{array}\right\} \qquad (1.2.15)$$

where G, S, GS, G_2S, ⋯, represent, respectively, the unadsorbed gaseous molecule, the vacant site of the adsorbent surface, single molecule adsorbed per vacant site, two molecules adsorbed per vacant site and so on.

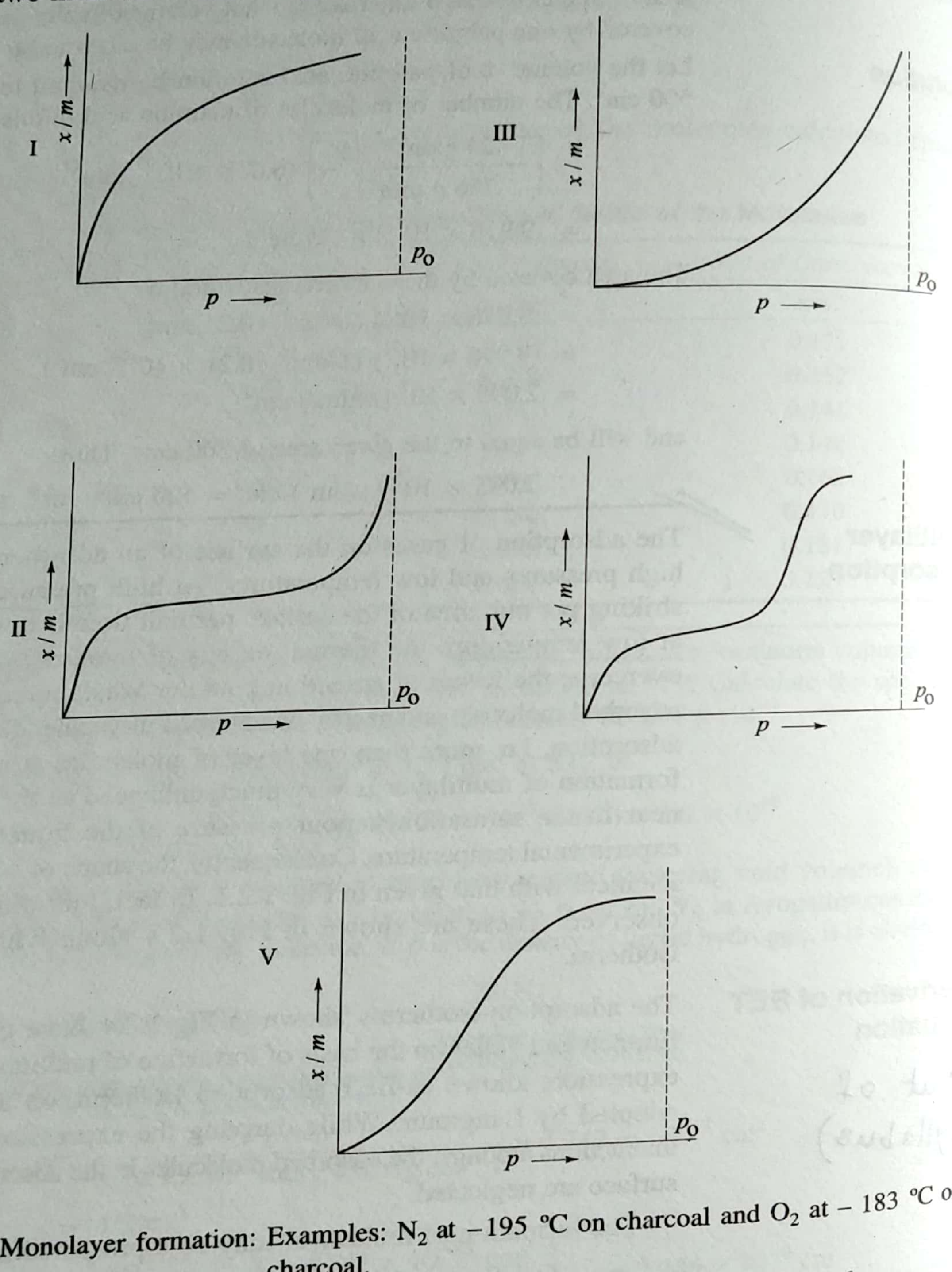


Fig. 1.2.4 Five different types of adsorption isotherms

I Monolayer formation: Examples: N_2 at −195 °C on charcoal and O_2 at − 183 °C on charcoal.

II Examples: N_2 at − 195 °C on Fe catalyst and N_2 at − 195 °C on silica gel.

III Examples: Br_2 at 79 °C on silica gel and I_2 at 79 °C on silica gel.

IV Example: Benzene on Fe_2O_3 at 50 °C.

V Example: Water vapour at 100 °C on charcoal.

The various equilibria of Eq. (1.2.15) may be characterized by the equilibrium constants defined as follows.

$$\left.\begin{aligned} K_1' &= \frac{[\mathrm{GS}]}{[\mathrm{G}]\,[\mathrm{S}]} \\ K_2' &= \frac{[\mathrm{G_2S}]}{[\mathrm{G}]\,[\mathrm{GS}]} \\ K_3' &= \frac{[\mathrm{G_3S}]}{[\mathrm{G}]\,[\mathrm{G_2S}]} \\ &\ldots\ldots\ldots\ldots\ldots\ldots, \text{ and so on.} \end{aligned}\right\} \tag{1.2.16}$$

Now, as usual, we will have:

(i) [G] ∝ pressure of the gas, that is,

$$[\mathrm{G}] \propto p$$

(ii) [S] ∝ the fraction of the free surface, that is,

$$[\mathrm{S}] \propto \theta_0$$

(iii) [GS] ∝ fraction of surface covered with single-molecule adsorption, that is,

$$[\mathrm{GS}] \propto \theta_1$$

(iv) $[\mathrm{G_2S}]$ ∝ fraction of surface covered with two-molecule adsorption, that is,

$$[\mathrm{G_2S}] \propto \theta_2$$

…………………, and so on.

With the above relations, the expressions of equilibrium constants (Eqs 1.2.16) become

$$\left.\begin{aligned} K_1 &= \frac{\theta_1}{p\theta_0} \\ K_2 &= \frac{\theta_2}{p\theta_1} \\ K_3 &= \frac{\theta_3}{p\theta_2} \\ &\ldots\ldots\ldots\ldots\ldots\ldots, \text{ and so on.} \end{aligned}\right\} \tag{1.2.17}$$

The value of constant K_1 is usually very large as compared to the rest of the equilibrium constants. The reason for this is that the interaction between the adsorbate and the adsorbent decreases very rapidly as the distance from the surface is increased. The remaining constants K_2, K_3, …, etc. though will not have the same values, but the difference between any two constants is generally much smaller than that between K_1 and K_2. It is for this reason, it can assumed that

$$K_2 \simeq K_3 \simeq K_4 \simeq \ldots \simeq K_L \tag{1.2.18}$$

where K_L is the equilibrium constant corresponding to the saturated vapour-liquid equilibrium and, by definition, is given as

$$\text{saturated vapour} \rightleftharpoons \text{liquid}$$

$$K_L = \frac{1}{p_0} \tag{1.2.19}$$

With the approximation given in Eq. (1.2.18), the various equilibrium constants of Eqs (1.2.17) are reduced to

$$\left.\begin{aligned} K_1 &= \frac{\theta_1}{p\theta_0} \\ K_2 &\simeq K_\mathrm{L} = \frac{\theta_2}{p\theta_1} \\ K_3 &\simeq K_\mathrm{L} = \frac{\theta_3}{p\theta_2} \\ &\ldots\ldots\ldots\ldots, \text{ and so on} \end{aligned}\right\} \quad (1.2.20)$$

Rearranging the above expressions and making use of Eq. (1.2.19), we get

$$\left.\begin{aligned} \theta_1 &= K_1 p\theta_0 \\ \theta_2 &= K_\mathrm{L} p\theta_1 = \left(\frac{1}{p_0}\right) p(K_1 p\theta_0) = K_1 p\left(\frac{p}{p_0}\right)\theta_0 \\ \theta_3 &= K_\mathrm{L} p\theta_2 = \left(\frac{1}{p_0}\right) p\left(K_1 p\frac{p}{p_0}\theta_0\right) = K_1 p\left(\frac{p}{p_0}\right)^2 \theta_0 \\ &\ldots\ldots\ldots\ldots, \text{ and so on.} \end{aligned}\right\} \quad (1.2.21)$$

If we assume that the entire adsorbent surface is covered, then the total coverage of the first layer will be given by

$$\theta_\text{total} = \theta_0 + \theta_1 + \theta_2 + \cdots = 1 \quad (1.2.22)$$

Substituting the values of θ_1, θ_2, $\cdots$ from Eqs (1.2.21), we have

$$\theta_\text{total} = \theta_0 + K_1 p\theta_0 + K_1 p\left(\frac{p}{p_0}\right)\theta_0 + K_1 p\left(\frac{p}{p_0}\right)^2 \theta_0 + \cdots = 1$$

$$= \theta_0\left[1 + K_1 p\left\{1 + \left(\frac{p}{p_0}\right) + \left(\frac{p}{p_0}\right)^2 + \cdots\right\}\right] = 1 \quad (1.2.23)$$

Since $p/p_0 \leq 1$, the expression within the curly brackets of Eq. (1.2.23) can be written as

$$1 + \left(\frac{p}{p_0}\right) + \left(\frac{p}{p_0}\right)^2 + \cdots = \left[1 - \left(\frac{p}{p_0}\right)\right]^{-1} = \frac{1}{1 - (p/p_0)} \quad (1.2.24)$$

Substituting Eq. (1.2.24) in Eq. (1.2.23), we get

$$\theta_\text{total} = \theta_0\left[1 + \frac{K_1 p}{1 - (p/p_0)}\right] = 1$$

or

$$\theta_0 = \frac{1}{1 + K_1 p/\{1 - (p/p_0)\}} = \frac{1 - p/p_0}{1 + K_1 p - p/p_0} \quad (1.2.25)$$

Now the total volume of the adsorbed gas (corrected to STP) will be given by

$$v_{\text{total}} = v_{\text{mono}}\,(\theta_1 + 2\theta_2 + 3\theta_3 + \cdots) \tag{1.2.26}$$

where v_{mono} is the volume required for the monolayer adsorption. Substituting the values of θ_1, θ_2, θ_3, ... from Eqs (1.2.21), we get

$$v_{\text{total}} = v_{\text{mono}}\,K_1 p\theta_0 \left[1 + 2\left(\frac{p}{p_0}\right) + 3\left(\frac{p}{p_0}\right)^2 + \cdots\right] \tag{1.2.27}$$

The expression within the bracket of Eq. (1.2.27) is simply a derivative of the expression within the curly bracket of Eq. (1.2.23). Thus in view of Eq. (1.2.24), we get

$$1 + 2\left(\frac{p}{p_0}\right) + 3\left(\frac{p}{p_0}\right)^2 + \cdots = \frac{1}{(1 - p/p_0)^2} \tag{1.2.28}$$

Substituting Eq. (1.2.28) in Eq. (1.2.27), we get

$$v_{\text{total}} = v_{\text{mono}}\,\frac{K_1 p\theta_0}{(1 - p/p_0)^2} \tag{1.2.29}$$

Substituting the expression of θ_0 from Eq. (1.2.25), we get

$$v_{\text{total}} = \frac{v_{\text{mono}} K_1 p}{(1 - p/p_0)(1 + K_1 p - p/p_0)} \tag{1.2.30}$$

The pressure p in the above expression may be replaced in terms of relative pressure (p/p_0) as shown below.

$$p = p_0\,\frac{p}{p_0} = \frac{1}{K_{\text{L}}}\left(\frac{p}{p_0}\right) \tag{1.2.31}$$

Thus, substitution of Eq. (1.2.31) in Eq. (1.2.30) gives

$$v_{\text{total}} = \frac{v_{\text{mono}}\,(K_1/K_{\text{L}})(p/p_0)}{(1 - (p/p_0)\{(K_1/K_{\text{L}})(p/p_0) - (p/p_0)\}} \tag{1.2.32}$$

The ratio K_1/K_{L} is designated by the symbol C. Thus, we have

$$v_{\text{total}} = \frac{v_{\text{mono}}\;C(p/p_0)}{(1 - (p/p_0)\{1 + C(p/p_0) - (p/p_0)\}} \tag{1.2.33}$$

Equation (1.2.33) is the required Brunauer, Emmett and Teller equation for multilayer adsorption of gaseous molecules (written in short as BET equation).

Equation (1.2.33) may be written in the form

$$\boxed{\frac{p}{v_{\text{total}}(p_0 - p)} = \frac{1}{v_{\text{mono}}C} + \frac{C - 1}{v_{\text{mono}}C}\,\frac{p}{p_0}} \tag{1.2.34}$$

Thus, a plot of $p/\{v_{\text{total}}(p_0 - p)\}$ against p/p_0 should give a straight line, whose intercept and slope are $1/(v_{\text{mono}}\,C)$ and $(C-1)/(v_{\text{mono}}\,C)$, respectively. The two constants v_{mono} and C can thus be evaluated. Knowing v_{mono}, the surface area of the adsorbent can be determined by following the method given earlier in this section (Eq. 1.2.13).

Physical Significance of the Constant C in BET Equation

The adsorption equilibrium constant K_1 is related to the standard change in the free energy ΔG° by the relation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_1^\circ$$

Therefore

$$K_1^\circ = \exp(\Delta_{\text{ads}}S_1^\circ/R)\exp(-\Delta_{\text{ads}}H_1^\circ/RT)$$

$$= g_1 \exp(\Delta_{\text{des}}H_1^\circ/RT)$$

where g_1 is the entropy factor and $\Delta_{\text{des}}H_1^\circ$ is the standard enthalpy of desorption of the monolayer formation. Similarly, for the equilibrium constant K_L, one can write

$$K_L^\circ = g_L \exp(\Delta_{\text{vap}}H_L^\circ/RT)$$

where $\Delta_{\text{vap}}H_L^\circ$ is the standard enthalpy of vaporization of the liquid adsorbate.

The ratio of these two equilibrium constants, which is equal to C in BET equation, is given by

$$C = \frac{K_1^\circ}{K_L^\circ} = \frac{g_1 \exp(\Delta_{\text{des}}H_1^\circ/RT)}{g_L \exp(\Delta_{\text{vap}}H_L^\circ/RT)} \simeq \exp\left(\frac{\Delta_{\text{des}}H_1^\circ - \Delta_{\text{vap}}H_L^\circ}{RT}\right) \tag{1.2.35}$$

Derivation of Langmuir Equation from BET Equation

Equation (1.2.34) may be written as

$$\frac{p\,p_0}{v_{\text{total}}(p_0 - p)} = \frac{1}{v_{\text{mono}}}\frac{p_0}{C} + \frac{1}{v_{\text{mono}}}\frac{C-1}{C}p \tag{1.2.36}$$

Now $C = \dfrac{K_1}{K_L}$ and $K_L = \dfrac{1}{p_0}$

Thus $C = \dfrac{K_1}{K_L} = \dfrac{K_1}{(1/p_0)} = p_0 K_1$

or $K_1 = \dfrac{C}{p_0}$

Substituting the above relation in Eq. (1.2.36), we get

$$\frac{p\,p_0}{v_{\text{total}}(p_0 - p)} = \frac{1}{v_{\text{mono}}\,K_1} + \frac{1}{v_{\text{mono}}}\frac{C-1}{C}p \tag{1.2.37}$$

Now if we assume that C is much greater than one and that p_0 is much greater than p, then Eq. (1.2.37) is modified to

$$\frac{p}{v_{\text{total}}} = \frac{1}{v_{\text{mono}}}\frac{1}{K_1} + \frac{p}{v_{\text{mono}}} \tag{1.2.38}$$

which is, in fact, the Langmuir equation (1.2.12).

8888 ← Pt

✓ Explanation of Isotherms of Fig. 1.2.4

The five isotherms shown in Fig. 1.2.4 can be explained on the basis of BET equation as described below.

Type I This type of adsorption is obtained whenever $p/p_0 \ll 1$ and $C \gg 1$. Note that under these conditions, we have deduced above the Langmuir equation (1.2.38) and hence the adsorption in the present case is monolayer.

Type II This type of adsorption is observed when C is considerably greater than one or, in other words, $\Delta_{\text{des}}H_1^\circ$ is greater than $\Delta_{\text{vap}}H_L^\circ$. The intermediate flattish portion corresponds to the formation of monolayer.

Type III This type of adsorption is observed when C is considerably smaller than one, or in the other words, $\Delta_{\text{des}}H_1^\circ$ is less than $\Delta_{\text{vap}}H_L^\circ$. There is no intermediate flattish portion indicating that the formation of multilayer takes place from the very beginning.

Type IV In the lower pressure region, the shape of the adsorption is very similar to that observed in the type II indicating the formation of monolayer followed by the development of multilayer. The essential condition of $\Delta_{\text{des}}H_1^\circ$ being greater than $\Delta_{\text{vap}}H_L^\circ$ is still satisfied. However, the shape of the adsorption as $p \rightarrow p_0$ differs from that observed in type II. In the present case, the adsorption reaches a limit at pressures well below the saturation vapour pressure. This has been explained on the basis of multilayer formation along with the possibility of filling the capillary pores as a result of condensation of the adsorbate at pressures appreciably below the saturation vapour pressure.

Type V Again, the lower portion of the diagram in this case is very similar to that observed in the type III indicating that $\Delta_{\text{des}}H_1^\circ$ is less than $\Delta_{\text{vap}}H_L^\circ$. The higher portion is identical to that of type IV indicating the saturation in adsorption at pressures below the saturation vapour pressure. This has been again explained on the basis of filling the capillary pores as a result of condensation of the adsorbate at pressures appreciably below the saturation vapour pressure.

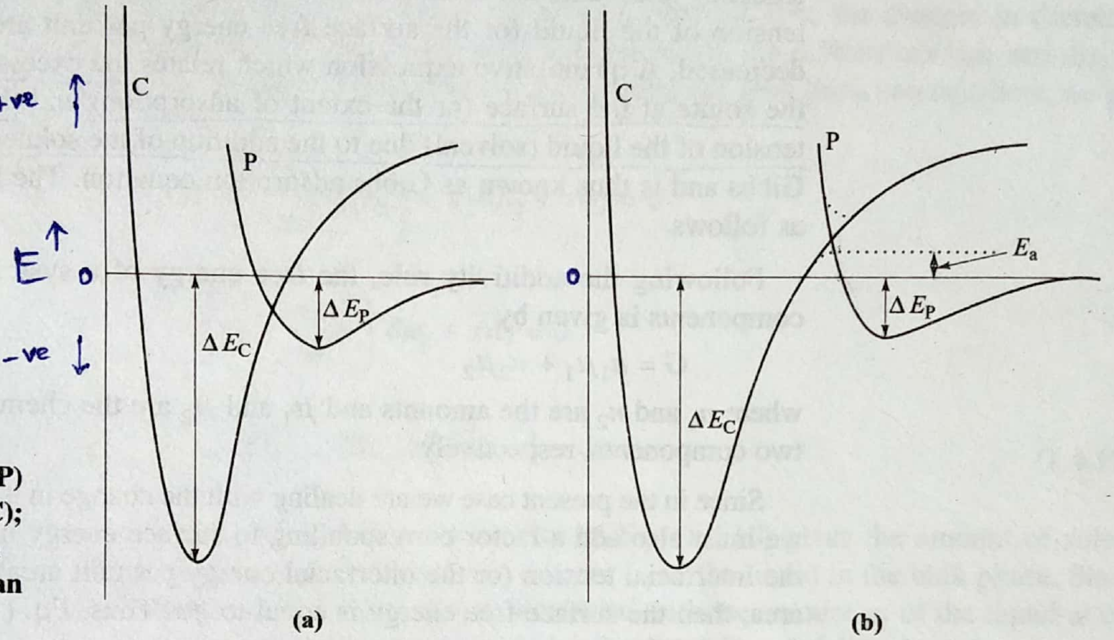
1.3 PHYSICAL ADSORPTION AND CHEMISORPTION

On the basis of forces of attraction between adsorbent and adsorbate, adsorption has been classified into two categories, namely, van der Waals adsorption (or physical adsorption) and chemisorption (or activated adsorption). The general characteristics of these adsorptions are described in Table 1.3.1.

Table 1.3.1 Characteristics of Physical Adsorption and Chemisorption

	Physical Adsorption	*Chemisorption*
1.	The forces of attraction between adsorbent and adsorbate are of van der Waals type (weak forces).	The forces of attraction between adsorbent and absorbate are of chemical nature (strong forces).
2.	This predominates at low temperatures.	This usually occurs at high temperature.
3.	Almost all gases show this type of adsorption at low temperatures.	It is highly specific in nature.
4.	The enthalpy of adsorption is low and has a value of about 20 kJ mol^{-1} or less.	The enthalpy of adsorption is high and has a value of the order of 80 to 420 kJ mol^{-1}.
5.	This type of adsorption attains equilibrium very rapidly on changing the temperature and pressure of the system.	This type of adsorption is relatively slower.
6.	This is reversible in nature.	This is usually irreversible in nature. For example, O_2 adsorbed on charcoal, when desorbed also contains CO and CO_2.
7.	The activation energy involved in this adsorption is small and is often less than 5 kJ mol^{-1}. It is for this reason, this is even attained at low temperatures.	The activation energy involved in this adsorption is high. It is for this reason this is attained only at high temperatures.
8.	Adsorption in this case is often multilayer.	Adsorption in this case is monolayer and thus Langmuir adsorption isotherm is applicable.

Sometimes physical adsoprtion can pass over to chemisorption on increasing the temperature of system. For example, hydrogen shows physical adsorption on a nickel surface at 73 K. On increasing temperature, the extent of adsorption decreases sharply as is to be expected. But very soon, the extent of adsorption starts increasing and attains a maximum value at about 173 K. Beyond 173 K, the extent of adsorption again starts decreasing. Thus, the physical adsorption which predominates at 73 K is passed over to chemisorption at 173 K. This transformation can be explained on the basis of intersections of potential energy curves of physical adsorption and chemisorption as shown in Fig. 1.3.1.



(a) (b)

Fig. 1.3.1 Potential energy diagram for physical adsorption (P) and chemisorption (C); (a) with no activation energy, and (b) with an activation energy

The potential energy diagram of physical adsorption shows a shallow minimum at a relatively long distance from the surface as compared to the larger minimum observed in case of chemisorption. The depths of these minima are in agreement with the enthalpies of adsorption involved in these two cases. It may be seen that at a distance very large from the surface, the gaseous molecules have zero potential energy in case of physical adsorption while those in case of chemisorption have a positive value. These suggest that the molecules in physical adsorption are not very much perturbed as a result of weak forces of attraction while those involved in cheimsorption are very much perturbed. The perturbation may be present even up to the extent of excited electronic state or a dissociated state and thus the molecule in chemisorption is altogether different from the ground state of the molecule. The two potential energy curves may intersect each other and at the point of intersection, both of them have the same energy. As in the interaction of two atomic orbitals to form bonding and antibonding orbitals, we have two different states, one with higher and one with a lower energy, as shown by the dashed curves in Fig. 1.3.1b. At round about these intersection points, the physical adsorption can pass over to the chemisorption. Now this passing over may or may not require activation energy. In the latter, the intersection occurs on the negative side of the potential energy of physical adsorption while in the former, it takes place on the positive side of potential energy. These two cases are also shown in Fig. 1.3.1.

1.4 ADSORPTION AT THE SURFACE OF A LIQUID

Gibbs Adsorption Equation

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 forces 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 the liquid, then it has a tendency to accumulate more at the surface of the liquid since this way the surface tension of the liquid (or the 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 the addition of the solute was derived by J.W. Gibbs and is thus known as Gibbs adsorption equation. The latter can be derived as follows.

Following the additivity rule, the free energy of a system consisting of two components is given by

$$G = n_1\mu_1 + n_2\mu_2 \tag{1.4.1}$$

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

Since in the present case we are dealing with the change in the surface free energy, we must also add a factor corresponding to surface energy in Eq. (1.4.1). If γ is the interfacial tension (or the interfacial energy per unit area) and s is the surface area, then the surface free energy is equal to γs. Thus, Eq. (1.4.1), in the present case, modifies to

$$G = n_1\mu_1 + n_2\mu_2 + \gamma s \tag{1.4.2}$$

The complete differential of Eq. (1.4.2) is given by

$$\mathrm{d}G = n_1\mathrm{d}\mu_1 + \mu_1\mathrm{d}n_1 + n_2\mathrm{d}\mu_2 + \mu_2\mathrm{d}n_2 + \gamma\mathrm{d}s + s\,\mathrm{d}\gamma \tag{1.4.3}$$

The function G will now depend on five independent variables, namely, T, p, n_1, n_2 and s, i.e.

$$G = \mathrm{f}(T, p, n_1, n_2, s) \tag{1.4.4}$$

The total differential of G will be given by

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{p,\,n_1,\,n_2,\,s}\mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{T,\,n_1,\,n_2,\,s}\mathrm{d}p + \left(\frac{\partial G}{\partial n_1}\right)_{T,\,p,\,n_2,\,s}\mathrm{d}n_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,\,p,\,n_1,\,s}\mathrm{d}n_2 + \left(\frac{\partial G}{\partial s}\right)_{T,\,p,\,n_1,\,n_2}\mathrm{d}s \tag{1.4.5}$$

or

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu_1\mathrm{d}n_1 + \mu_2\mathrm{d}n_2 + \gamma\mathrm{d}s \tag{1.4.6}$$

At constant temperature and pressure, Eq. (1.4.6) reduces to

$$\mathrm{d}G_{T,\,p} = \mu_1\mathrm{d}n_1 + \mu_2\mathrm{d}n_2 + \gamma\mathrm{d}s \tag{1.4.7}$$

From Eqs. (1.4.7) and (1.4.3), we get

$$n_1 \mathrm{d}\mu_1 + n_2 \mathrm{d}\mu_2 + s\,\mathrm{d}\gamma = 0 \qquad (1.4.8)$$

The corresponding expression for the bulk of the liquid is

$$n_1^0\, \mathrm{d}\mu_1 + n_2^0\, \mathrm{d}\mu_2 = 0 \qquad (1.4.9)$$

where n_1^0 and n_2^0 are the respective amounts of the liquid and solute in the bulk phase.

Now since 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 equilibrium, then the changes in chemical potentials must be identical in both the phases, i.e. the differentials $\mathrm{d}\mu_1$ and $\mathrm{d}\mu_2$ in Eqs. (1.4.8) and (1.4.9) are identical. Eliminating $\mathrm{d}\mu_1$ from these two equations, we get

$$n_1\left(-\frac{n_2^0}{n_1^0}\,\mathrm{d}\mu_2\right) + n_2 \mathrm{d}\mu_2 + s\,\mathrm{d}\gamma = 0$$

or

$$\left(n_2 - \frac{n_1 n_2^0}{n_1^0}\right)\mathrm{d}\mu_2 + s\,\mathrm{d}\gamma = 0$$

or

$$-\frac{\mathrm{d}\gamma}{\mathrm{d}\mu_2} = \frac{n_2 - (n_1 n_2^0/n_1^0)}{s} \qquad (1.4.10)$$

The expression within the bracket of Eq. (1.4.10) gives the amount of solute that would be associated with the amount n_1 of the liquid in the bulk phase. Since n_2 is the amount of solute that is associated with the amount n_1 of the liquid at the surface, the numerator on the right-hand side of Eq. (1.4.10) gives the excessive amount of solute that is present in the surface of the liquid. Dividing this quantity with s gives the excessive concentration of solute per unit area of surface. This quantity is represented by the symbol Γ_2. Thus, we have

$$\Gamma_2 = -\frac{\mathrm{d}\gamma}{\mathrm{d}\mu_2} \qquad (1.4.11)$$

Equation (1.4.11) is the required *Gibbs adsorption equation*. If we eliminate $\mathrm{d}\mu_2$ instead of $\mathrm{d}\mu_1$ from Eqs (1.4.8) and (1.4.9), we would have got the Gibbs adsorption equation as applicable to the liquid. It has a form

$$\Gamma_1 = \frac{\mathrm{d}\gamma}{\mathrm{d}\mu_1} \qquad (1.4.12)$$

where Γ_1 is the surface excessive concentration of the solvent at the surface of liquid.

The chemical potential of the solute is given by

$$\mu_2 = \mu_2^*(1) + RT \ln a_2$$

where $\mu_2^*(1)$ is the chemical potential of pure solute in liquid phase. Hence

$$\mathrm{d}\mu_2 = RT\,\mathrm{d}\ln a_2 \qquad (1.4.13)$$

Substituting Eq. (1.4.13) in Eq. (1.4.11), we get

$$\Gamma_2 = -\frac{1}{RT}\,\frac{\mathrm{d}\gamma}{\mathrm{d}\ln a_2} = -\frac{a_2}{RT}\,\frac{\mathrm{d}\gamma}{\mathrm{d}a_2} \tag{1.4.14}$$

For a dilute solution, we have

$$\boxed{\Gamma_2 = -\frac{1}{RT}\,\frac{\mathrm{d}\gamma}{\mathrm{d}\ln (c_2/c^\circ)} = -\frac{c_2}{RT}\,\frac{\mathrm{d}\gamma}{\mathrm{d}c_2}} \tag{1.4.15}$$

where c° is standard unit concentration.

Thermodynamic Treatment of Adsorption

Jura and Harkins extended thermodynamically derived Gibbs equation (see Section 1.4) to the adsorption of gases on solids on the assumption that the adsorbed films of gases on solid surfaces are similar to those at liquid-vapour interfaces. The Gibbs equation is given by

$$\Gamma = -\frac{1}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}\ln a} \tag{1.2.39}$$

where Γ is the excess concentration of solute per unit area at the surface.

For the adsorption of gases, Eq. (1.2.39) takes the form

$$\Gamma = \frac{1}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}\ln(p/p^\circ)} \tag{1.2.40}$$

where p is the pressure of the gas and p° is the standard unit pressure. Now the excess concentration of solute per unit area at the surface will be equal to concentration of adsorbed gas since the concentration of gas in the bulk of adsorbent is zero. If υ is the volume of gas adsorbed per unit mass of solid and σ is the surface area of the solid per unit of mass, then

$$\text{Volume of gas adsorbed per unit surface area of adsorbent} = \frac{\upsilon}{\sigma}$$

Now, if V_m is the molar volume of the gas, we will have

$$\text{Amount of gas adsorbed per unit surface area of adsorbent} = \frac{1}{V_\mathrm{m}}\left(\frac{\upsilon}{\sigma}\right)$$

and this will be equal to surface excess concentration at the surface. Thus

$$\Gamma = \frac{1}{V_\mathrm{m}}\left(\frac{\upsilon}{\sigma}\right) \tag{1.2.41}$$

Substituting Eq. (1.2.41) in Eq. (1.2.40), we get

$$\frac{\upsilon}{\sigma V_\mathrm{m}} = -\frac{1}{RT}\,\frac{\mathrm{d}\gamma}{\mathrm{d}\ln(p/p^\circ)} \tag{1.2.42}$$

or $$\mathrm{d}\gamma = -\frac{\upsilon RT}{\sigma V_\mathrm{m}}\,\mathrm{d}\ln(p/p^\circ) \tag{1.2.43}$$

The change in surface tension $\mathrm{d}\gamma$ of absorbent may be correlated with the area of cross-section of the absorbed molecules. Lesser the area, larger the number of molecules absorbed per unit area of the adsorbent and hence larger the decrease in the surface tension of the latter. The dependence of surface tension γ on the cross-sectional area A of the molecule of adsorbate may be represented as

$$\gamma_0 - \gamma = b - aA \tag{1.2.44}$$

where b and a are constants. From Eq. (1.2.44), we have

$$\mathrm{d}\gamma = a\,\mathrm{d}A \tag{1.2.45}$$

Now

Number of molecules of gas adsorbed per unit area of adsorbent

$$= N_\mathrm{A}\Gamma = \frac{N_\mathrm{A}\upsilon}{\sigma V_\mathrm{m}}$$

Thus

Area of cross-section of a molecule of gas absorbed

$$A = \frac{1}{N_\mathrm{A}\Gamma} = \frac{\sigma V_\mathrm{m}}{N_\mathrm{A}\upsilon}$$

Hence, $$\mathrm{d}A = -\frac{\sigma V_\mathrm{m}}{N_\mathrm{A}\upsilon^2}\,\mathrm{d}\upsilon$$

Substituting $\mathrm{d}A$ in Eq. (1.2.45), we get

$$\mathrm{d}\gamma = a\mathrm{d}A = -\frac{a\sigma V_\mathrm{m}}{N_\mathrm{A}\upsilon^2}\,\mathrm{d}\upsilon \tag{1.2.46}$$

Substituting Eq. (1.2.46) in Eq. (1.2.43), we get

$$-\frac{a\sigma V_\mathrm{m}}{N_\mathrm{A}\upsilon^2}\,\mathrm{d}\upsilon = -\frac{\upsilon RT}{\sigma V_\mathrm{m}}\,\mathrm{d}\ln(p/p^\circ)$$

or $$\frac{a\sigma^2 V_\mathrm{m}^2}{N_\mathrm{A}RT}\,\frac{\mathrm{d}\upsilon}{\upsilon^3} = \mathrm{d}\ln(p/p^\circ)$$

Integrating the above expression, we have

$$-\frac{a\sigma^2 V_\mathrm{m}^2}{2N_\mathrm{A}RT}\,\frac{1}{\upsilon^2} + I = \ln(p/p^\circ) \tag{1.2.47}$$

where I is a constant of integration. Thus, if $\ln(p/p^\circ)$ is plotted against $1/\upsilon^2$, we get a straight line with slope equal to $(-a\sigma^2 V_\mathrm{m}^2/2N_\mathrm{A}RT)$.

Surface Area of Adsorbent by Harkins and Jura Method

According to Eq. (1.2.47), the slope of the graph of log $(p/p°)$ versus $1/\upsilon^2$ is given by

$$\text{slope} = -\frac{a\sigma^2 V_{\mathrm{m}}^2}{2N_{\mathrm{A}}RT}\,\frac{1}{2.303}$$

Hence, $$\sigma^2 = \left(\frac{2 \times 2.303 \times N_{\mathrm{A}}RT}{a\,V_{\mathrm{m}}^2}\right)(-\text{ slope})$$

or $$\sigma = \left(\frac{2 \times 2.303 \times N_{\mathrm{A}}RT}{a\,V_{\mathrm{m}}^2}\right)^{1/2}(-\text{ slope})^{1/2}$$

$$= k_1\,(-\text{ slope})^{1/2} \qquad (1.2.48)$$

where k_1 is a constant and is equal to $(2 \times 2.303 \times N_{\mathrm{A}}RT/aV_{\mathrm{m}}^2)^{1/2}$. For area in square metre per gram of adsorbent, k_1 is equal to $4.06 \times 10^6\ \mathrm{m}^{-1}$ for nitrogen at −195.8 °C.