

<b>Subject</b>	<b>Chemistry</b>
<b>Paper No and Title</b>	<b>10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)</b>
<b>Module No and Title</b>	<b>23: Surface area of adsorbent and BET adsorption isotherm</b>
<b>Module Tag</b>	<b>CHE_P10_M23</b>

<b>Principal Investigator</b>		<b>Co- Principal Investigator and Technical Coordinator</b>
<b>Prof A.K.Bakhshi</b> Sir Shankar Lal Professor, Department of Chemistry, University of Delhi, Delhi		<b>Dr Vimal Rarh</b> Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi  <i>Specialised in : e-Learning and Educational            Technologies</i>
<b>Paper Coordinator</b>	<b>Content Writer</b>	<b>Reviewer</b>
<b>Prof A.K.Bakhshi</b> Sir Shankar Lal Professor, Department of Chemistry, University of Delhi, Delhi	<b>Dr. Deepika Kansal</b> Associate Professor, P. G. Govt. College for Girls, Punjab University, Chandigarh <b>Dr. Aditi Gupta</b> Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi, Delhi	<b>Prof A.K.Bakhshi</b> Sir Shankar Lal Professor, Department of Chemistry, University of Delhi, Delhi
<b>Anchor Institute : SGTB Khalsa College, University of Delhi</b>		

**CHEMISTRY**
**Paper No.10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)**
**Module No. 23: Surface area of adsorbent and BET adsorption isotherm**

## TABLE OF CONTENTS

1. Learning outcomes
2. Determination of surface area of adsorbent
3. Multilayer adsorption
  - 3.1 BET adsorption isotherm
  - 3.2 Derivation of BET adsorption isotherm
  - 3.3 Physical significance of constant C
  - 3.4 Explanation of different types of adsorption isotherms
  - 3.5 Advantages and Disadvantages
4. Determination of thermodynamic parameters of adsorption process
5. Summary

**CHEMISTRY**

**Paper No.10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics**

**Module No. 23: Surface area of adsorbent and BET adsorption isotherm**

## 1. Learning outcomes

After studying this module, you shall be able to:

- Determine the total surface area of an adsorbent
- Know about multilayer adsorption and BET adsorption isotherm
- Know how BET equation explains various adsorption isotherms
- Know how to determine the thermodynamic parameters of adsorption process

## 2. Determination of surface area of adsorbent

We know that volume occupied by one mole of an idea gas = 22.414 dm<sup>3</sup>

Or, number of molecules occupying 22.414 dm<sup>3</sup> volume =  $6.023 \times 10^{23}$

Therefore, number of molecules, N, corresponding to  $V_{mono} = \frac{V_{mono}}{22.414} \times 6.023 \times 10^{23}$  (1)

The total surface area of the adsorbent can be obtained if we multiply the above number N by the area of cross section of a single molecule, A. The latter can be obtained from the density measurements.

Assuming close packing with negligible void volume, the volume,  $v$ , occupied by a single molecule can be obtained from density,  $\rho$ , as follows:

$$\rho = \frac{M}{v N_A} \quad (2)$$

where,  $N_A$  = Avogadro's constant,  $6.023 \times 10^{23}$

or, 
$$v = \frac{M}{\rho N_A} \quad (3)$$

**CHEMISTRY**

**Paper No.10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)**

**Module No. 23: Surface area of adsorbent and BET adsorption isotherm**

If the molecule is assumed to be spherical with radius,  $r$ , then,

$$v = \frac{4}{3} \pi r^3 = \frac{M}{\rho N_A} \quad (4)$$

or, 
$$r = \left[ \frac{3}{4\pi} \frac{M}{\rho N_A} \right]^{1/3} \quad (5)$$

Therefore, 
$$A = \pi r^2 = \left[ \frac{3}{4\pi} \frac{M}{\rho N_A} \right]^{2/3} \quad (6)$$

However, the area of cross-section obtained from the above relation (6) is not accurate.

This is because, we have made use of the following approximations:

- We have assumed a close packing, since we do not have the data on the exact nature of packing of the adsorbate molecules on the surface of the adsorbent
- The void volume is neglected
- The adsorbate molecules are assumed to be perfectly spherical, with no distortions

The results can be significantly improved if we have detailed knowledge about the crystal structure.

Emmett and Brunauer made use of the following approximation to calculate the area of cross-section of a single molecule: 'the average cross section of the adsorbate molecules is the same as that of the molecules in the corresponding plane of closest packing in the solidified gas'

$$A = 4 \times 0.86 \times \left[ \frac{1}{4\sqrt{2}} \frac{M}{\rho N_A} \right]^{2/3} \quad (7)$$

Once the value of the area of cross-section of a single molecule is obtained,

The total surface area of the adsorbent =  $A \times N$  (8)

### 3. Multilayer adsorption

In the Langmuir adsorption, a monolayer formation of adsorbate gas molecules on the surface of the adsorbent is assumed at low pressure and moderately high temperatures. This assumption, however, is not valid at high pressures and low temperatures. When the gas pressure is high, greater number of adsorbate molecules strike unit surface area of the adsorbent in unit time. And when the temperatures are low, the thermal energies of the gas molecules are low, insufficient to overcome the Van der waals forces of attraction between the adsorbed molecules and the surrounding unadsorbed molecules. As a result of these two effects, the solid adsorbent holds on many layers of gas molecules on to its surface, resulting into what is called as a multilayer adsorption.

Multilayer adsorption is especially prevalent at gas pressures close to gas saturation pressure, at a particular temperature. Therefore, what we observe is not only type I adsorption isotherm, but also type II, III, IV and V adsorption isotherms.

One of the most successful theories to explain multilayer adsorption is the BET adsorption isotherm.

#### 3.1 BET adsorption isotherm

In 1938, Brunauer, Emmett and Teller gave the true picture of adsorption as being multilayer in nature.

The various postulates of BET adsorption isotherm are as follows:

- 1) The adsorption involves the formation of multimolecular layer of adsorbate molecules on the surface of the solid adsorbent, unlike in Langmuir adsorption, whereby only unimolecular layer formation takes place.

The multilayer adsorption takes place in the following manner:



Vapor + Double complex

---→ Triple complex

--→ --→ --→ Multilayer formation

- 2) The Langmuir concept of fixed number of adsorption sites being available on the surface of solid adsorbent, applies to each layer.
- 3) The interactions between the adsorbate molecules in the adsorbed layer are neglected.
- 4) For the formation of single complexes, the assumptions made by Langmuir model still hold true.
- 5) The concept of dynamic equilibrium adopted by Langmuir holds in each layer holds valid, i.e., the rate of desorption from the first layer is equal to the rate of adsorption in the preceding layer.
- 6) The forces that produce condensation are responsible for binding energy in the successive layers
- 7) The heat of adsorption in the first layer is constant. After the formation of first layer, the heat of adsorption is assumed to be equal to the latent heat of condensation of vapors.

### 3.2 Derivation of BET adsorption isotherm

On the basis of above postulates, Brunauer, Emmett and Teller derived the BET equation as follows.

We can represent the formation of multilayer of gas molecules on the adsorbent surface with the help of following equilibrium equations:



Where M is the unadsorbed gas molecules, S is the active site on the adsorbent surface, MS is the single complex formed, M<sub>2</sub>S is the double complex formed, and so on.

The equilibrium constants for the above equilibrium reactions can be written as follows:

$$\begin{array}{l}
 K'_1 = \frac{[MS]}{[M][S]} \\
 K'_2 = \frac{[M_2S]}{[M][MS]} \\
 K'_3 = \frac{[M_3S]}{[M][M_2S]} \\
 \dots\dots\dots, \text{ and so on}
 \end{array}
 \quad \left. \vphantom{\begin{array}{l} K'_1 \\ K'_2 \\ K'_3 \\ \dots \end{array}} \right\} \quad (10)$$

Now,

[M] ∞ pressure of the gas, p

[S] ∞ fraction of freely available adsorbent surface, θ<sub>0</sub>

[MS] ∞ fraction of adsorbent surface having unimolecular coverage, θ<sub>1</sub>

[M<sub>2</sub>S] ∞ fraction of adsorbent surface having bimolecular coverage, θ<sub>2</sub>

-----, and so on

Substituting for above proportionalities in equations 10, we get,

$$\left. \begin{aligned}
 K_1 &= \frac{\theta_1}{p\theta_0} \\
 K_2 &= \frac{\theta_2}{p\theta_1} \\
 K_3 &= \frac{\theta_3}{p\theta_2} \\
 &\dots\dots\dots, \text{ and so on}
 \end{aligned} \right\} \quad (11)$$

The value of  $K_1$  is usually very large as compared to other equilibrium constants. This is due to the fact that with increase in the distance from the adsorbent surface, the interaction between the gas molecules and solid adsorbent decreases. Therefore, the constants,  $K_2, K_3, K_4, \dots$ etc., although with different numerical values, will be much smaller than the constant  $K_1$ . In other words, the difference between these equilibrium constants will be much smaller as compared to difference between  $K_1$  and  $K_2$ .

Therefore, we can have the following assumption:

$$K_2 \approx K_3 \approx K_4 \approx \dots \approx K_L \quad (12)$$

where,  $K_L$  is the equilibrium constant corresponding to the saturated vapor-liquid equilibrium, given as,



$$K_L = \frac{1}{p_0} \quad (13)$$

Using the approximation from equation (12), the various equilibria in equation (11) can be written as:



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

(14)

Rearranging the above expressions and making use of equation (13), we get,

$$\left. \begin{aligned} \theta_1 &= K_1 p \theta_0 \\ \theta_2 &= K_L p \theta_1 = \left(\frac{1}{p_0}\right) p (K_1 p \theta_0) = K_1 p \left(\frac{p}{p_0}\right) \theta_0 \\ \theta_3 &= K_L p \theta_2 = \left(\frac{1}{p_0}\right) p \left(K_1 p \frac{p}{p_0} \theta_0\right) = K_1 p \left(\frac{p}{p_0}\right)^2 \theta_0 \\ &\dots\dots\dots, \text{ and so on} \end{aligned} \right\} \quad (15)$$

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

$$\theta_{\text{total}} = \theta_0 + \theta_1 + \theta_2 + \dots = 1 \quad (16)$$

Substituting equations (15) in equation (16), we get,

$$\begin{aligned} \theta_{\text{total}} &= (\theta_0 + K_1 p \theta_0 + K_1 p \left(\frac{p}{p_0}\right) \theta_0 + K_1 p \left(\frac{p}{p_0}\right)^2 \theta_0 + \dots) = 1 \\ &= \theta_0 \left[ 1 + K_1 p \left\{ 1 + \left(\frac{p}{p_0}\right) + \left(\frac{p}{p_0}\right)^2 + \dots \right\} \right] = 1 \end{aligned} \quad (17)$$

Since  $p/p_0$  is  $\leq 1$ , the expression within the curly brackets of above equation 9, can be written as

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

(18)

Substituting equation (18) in equation (17), we get,

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

or  $\theta_0 = \frac{1}{1 + K_1 p / \{1 - (p/p_0)\}} = \frac{1 - p/p_0}{1 + K_1 p - p/p_0}$  (19)

The total volume of the adsorbed gas (corrected to STP) is given by

$$V_{\text{total}} = V_{\text{mono}} (\theta_1 + 2\theta_2 + 3\theta_3 + \dots)$$

(20)

where,  $V_{\text{mono}}$  is the volume required for the monolayer adsorption

Substituting the values of  $\theta_1, \theta_2, \theta_3, \dots$  from equation (15), we get,

$$V_{\text{total}} = V_{\text{mono}} K_1 p \theta_0 \left[1 + 2 \left(\frac{p}{p_0}\right) + 3 \left(\frac{p}{p_0}\right)^2 + \dots\right]$$

(21)

The expression within the bracket of above equation (21) is a derivative of the expression within the curly bracket of equation (17). Thus in view of equation (18), we get,

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

(22)

Substituting equation (22) in equation (21), we get,

$$V_{\text{total}} = V_{\text{mono}} \frac{K_1 p \theta_0}{(1 - p/p_0)^2} \quad (23)$$

Substituting the value of  $\theta_0$  from equation (19), we get,

$$V_{\text{total}} = \frac{V_{\text{mono}} K_1 p}{(1 - p/p_0)(1 + K_1 p - p/p_0)} \quad (24)$$

The pressure  $p$  in the above equation (24) may be replaced in terms of relative pressure  $p/p_0$  as shown:

$$p = p_0 \frac{p}{p_0} = \frac{1}{K_L} \left( \frac{p}{p_0} \right) \quad (25)$$

The substitution of equation (25) in equation (24) gives,

$$V_{\text{total}} = \frac{V_{\text{mono}} (K_1 / K_L) (p/p_0)}{1 - (p/p_0) \{ (K_1 / K_L) (p/p_0) - (p/p_0) \}} \quad (26)$$

The ratio  $K_1/K_L$  is designated as constant  $C$ .

Therefore we get,

$$V_{\text{total}} = \frac{V_{\text{mono}} C (p/p_0)}{1 - (p/p_0) \{ 1 + C(p/p_0) - (p/p_0) \}} \quad (27)$$

Equation (27) is the required BET equation for multilayer adsorption of gaseous molecules on adsorbent surface.

Equation (27) can be written as

$$\frac{p}{V_{total}(p/p_o)} = \frac{1}{V_{mono}C} + \frac{C-1}{V_{mono}C} \frac{p}{p_o} \quad (28)$$

where,

$V_{total}$  = Volume of gas adsorbed under given conditions of temperature and pressure, reduced to standard conditions

$V_{mono}$  = Volume of gas required to form a monolayer on the adsorbent surface, reduced to standard conditions

$C$  = Characteristic constant for a particular adsorbate-adsorbent system

The validity of BET adsorption isotherm can be proved by plotting a graph between

$\frac{P}{V_{total}(P_o-P)}$  and  $\frac{P}{P_o}$  (Fig. 1)

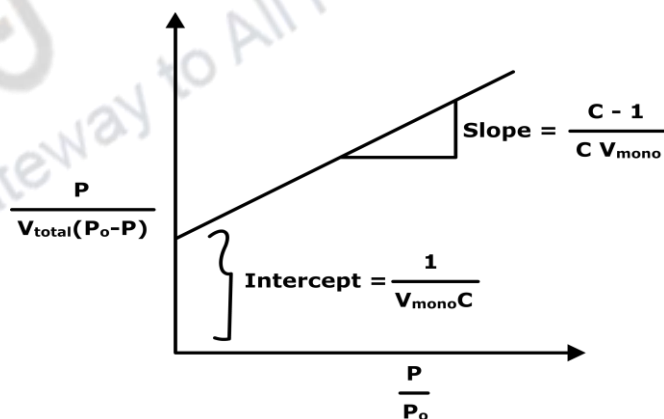


Fig. 1: BET isotherm

**CHEMISTRY**

**Paper No.10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)**

**Module No. 23: Surface area of adsorbent and BET adsorption isotherm**

A straight line plot with slope,  $\frac{C-1}{C V_{mono}}$ , and intercept,  $\frac{1}{V_{mono} C}$ , validates BET adsorption isotherm.

The two constants  $V_{mono}$  and  $C$ , can be therefore evaluated.

After  $V_{mono}$  is known, the surface area of the adsorbent can also be evaluated as discussed above.

The plot between  $\frac{P}{V_{total} (P_0 - P)}$  and  $\frac{P}{P_0}$  gives a straight line till the gas pressure is less than one-third the gas saturation pressure. It is observed that at high pressures, deviations are obtained.

### 3.3 Physical significance of constant C

The relation between the standard free energy change for adsorption  $\Delta G^\circ$  and the adsorption equilibrium constant  $K_1^\circ$  can be written as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln k_1^\circ$$

$$\text{Therefore, } \ln k_1^\circ = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\text{or } k_1^\circ = \exp \left( \frac{\Delta S_{ads}^\circ}{R} - \frac{\Delta H_{ads}^\circ}{RT} \right)$$

$$k_1^\circ = \left( \exp \left( \frac{\Delta_{ads} S^\circ}{R} \right) \right) \left( \exp \left( \frac{-\Delta_{ads} H^\circ}{RT} \right) \right) \quad (29)$$

Where,  $\Delta_{ads} S^\circ$  and  $\Delta_{ads} H^\circ$  are the standard entropy and standard enthalpy change for adsorption, respectively, for monolayer formation of gas molecules on adsorbent surface.

$$k_1^\circ = g_1 \exp\left(\frac{-\Delta_{\text{ads}}H_1^\circ}{RT}\right) = g_1 \exp\left(\frac{\Delta_{\text{des}}H_1^\circ}{RT}\right) \quad (30)$$

Where,  $g_1$  is the entropy factor and  $\Delta_{\text{des}}H_1^\circ$  is the standard enthalpy change for desorption for monolayer formation of gas molecules on adsorbent surface

We can write similar equations for equilibrium constant  $K_L$  as follows:

$$k_L^\circ = g_L \exp\left(\frac{-\Delta_{\text{con}}H_L^\circ}{RT}\right) = g_L \exp\left(\frac{\Delta_{\text{vap}}H_L^\circ}{RT}\right) \quad (31)$$

Where,  $g_L$  is the entropy factor

And  $\Delta_{\text{cond}}H_L^\circ$  is the standard enthalpy change for condensation of gas molecules on adsorbent surface,

$\Delta_{\text{vap}}H_L^\circ$  is the standard enthalpy change for vaporization of liquid adsorbed on adsorbent surface

The ratio between these two equilibrium constants gives the constant 'C' in the BET equation:

$$C = \frac{K_1^\circ}{K_L^\circ} = \frac{g_1 \exp(-\Delta_{\text{ads}}H_1^\circ / RT)}{g_L \exp(-\Delta_{\text{con}}H^\circ / RT)} = \frac{g_1 \exp(\Delta_{\text{des}}H_1^\circ / RT)}{g_L \exp(\Delta_{\text{vap}}H_L^\circ / RT)}$$

$$C \approx \exp \left[ \frac{(-\Delta_{\text{ads}}H_1^\circ) - (-\Delta_{\text{con}}H_L^\circ)}{RT} \right]$$

$$\text{or } \approx \exp \left[ \frac{\Delta_{\text{des}}H_1^\circ - \Delta_{\text{vap}}H_L^\circ}{RT} \right] \quad (32)$$

In simple term

$$C = e^{\left( \frac{E_1 - E_L}{RT} \right)}$$

where  $E_1$  = enthalpy of adsorption of gas in tint layer

where  $E_L$  = enthalpy of condensation of gas

$$E_1 - E_L = \text{net heat of adsorption} \quad (33)$$

### 3.4 Explanation of different types of adsorption isotherms

We have the BET equation from equation 28 is:

$$\frac{P}{V_{\text{total}} (P_o - P)} = \frac{1}{V_{\text{mono}} C} + \frac{C - 1}{C V_{\text{mono}}} \frac{P}{P_o}$$

Multiplying equation (28) throughout by  $P_o$

$$\frac{P P_o}{V_{\text{total}} (P_o - P)} = \frac{P_o}{V_{\text{mono}} C} + \frac{C - 1}{C V_{\text{mono}}}$$

$$\text{Now, } C = \frac{K_1}{K_L} \text{ and } K_L = \frac{1}{P_o} \quad (34)$$

$$\text{Thus, } C = K_1 P_o$$

Or, 
$$K_1 = \frac{C}{P_o} \quad (35)$$

Substituting this value of  $K_1 = \frac{C}{P_o}$  from equation (35) in the above equation (34), we get

$$\frac{P P_o}{V_{total} (P_o - P)} = \frac{1}{V_{mono} K_1} + \frac{C-1}{C V_{mono}} P \quad (36)$$

If we assume,

$$C \gg 1 \text{ and}$$

$P_o \gg P$ , then the above equation (36) gets modified to

$$\frac{P}{V_{total}} = \frac{1}{V_{mono} K_1} + \frac{P}{V_{mono}} \text{ which is the Langmuir equation}$$

Thus, under the assumptions,  $C \gg 1$  and  $P_o \gg P$ , BET equation can be reduced to the Langmuir adsorption equation. Under these circumstances, BET equation can satisfactorily explain the monolayer adsorption as in type I adsorption isotherm.

Type II adsorption isotherm is observed when  $C > 1$ , i.e.,  $\Delta_{des} H^{\circ}_1 > \Delta_{vap} H^{\circ}_L$ . Here the monolayer formation starts, it gets completed and then the multilayer formation starts.

Type III adsorption isotherm can be explained by the condition:  $C < 1$ , i.e.,  $\Delta_{des} H^{\circ}_1 < \Delta_{vap} H^{\circ}_L$ . Here, the multilayer formation starts even before the monolayer formation is complete.

**CHEMISTRY**

**Paper No.10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics**

**Module No. 23: Surface area of adsorbent and BET adsorption isotherm**



Type IV adsorption isotherm, which is a duplicate of type II adsorption isotherm, can again be explained by the condition  $\Delta_{\text{des}}H^{\circ}_1 > \Delta_{\text{vap}}H^{\circ}_L$ . In this, the adsorption reaches a saturation value much before the gas saturation pressure is attained. This is explained by the fact that, in addition to the multilayer formation taking place on the adsorbent surface, adsorption also takes place in capillary pores, cracks and crevices of the adsorbent.

In type V adsorption isotherm, the lower portion of the isotherm matches with that of type III adsorption isotherm. Therefore, this can be explained by the condition  $\Delta_{\text{des}}H^{\circ}_1 < \Delta_{\text{vap}}H^{\circ}_L$ . The isotherm at higher pressures matches with type IV isotherm, again indicating that adsorption reaches a saturation value much before the gas saturation pressure is attained. This can be explained by the fact that, capillary condensation takes place in addition to the multilayer formation on the adsorbent surface.

### 3.5 Limitations of BET isotherm

Although BET adsorption isotherm can successfully explain the different types of adsorption isotherms, yet it is associated with the following limitations:

- BET equation holds good when the ratio  $\frac{P}{P_0}$  lies between 0.05- 0.35. Out of this range, deviations from linearity set in
- An inherent assumption of BET isotherm is that the gas adsorbate has liquid properties. However, this is true only when the critical temperature is high. But permanent gases like hydrogen, oxygen, nitrogen, etc. have low critical temperatures

#### 4. Determination of thermodynamic parameters of adsorption process

We can derive the relations for change in the enthalpy, entropy and free energy on adsorption process as follows:

From the Langmuir equation, we have

$$k_1 = \frac{\theta}{1-\theta} \frac{1}{P} \quad (37)$$

In this equation, the equilibrium constant  $K_1$  is a function of temperature only.

The temperature dependence of  $K_1$  can be obtained by the Van't Hoff's equation:

$$\frac{\partial \ln K_1}{\partial T} = \frac{\Delta_{ad} H^\circ}{RT^2} \quad (38)$$

From equation (37), we get,

**At constant  $\theta$ ,  $k_1 P = \text{constant}$**

**$\ln k_1 + \ln P = \text{constant}$**

Differentiating with respect to T, at constant  $\theta$ , and using equation (38), we get,

$$\begin{aligned} \left[ \frac{d(\ln k_1)}{dt} \right]_{\theta} &= - \left[ \frac{d(\ln P/P^\circ)}{dt} \right]_{\theta} \\ \Rightarrow \left[ \frac{d(\ln P/P^\circ)}{dt} \right]_{\theta} &= - \left[ \frac{d(\ln k_1)}{dt} \right]_{\theta} = - \frac{\Delta_{ad} H^\circ}{RT^2} \\ \Rightarrow \frac{d(\ln P/P^\circ)}{dT} &= - \left[ \frac{\Delta_{ad} H^\circ}{RT^2} \right] \quad \text{or } d(\ln P/P^\circ) = \frac{-\Delta_{ad} H^\circ}{RT^2} dT \end{aligned}$$

$$\text{or Integrating } (\ln P/P^\circ) = \frac{\Delta_{ad} H^\circ}{RT} + \text{constant} \quad (39,40)$$

A plot between  $\ln (P/P^{\circ})$  vs  $1/T$  gives a straight line with a negative slope equal to  $\Delta H/R$  as shown in Fig. 2:

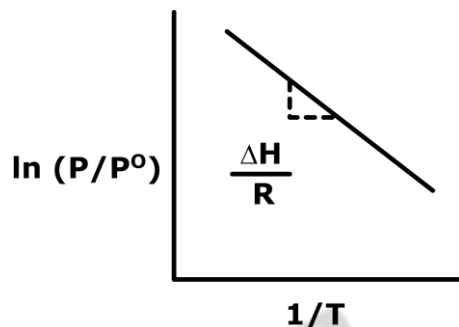


Fig. 2: A plot between  $\ln (P/P^{\circ})$  vs  $1/T$

The value of  $\Delta H$  obtained from the slope of the graph is called the isotheric enthalpy of adsorption.

Integrating equation (39) within limits, we get:

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{-\Delta H}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{ad}H}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \quad (41)$$

The change in free energy and entropy of adsorption can be calculated from the relations as follows:

$$\Delta_{ad}G^{\circ} = -RT \ln k_1^{\circ}$$

$$\Delta_{ad}S^{\circ} = \frac{\Delta_{ad}H^{\circ} - \Delta_{ad}G^{\circ}}{T} \quad (42)$$

## 5. Summary

- Total surface area of the adsorbent can be obtained if we multiply the number of molecules corresponding to  $V_{mono}$  by the area of cross section of a single molecule
- Brunauer, Emmett and Teller gave the true picture of adsorption as being multilayer in nature
- BET adsorption isotherm is based on certain postulates which gave the BET equation as

$$\frac{P}{V_{total} (P_o - P)} = \frac{1}{V_{mono} C} + \frac{C - 1}{C V_{mono}} \frac{P}{P_o}$$

- BET adsorption equation can successfully explain type I, II, III, IV and V isotherms. However, it is associated with certain limitations
- The thermodynamic parameters of adsorption process can be determined using the following relations:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\Delta_{ad}G^\circ = -RT \ln k_1^\circ$$

$$\Delta_{ad}S^\circ = \frac{\Delta_{ad}H^\circ - \Delta_{ad}G^\circ}{T}$$

**CHEMISTRY**

**Paper No.10: Physical Chemistry –III (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface Chemistry, Fast Kinetics)**

**Module No. 23: Surface area of adsorbent and BET adsorption isotherm**