Module 5: "Adsoption"

Lecture 26: ""

The Lecture Contains:

- BET (Brunauer Emmet Teller) Adsorption Isotherm
  - Assumptions in the BET theory
  - Practically useful form
  - Drawbacks of BET adsorption theory
- Application in Surface Phenomenon
- Reference

Previous Next

BET (Brunauer Emmet Teller) Adsorption Isotherm

Stephen Brunauer, Paul Emmet and Edward Teller published this theory in 1938. It is a theory for multi-layer physisorption and is of profound significance in the development of this field.

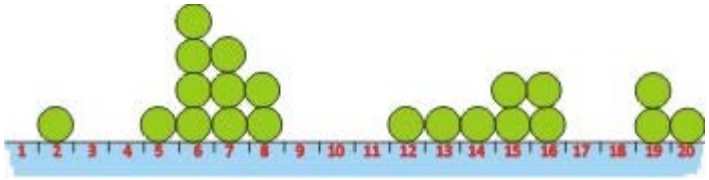

Fig. 7.7: Active sites in BET adsorption

To derive the BET adsorption isotherm equation let us propose the following:

Consider the surface of adsorbent to be made up of N_T sites (in the above figure N_T=20)

Let number of sites which have adsorbed 0 molecules be = n_0 (in the above figure n_0= 8; viz. site number 1, 3, 4, 9, 10, 11, 17, 18)

Let number of sites which have adsorbed 1 molecule be = n_1 (in the above figure n_1 = 6; viz. sites number 2, 5, 12, 13, 14, 20)

Let number of sites which have adsorbed 2 molecules be = n_2 (in the above figure n_2 = 4; viz. sites number 8, 15, 16, 19)

……..
…….. (and so on)
……..

Let number of sites which have adsorbed i molecules be = n_i
Therefore, total number of sites N_T has to be $N_T = \sum_{i=0}^{\infty} n_i$
In the above example it can be verified that 20 = 8 + 6 + 4 + 1 + 1 $(n_0 + n_1 + n_2 + n_3 + n_4)$
Also it is easy to note that the total number of molecules adsorbed N is given by

$$N = \sum_{i=0}^{\infty} i.n_i \qquad (7.7)$$

In the above figure N = 0*8 + 1*6 +2*4 + 3*1 + 4*1 = 21 molecules (which can be verified by counting)
NOTE: Here, for mathematical completeness and without loss of generality we assume that infinite molecules can be adsorbed on one site though practically it is not possible. Hence, the summation goes upto infinity.

Previous Next

Assumptions in the BET theory

- Multilayer adsorption is possible. However, owing to the influence of the adsorbent, the van der Waals forces on the surface of the adsorbent will be stronger than the van der Waals forces between molecules of the gas phase. So the forces of adsorption are much higher for the first layer and constant for the subsequent layers. This implies that the heat of adsorption of the 1st layer is greater than that of the 2nd and higher layers.
- There is again no lateral interaction as in the case of Langmuir.
- The surface in homogeneous

According to the BET theory

- At equilibrium the rate of adsorption is equal to the rate of desorption.
- The rate of adsorption of the ith layer is proportional to the number of sites in the lower $(i-1)^{th}$ layer and the gas phase pressure.
- The rate of desorption from the ith layer is proportional to the number of sites occupied by the ith layer but not occupied by molecules of higher layers (i.e there should be only i molecules on that site).

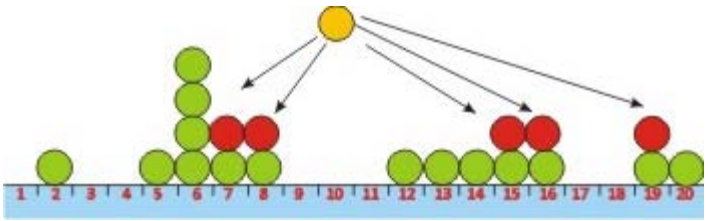

Fig. 7.8: BET theory

Previous Next

For instance, to form a layer i =3, the molecule in gas phase have sites only with i=2 molecules available for adsorption. Hence the rate for i=3 is proportional to number of sites having i=2 molecules.

At equilibrium,

Rate of formation of ith layer = Rate of destruction of ith layer

What are the ways in which i^{th} layer can be formed??

- If adsorption takes place on $(i-1)^{th}$ layer – Rate = $(k_a)_i n_{i-1} p$
- If desorption takes place on $(i+1)^{th}$ layer – Rate = $(k_d)_{i+1} n_{i+1}$

Assume rate constant for adsorption is k_a and for desorption is k_d

What are the ways in which an ith layer can be destroyed??

- Adsorption takes place on the ith layer – Rate = $(k_a)_{i+1} n_i p$
- Desorption takes place from the ith layer – Rate = $(k_d)_i n_i$

Previous Next

Therefore, equating the rates for formation and destruction of ith layer we get

$$(k_a)_i n_{i-1} p + (k_d)_{i+1} n_{i+1} = (k_a)_{i+1} n_i p + (k_d)_i n_i \qquad (7.9)$$

Write this equation for all the layers and then add

$$(k_a)_1 n_0 p + (k_d)_2 n_2 = (k_a)_2 n_1 p + (k_d)_1 n_1$$

$$(k_a)_2 n_1 p + (k_d)_3 n_3 = (k_a)_3 n_2 p + (k_d)_2 n_2$$

$$(k_a)_3 n_2 p + (k_d)_4 n_4 = (k_a)_4 n_3 p + (k_d)_3 n_3$$

.....

.....

$$(k_d)_{i+1} n_{i+1} = (k_a)_{i+1} n_i p \qquad (7.9)$$

$n_{i+1} = x.n_i$ where, $x = \frac{(k_a)_{i+1}}{(k_d)_{i+1}} p$

However, as mentioned above according to the BET theory the forces of adsorption are much greater for the very first layer and then constant afterwards. Hence, to compensate for that we multiply by an extra constant c for the i=0 equation.

$$n_1 = c.x.n_0 \qquad (7.10)$$

Previous Next

From the second layer onwards, the forces are almost of the same magnitude which implies that

$$\frac{(k_a)_{i+1}}{(k_d)_{i+1}} = \frac{k_a}{k_d} \tag{7.11}$$

Also, for a liquid or condensed phase where bulk saturation takes place,

$k_a p_0 = k_d$ where p_0 is the saturated vapour pressure of the adsorbate phase.

Therefore, from the above arguments,

$$x = \frac{k_a}{k_d} p = \frac{p}{p_0} \tag{7.12}$$

Now, all the physical concepts being in place we now use some simple mathematics to manipulate the above equations and to arrive at the final BET isotherm

$$n_i = x.n_{i-1} = x^2.n_{i-2} = x^3.n_{i-3} = \cdots = x^{i-1}.n_1 = c.x^i.n_0$$

$$\therefore\ n_i = c.x^i.n_0 \tag{7.13}$$

Now we know that the total number of molecules adsorbed N is given by

$$N = \sum_{i=0}^{\infty} i.n_i = cn_0 \sum_{i=0}^{\infty} i.x^i = cn_0 x \left(\frac{d}{dx}\sum_{i=1}^{\infty} x^i\right) \tag{7.14}$$

Also the total number of sites NT is given by

$$N_T = \sum_{i=0}^{\infty} n_i = n_0 + \sum_{i=1}^{\infty} n_i = n_0 + c.n_0 \sum_{i=1}^{\infty} x^i = n_0\left(1 + c\sum_{i=1}^{\infty} x^i\right) \tag{7.15}$$

It is obvious that x < 1 as p <p_0 Therefore, the sum of the infinite series is given by

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x} \tag{7.16}$$

And therefore,

$$\frac{d}{dx}\sum_{i=1}^{\infty} x^i = \frac{d}{dx}\left(\frac{x}{1-x}\right) = \frac{1}{(1-x)^2} \tag{7.17}$$

Thus, substituting above expressions for N and N_T

$$N = \frac{c.n_0.x}{(1-x)^2}$$

$$N_T = n_0\left(1 + \frac{c.x}{1-x}\right) \tag{7.18}$$

The total number of sites N_T is proportional to the monolayer volume v_m which is the volume of gas adsorbed when the entire surface is covered with a complete monolayer.

Also, total number of adsorbed molecules N is proportional to the volume v of the adsorbed molecules.

Previous Next

Hence,

$$\frac{N}{N_T} = \frac{v}{v_m} = \frac{\frac{c.n_0.x}{(1-x)^2}}{n_0\left(1+\frac{c.x}{1-x}\right)} = \frac{c.x}{(1-x).(1-x+c.x)}$$

$$\frac{v}{v_m} = \frac{c.x}{(1-x).(1-x+c.x)}$$

This is the equation for BET adsorption isotherm. (7.19)

It has two constants v_m and c. The constant c is related to the ratio of heats of adsorptions for the first layer and second layer. (Since according to BET theory the heat of adsorption for 1st layer is large compared to subsequent layers) Since heats of adsorption is sort of a potential or activation barrier it follows Arrhenius equation

$$\therefore c \propto \exp\left(\frac{q_1-q_2}{RT}\right) \quad (7.20)$$

The authors of the BET theory assumed the constant of proportionality to be approximately one.

Hence,

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Previous Next

Practically useful form

The BET equation is usually linearized by rearranging the equation as follows

$$\frac{1}{v(1-x)} = \frac{1}{v_m} + \frac{1}{v_m.c}\frac{1-x}{x} \qquad (7.21)$$

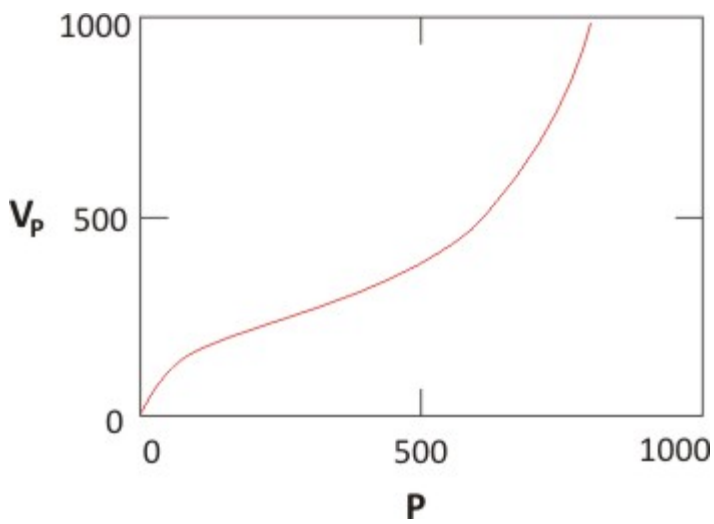
Plotting of $\frac{1}{v(1-x)}$ vs $\frac{1-x}{x}$ gives a straight line whose slope and intercept can be used to find the values of c and v_m . This can be used to calculate the surface area and the heats of adsorption.

NOTE: *An important point to note here is as* $v \to \infty$ *x goes to 1, which implies* $x = p/p_o$ *goes to 1 i.e.* $p \to p_0$ *where* p_0 *is the equilibrium vapour pressure where condensation begins on the surface.*

$$\therefore 1 = x = \frac{k_a}{k_d}p_0 \quad \to \quad p_0 = \frac{k_d}{k_a} \qquad (7.22)$$

NOTE: For large c, x can be neglected and the BET equation becomes

$\frac{v}{v_m} = \frac{cx}{1+cx}$ which is similar to the Langmuir equation.



Drawbacks of BET adsorption theory

- Surface is assumed to be homogenous which the case is not always.
- Lateral interaction between the adsorbed molecules in neglected.
- Heat of adsorption from 2nd layer onwards to be equal to subsequent layers which is not usually true.

Previous Next

Application in Surface Phenomenon

Now consider a normal surface with a drop placed on it. If adsorption takes place on this surface, the internal contact angle θ also changes. This phenomenon is called autophobicity.

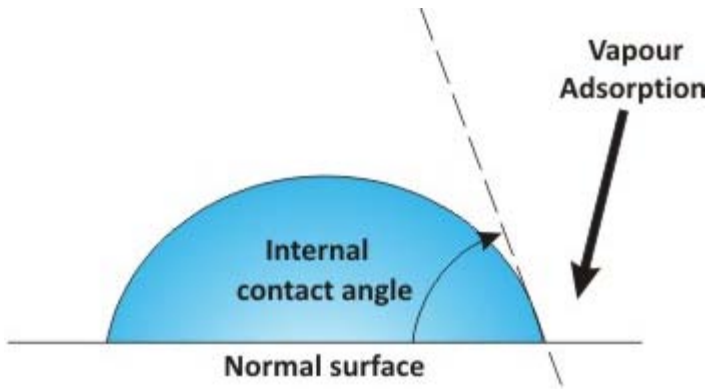


Fig. 7.10: Drop on a surface with adsorption

Now we would like to calculate the surface energy of the above system

We know that

$$-d\gamma = RT\Gamma d(lnP)$$

$$-d\gamma = RT\left(\frac{n}{A}\right)(lnP)$$

$$\therefore\ -d\gamma = \frac{RT}{A_{sp}}\frac{n}{W}(lnP) \qquad (7.23)$$

Where

γ = surface tension

R= gas constant
T= Temperature
n= Number of moles of gas / area
W= weight of an adsorbed particle
A_{sp} = Specific surface area

Previous Next

The previous equation can be integrated to find the energy

$$-\int_{\gamma_0}^{\gamma} d\gamma = \int_0^P \frac{RT}{A_{sp}}\left(\frac{n}{W}\right) d(lnP)$$

$$\gamma_0 - \gamma = \pi = \frac{RT}{A_{sp}}\int_0^P \left(\frac{n}{W}\right) d(lnP) \qquad (7.24)$$

Now we need to find (n/W) as a function of pressure P. This can be done from the BET adsorption isotherm observations as follows

$$\frac{v_m}{W} = \frac{n}{W} * 22414\ cm^3 \text{ @ STP}$$

Now we need to calculate the specific surface area A_{sp}

$$A_{sp} = A/W$$

v_m is the monolayer volume coverage

Hence $\frac{v_m}{22414}$ is the number of moles of monolayer

$A = \sigma^*$ Number of molecules in mono layer

(where, σ = diameter of a single molecule)

$$\therefore A = \sigma * \frac{v_m}{22414} * N_A$$

$$A_{sp} = \frac{\sigma}{W} * \frac{v_m}{22414} * N_A \qquad (7.25)$$

With this knowledge we can calculate the change in surface tension of the drop and using the Young's equation we can calculate the change in the contact angle.

Previous Next

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Previous Next