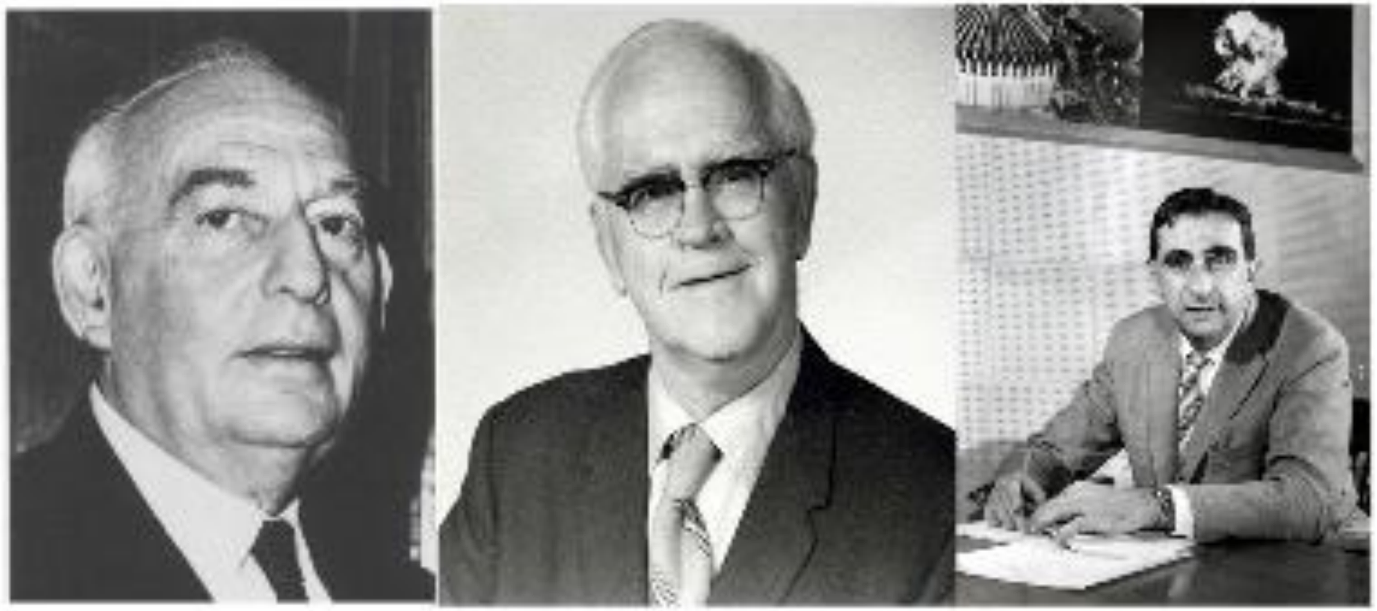
BET ADSORPTION ISOTHERM

- Brunauer–Emmett–Teller (BET) theory explains the physical adsorption of gas molecules on a solid surface.
- The BET theory applies to systems of multilayer adsorption.
- An important analysis technique for the measurement of the specific surface area of materials.



Stephen Brunauer **Paul Emmett** **Edward Teller**

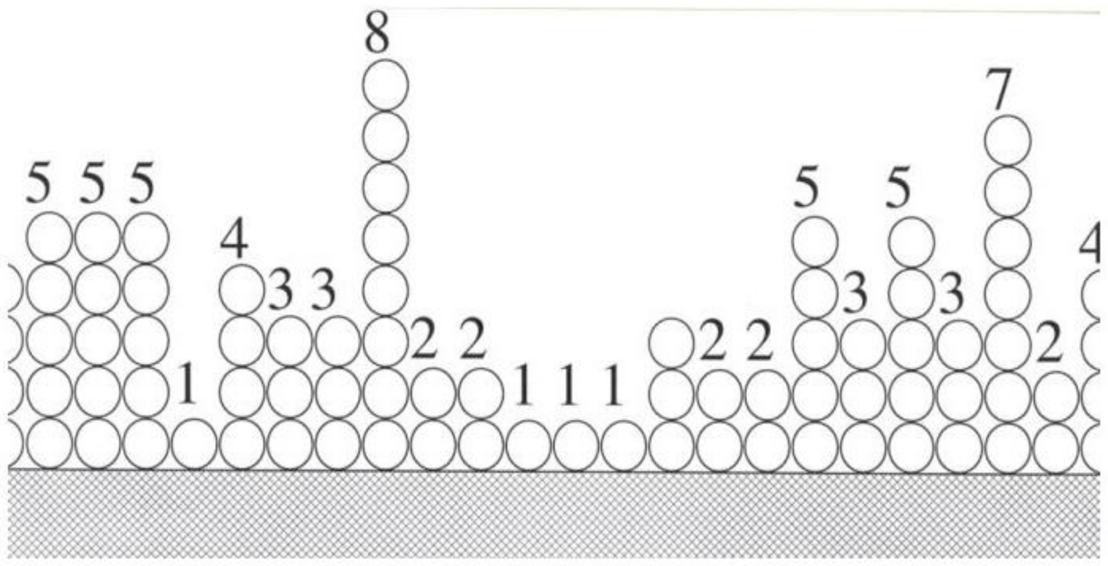
$$\frac{V}{V_m} = \frac{cx}{(1-x)\left[1+(c-1)\right]x}$$

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

ASSUMPTIONS OF BET THEORY

- The gas molecules undergo multilayer adsorption on solid surface.
- The principle of Langmuir theory can be applied to each layer.
- A dynamic equilibrium exists between successive layers. The rate of evaporation from a particular layer is equal to the rate of condensation of the preceding layer.
- The enthalpy of adsorption of the first layer (E_1) is a constant, whereas that of any layer above the first layer is the energy of liquefaction of the adsorbate (E_L)
- Condensation forces are the principal forces of attraction.

MODELLING OF ADSORPTION ACCORDING TO BET THEORY



S_0, S_0, S_2, S_3 ……S_i represent the surface area of the adsorbent covered by 0, 1, 2, 3 …..i layers of adsorbates.

Rate of condensation on the bare surface = a_1PS_0

Rate of evaporation from the first layer = $b_1S_1e^{-E_1/RT}$

$$a_1PS_0 = b_1S_1e^{-E_i/RT}$$

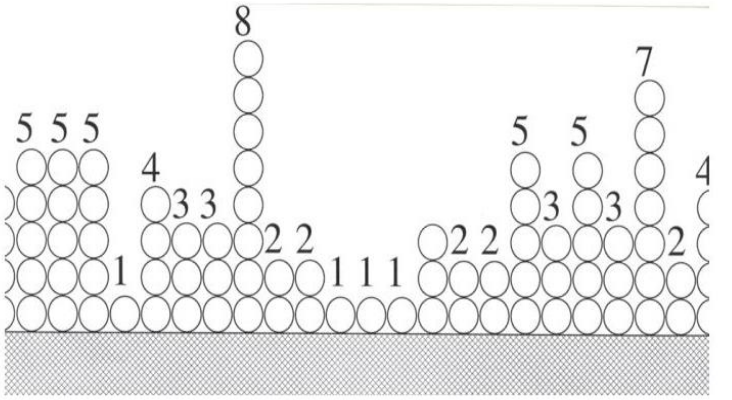
According to assumption (iii) of BET

$$a_2 P S_1 = b_2 S_2 e^{-E_2/RT}$$

$$a_3 P S_2 = b_3 S_3 e^{-E_3/RT}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$a_i P S_{i-1} = b_i S_i e^{-E_i/RT}$$



Total surface area of the adsorbent $A = \sum_{i=0}^{\infty} S_i$

Total volume of the adsorbed gas $V = V_0 \sum_{i=0}^{\infty} i S_i$

V_0 is the volume of the gas adsorbed on 1 cm^2 of the adsorbent surface monolayer coverage.

$$\frac{V}{A}=\frac{V_0\sum_{i=0}^{\propto} iS_i}{\sum_{i=0}^{\propto} S_i} \;\Rightarrow\; \frac{V}{AV_0}=\frac{\sum_{i=0}^{\propto} iS_i}{\sum_{i=0}^{\propto} S_i} \;\Rightarrow\; \frac{V}{V_m}=\frac{\sum_{i=0}^{\propto} iS_i}{\sum_{i=0}^{\propto} S_i}$$

V_m is the volume of the gas for monolayer coverage.

Approximations by Stephen Brunauer, Paul Emmett and Edward Teller made a couple of approximations

$$E_2=E_3=E_4.........=E_i=E_L$$

$$\frac{b_2}{a_2}=\frac{b_3}{a_3}=\frac{b_4}{a_4}=........=\frac{b_i}{a_i}=g$$

$$S_1 = \left(\frac{a_1}{b_1}\right) \cdot Pe^{E_1/RT} \cdot S_0$$

$$S_1 = yS_0$$

$$y = \left(\frac{a_1}{b_1}\right) \cdot Pe^{E_1/RT}$$

$$S_2 = \left(\frac{a_2}{b_2}\right) \cdot Pe^{E_2/RT} \cdot S_1$$

$$S_2 = \left(\frac{P}{g}\right) \cdot e^{E_L/RT} \cdot S_1$$

$$S_2 = x \cdot S_1$$

$$x = \left(\frac{P}{g}\right) \cdot e^{E_L/RT}$$

$$S_2 = x \cdot yS_0$$

Putting the value of S_1 in the equation for S_2,

$$a_1PS_0 = b_1S_1e^{-E_i/RT}$$

$$a_2PS_1 = b_2S_2e^{-E_2/RT}$$

$$a_3PS_2 = b_3S_3e^{-E_3/RT}$$

....

$$a_iPS_{i-1} = b_iS_ie^{-E_i/RT}$$

$$E_2 = E_3 = E_4 \ldots\ldots\ldots = E_i = E_L$$

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \frac{b_4}{a_4} = \ldots\ldots\ldots = \frac{b_i}{a_i} = g$$

$$S_3 = x \cdot S_2$$

$$S_3 = x \cdot x \cdot S_1 = x^2 \cdot S_1$$ by putting $S_2 = x \cdot yS_0$

$$S_3 = x^2 \cdot yS_0$$ by putting $S_1 = yS_0$

$$S_4 = x^3 \cdot yS_0$$

$$S_i = x^{i-1} \cdot yS_0$$

$$S_i = x^i \cdot c \cdot S_0$$

$$c = \frac{y}{x} = \frac{\left(\frac{a_1}{b_1}\right) \cdot Pe^{E_1/RT}}{\left(\frac{P}{g}\right) \cdot e^{E_L/RT}} = \left(\frac{a_1}{b_1}\right) \cdot ge^{(E_1 - E_L)/RT}$$

$$\frac{V}{V_m} = \frac{\sum_{i=0}^{\propto} iS_i}{\sum_{i=0}^{\propto} S_i}$$

$$\frac{V}{V_m} = \frac{\sum_{i=0}^{\propto} iS_i}{\sum_{i=0}^{\propto} S_i} = \frac{0 + \sum_{i=1}^{\propto} iS_i}{S_0 + \sum_{i=1}^{\propto} S_i}$$

$$S_i = x^i \cdot c \cdot S_0$$

$$\frac{V}{V_m} = \frac{\sum_{i=1}^{\propto} i \cdot x^i c S_0}{S_0 + \sum_{i=1}^{\propto} x^i c S_0} = \frac{cS_0 \sum_{i=1}^{\propto} i \cdot x^i}{S_0 + cS_0 \sum_{i=1}^{\propto} x^i}$$

$$\frac{V}{V_m}=\frac{c\sum_{i=1}^{\infty} i\cdot x^i}{1+c\sum_{i=1}^{\infty} x^i}$$

Applying the expressions for summations $\sum_{i=1}^{\infty} i\cdot x^i=\frac{x}{(1-x)^2}$ and $\sum_{i=1}^{\infty} x^i=\frac{x}{(1-x)}$

$$\frac{V}{V_m}=\frac{c\frac{x}{(1-x)^2}}{1+c\frac{x}{(1-x)}}=\frac{\frac{cx}{(1-x)}}{(1-x)+cx}=\frac{\frac{cx}{(1-x)}}{1+(c-1)x}$$

$$\frac{V}{V_m}=\frac{cx}{(1-x)\left[1+(c-1)x\right]}$$

$$\frac{x}{(1-x)V} = \frac{\left[1+(c-1)x\right]}{cV_m}$$

$$\frac{x}{(1-x)V} = \frac{1}{cV_m} + \frac{(c-1)}{cV_m}x$$

Different forms of BET equation

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

$$x = \frac{p}{p^0}$$

p is the equilibrium pressure of the gas over the surface

p^0 is the saturated vapour pressure of the gas at experimental conditions

BET equation and Langmuir equation:

$$\frac{V}{V_m}=\frac{cx}{(1-x)}\left[\frac{1-(n+1)x^n+nx^{n+1}}{1+(c-1)x-cx^{n+1}}\right]$$

$$\frac{x}{(1-x)V}=\frac{1}{cV_m}+\frac{(c-1)}{cV_m}x$$

For Langmuir adsorption isotherm, n=1, then

$$\frac{V}{V_m}=\frac{cx}{(1-x)}\left[\frac{1-2x+x^2}{1+(c-1)x-cx^2}\right]$$

$$\frac{V}{V_m}=\frac{cx}{(1-x)}\times\frac{(1-x)^2}{\left[1+(c-1)x-cx^2\right]}=\frac{cx}{(1-x)}\times\frac{(1-x)^2}{\left[1+cx-x-cx^2\right]}=\frac{cx}{(1-x)}\times\frac{(1-x)^2}{\left[(1-x)+cx(1-x)\right]}$$

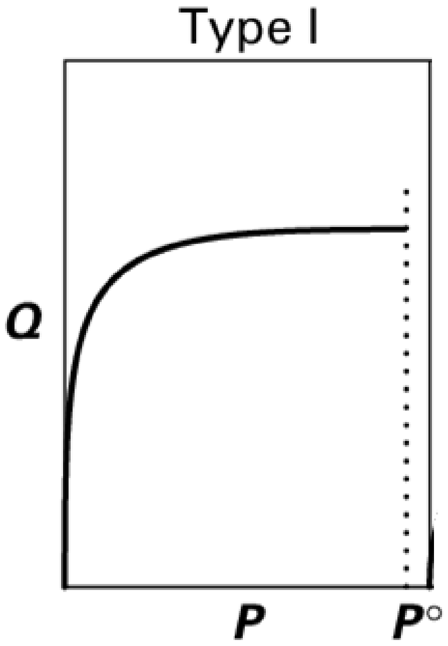
$$\frac{V}{V_m}=\frac{cx}{(1-x)}\times\frac{(1-x)^2}{(1-x)(1+cx)} \longrightarrow \frac{V}{V_m}=\frac{cx}{(1+cx)}$$

Explanations of Different isotherms by BET Theory:

i) When $E_1 >>> E_L$, the value of 'c' becomes very large.

The BET equation reduces to Langmuir isotherm for monolayer adsorption. Hence Type I isotherm is explained.

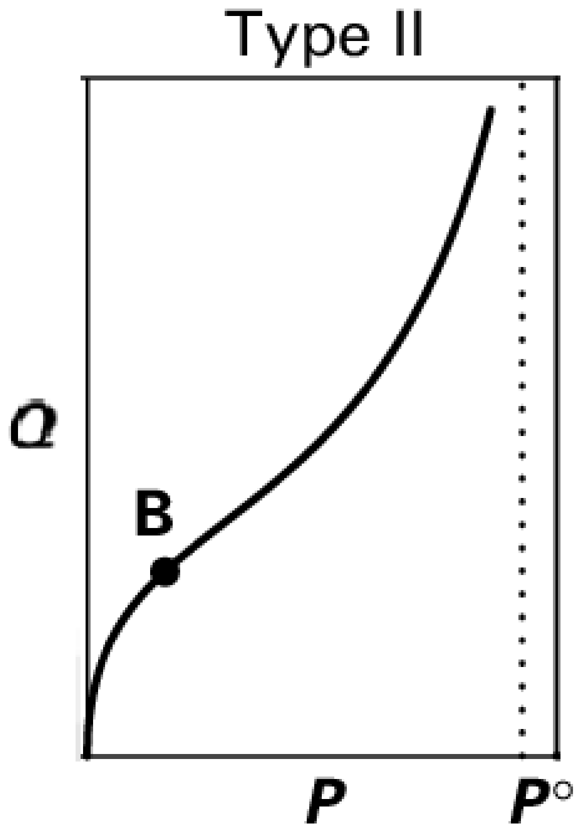
$$c = \left(\frac{a_1}{b_1}\right) \cdot g e^{(E_1 - E_L)/RT}$$



When $E_1 > E_L$, an intermediate value of ‘c’ is obtained.

This gives Type II adsorption isotherm indicating multilayer adsorption.

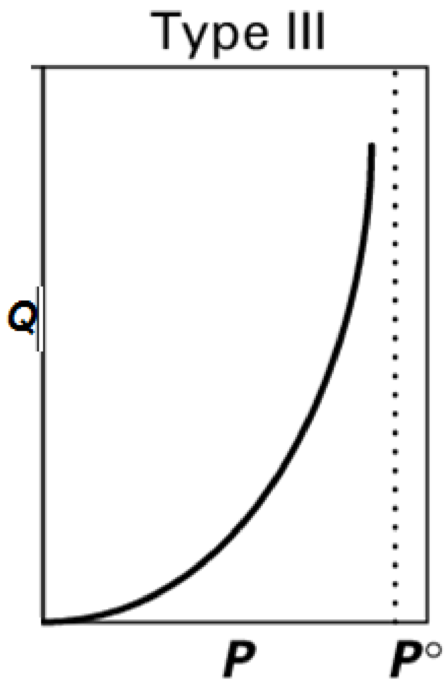
$$c = \left(\frac{a_1}{b_1}\right) \cdot g e^{(E_1 - E_L)/RT}$$



When $E_1 < E_L$, small values of 'c' are obtained.

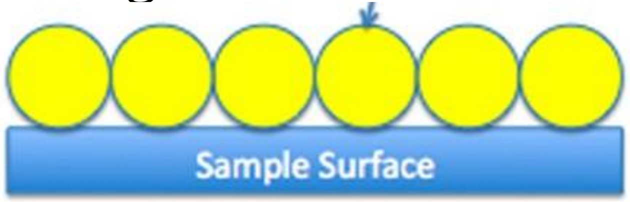
$$c = \left(\frac{a_1}{b_1}\right) \cdot g e^{(E_1 - E_L)/RT}$$

This results in Type III adsorption isotherm, where multilayer adsorption begins even before the completion of monolayer adsorption.



DETERMINATION OF SURFACE AREA

- Surface area of the adsorbent can be obtained by calculating the volume of monolayer coverage (V_m) using BET and Langmuir isotherms.



V_m - The volume of the gas at STP required to cover the whole surface of adsorbent by monolayer adsorption.

Number of gas molecules in 22.414 dm^3 of adsorbate gas at STP = N_0 (*Avogadro number*)

Number of gas molecules in V_m dm^3 of adsorbate gas at STP = $\frac{N_0}{22.414} \times V_m$

'S m^2 - The area of single adsorbate gas molecule occupying the surface of adsorbent

Area occupied by $\frac{N_0}{22.414} \times V_m$ number of particles = $\frac{N_0 \cdot V_m \cdot S}{22.414} m^2$

Surface area of the adsorbent = $\frac{N_0 \cdot V_m \cdot S}{22.414} m^2$

Nitrogen gas is generally used for finding out the surface area. The cross sectional area of nitrogen is usually taken as 1.62×10^{-19} m^2

The value of V_m can be obtained from graphical methods.

From Langmuir Isotherm

$$\theta = \frac{bP}{1+bP}$$

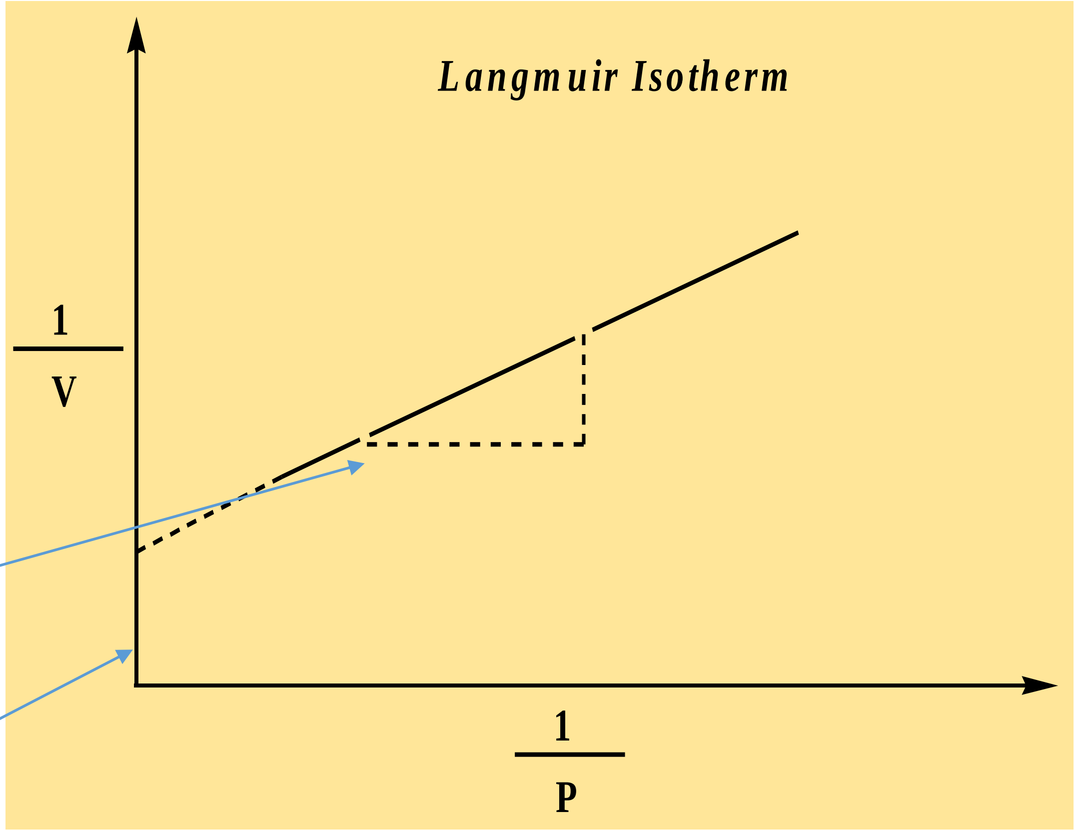
$$\frac{1}{\theta} = \frac{1}{bP} + 1$$

$$\theta = \frac{V}{V_m}$$

$$\frac{V_m}{V} = \frac{1}{bP} + 1$$

$$\frac{1}{V} = \frac{1}{bPV_m} + \frac{1}{V_m}$$

Graph between $\left(\frac{1}{V}\right)$ and $\left(\frac{1}{P}\right)$



$$\text{Slope} == \frac{1}{bV_m}$$

$$\text{Inercept} = \frac{1}{V_m}$$

From BET Isotherm

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

Plot a graph between $\dfrac{P}{V\left(P^0 - P\right)}$ and $\dfrac{P}{P^0}$

$$\text{Slope} = \frac{\left(c-1\right)}{cV_m}$$

$$\text{Inercept} = \frac{1}{cV_m}$$