Course: Adsorption Science and Technology: Fundamentals and Applications

Instructor: Prof Sourav Mondal

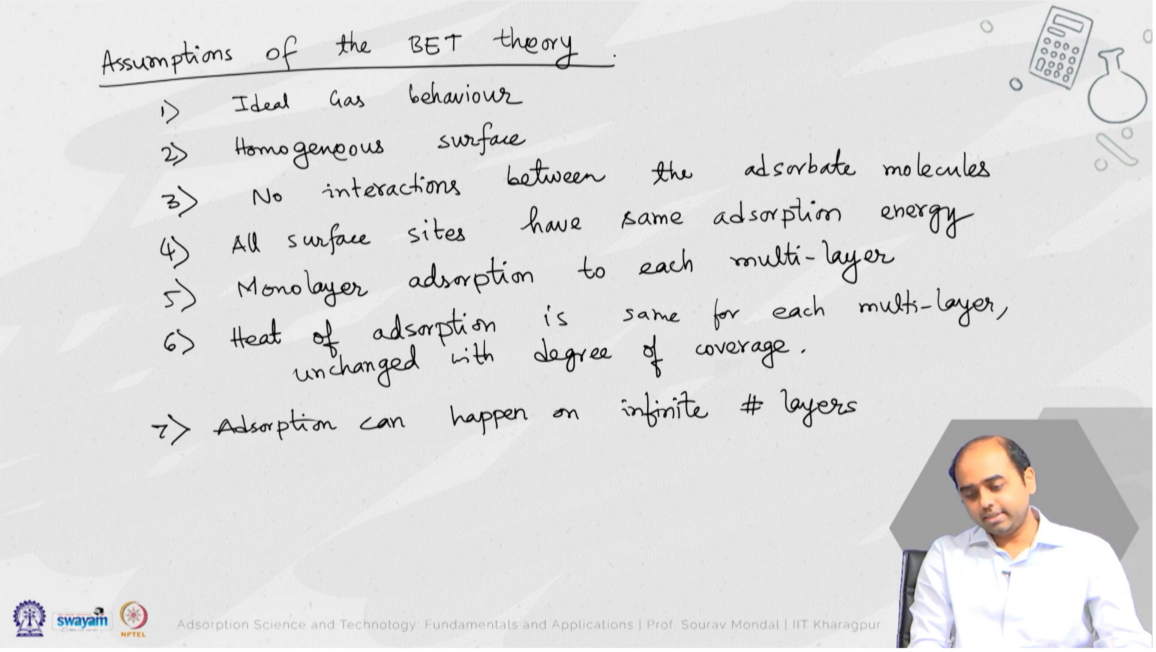
Department: Chemical Engineering

Institute: Indian Institute of Technology Kharagpur

Week 03

Lecture 12 | Gas Sorption

Hello everyone, welcome through to this second lecture on you know BET analysis. In this lecture today itself we will talk about the details of the BET isotherm and how it is evolved considering the multilayer adsorption phenomena. So, the gas adsorption profile is multilayer in nature and the BET isotherm essentially captures this effect. So, we will see that how the BET isotherm model is essentially developed in the gas as one of the famous and popular adsorption model which accounts for multilayer adsorption and this very well takes in care of all the different types of adsorption profiles that we have already discussed in the previous lecture now to begin with there are some assumptions of course which is involved in this bet isotherm model so this assumptions include the major assumptions is something that I will try to list here this assumptions of the BET theory. So, this includes the first that ideal gas behavior, second is this surface is homogeneous. No interaction between the adsorbate molecules, all surface sites have same adsorption energy.



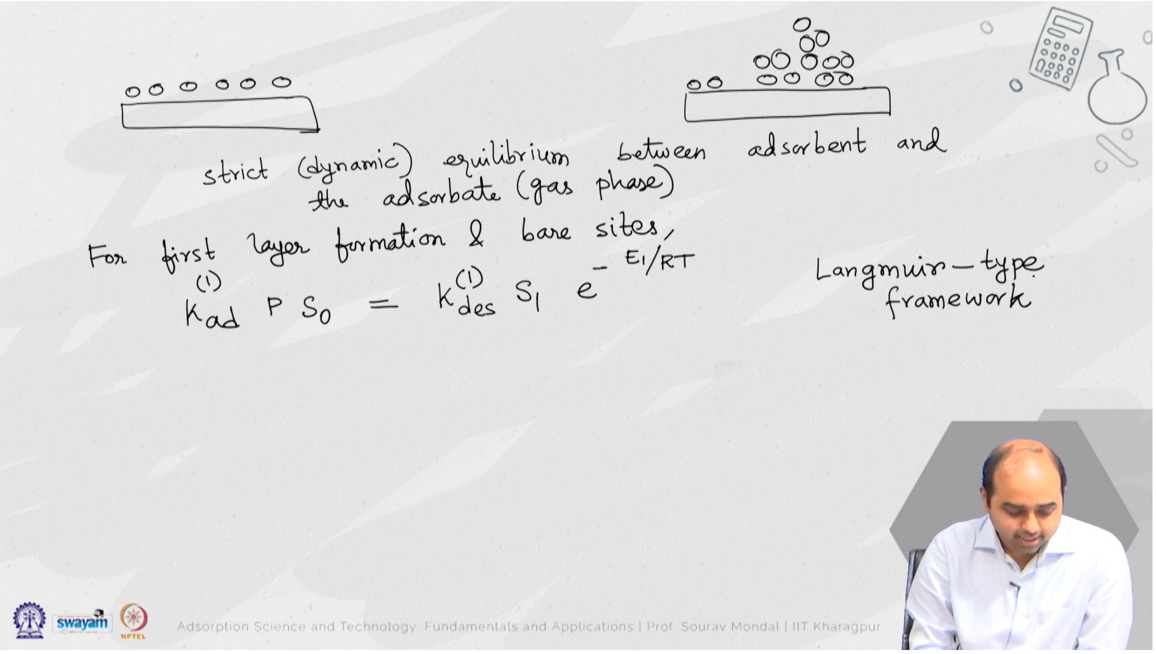
Assumptions of the BET theory.

1> Ideal Gas behaviour
2> Homogeneous surface
3> No interactions between the adsorbate molecules
4> All surface sites have same adsorption energy
5> Monolayer adsorption to each multi-layer
6> Heat of adsorption is same for each multi-layer, unchanged with degree of coverage.
7> Adsorption can happen on infinite # layers

So, all the sites are equally probable. monolayer adsorption to each multilayers or in other words it suggest that there is formation of monolayers or this whatever the assumptions involved in the monolayer adsorption is applied to each of these multilayers. This heat of adsorption is same for each multilayer and this is unchanged with degree of coverage and adsorption can happen on infinite number of layers. So, there is a possibility that that infinite number of multilayers can be formed in this process.

Now, let us try to look into this BET theory or how the BET isotherm is originally a you know developed or is represented. So, this theory of course, as you understand is suitable or is actually developed to explain multiple layers and that is where you see most of these different types of adsorption profiles in this case. Let us try to explain this formation of the multilayer. So, this is I draw a picture of the single layer and I draw a picture of the multilayers. So, typically there exist a strict dynamic equilibrium between adsorbate and gas phase.

Sorry between the adsorbent and the adsorbate which is the gas phase and this is generally characterized by the rates of their adsorption and the rates of their desorption so for the case of the fast layer or the bare sites right for fast layer formation for fast layer formation and bare site. We already have seen that we can write this kind of this rate of adsorption defined by the this constant K for adsorption. Then we have the pressure and then we have the surface coverage for this you know phase which is equal to this sorry this is the not the surface coverage this is the vacant site. So, we write this as S 0 and similarly we have the this is equal to the desorption constants which is multiplied with the surface coverage and that is S 1. This index 0 1 represents the number of layers.



strict (dynamic) equilibrium between adsorbent and the adsorbate (gas phase)

For first layer formation & bare sites,

$$k_{ad}^{(1)} P S_0 = k_{des}^{(1)} S_1 e^{-E_1/RT}$$

Langmuir-type framework

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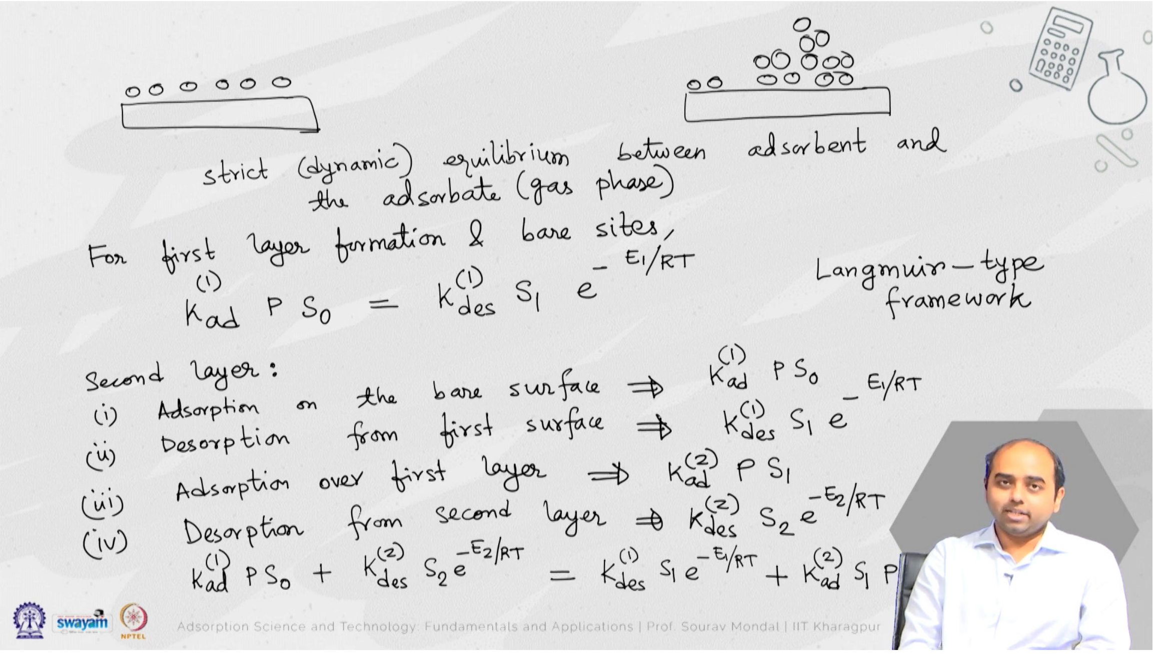
So, 0 represents the bare surface 1 represents the first layer 2 3 4 etcetera represents the subsequent layers. Similarly, we also identify the constants k desorption and adsorption this is for first layer only so from their superscript. Now, often to this the to take into account for the you know type of chemisorption behavior where there is a role of some sort of activation energy for the process we can this this exponential or the Arrhenius type format can also be represented. So, this is what represents a first layer purely Langmuir type equation for the formation of the first layer. So, now we can look into the situation when the second layer starts to form over the first layer.

So in this case there would be four processes that is happening so one is so after the first layer when we start to see for the second layer how does the situation change. So in the second layer there are four processes that happens. So, one is adsorption of particle or whatever adsorbate on the bare surface. So, that is represented by this because there will be some uncovered site still when the second layer formation starts. Then desorption from first surface this can happen and this we write as S 1 e to the power this the third process which happens in the formation is adsorption on first layer or let us say over first layer.



strict (dynamic) equilibrium between adsorbent and the adsorbate (gas phase)

For first layer formation & bare sites,

$$K_{ad}^{(1)} P S_0 = K_{des}^{(1)} S_1 e^{-E_1/RT}$$

Langmuir-type framework

Second layer:

(i) Adsorption on the bare surface ⇒ $K_{ad}^{(1)} P S_0$

(ii) Desorption from first surface ⇒ $K_{des}^{(1)} S_1 e^{-E_1/RT}$

(iii) Adsorption over first layer ⇒ $K_{ad}^{(2)} P S_1$

(iv) Desorption from second layer ⇒ $K_{des}^{(2)} S_2 e^{-E_2/RT}$

$$K_{ad}^{(1)} P S_0 + K_{des}^{(2)} S_2 e^{-E_2/RT} = K_{des}^{(1)} S_1 e^{-E_1/RT} + K_{ad}^{(2)} S_1 P$$

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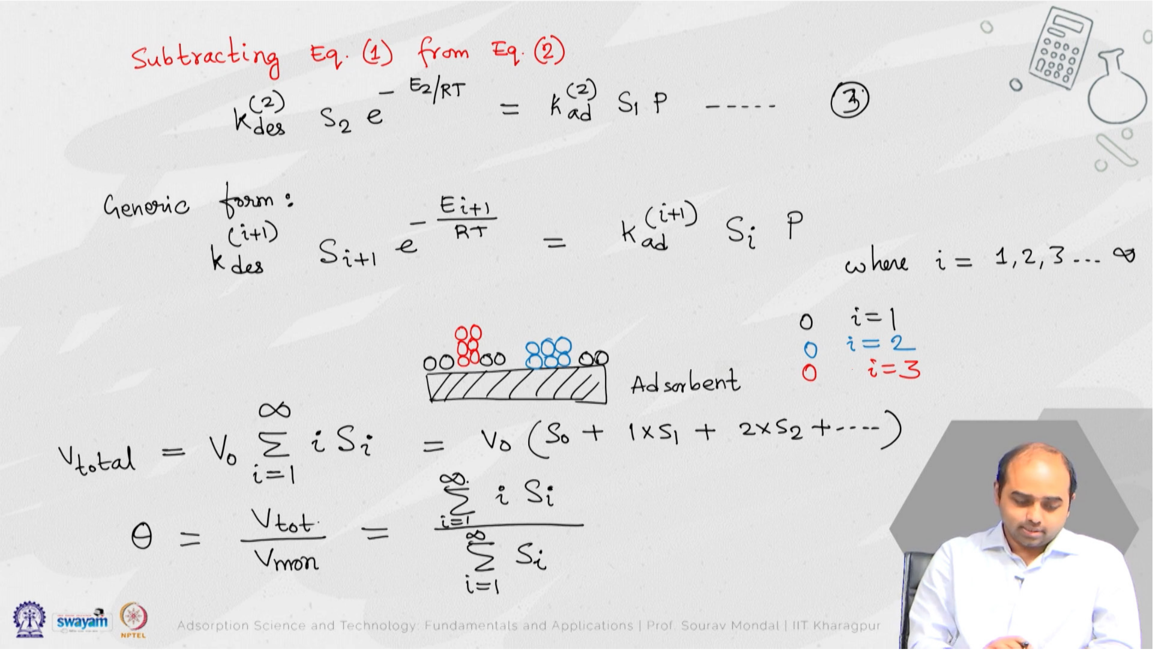
So, in this case the adsorption rate constants are defined by 2 and then we have P and then we have S 1 right. So, which is like the the available surface area on the first layer and then desorption from second layer. k desorption from second layer is S 2, e to the power minus this second layer activation energies. So, when the second layer so, in the case of the first layer there are only two processes which is happening one is adsorption on the bare surface and one is desorption from the first layer. But now starting into the when we move to the second layer, there are four processes which is happening one is adsorption onto the bare surface because there will be still some uncovered you know sites in the bare surface of the zeroth surface the bare surface represent the 0 surface by index there is nothing called 0 by index and then desorption from the first surface which is formed. So, these two processes very similar to the formation of the first layer. The additional two comes because of the presence of the second layer. One is the addition or attachment to the first layer that is step 3 or the process 3 and also there is a possibility of desorption when second layer has already formed. So, this third and the fourth are additional steps or additional process which is present when the second layer starts to form.

Similarly, when we go to the third layer there will be formation of additional two more steps in addition to that is from the adsorption over the second layer and desorption from the third layer in addition to this case. So, now to write the balance equation, so we will be writing the adsorption rates and the desorption rates at equilibrium. So, adsorption of you know this for this part would be this is adsorption on the bare surface plus the desorption rate from the second surface is important and why I am writing this I will just explain let me write it first. This is equated to the desorption from first surface and adsorption onto the first surface. One important thing we should note here that while I am writing this equation the the key idea is that the surface area S 1 should not change.

So, that at equilibrium, we ensure now there since the rates are different I cannot equate the total adsorption is equal to total desorption that is not happening in this scenario. What is happening is this with this four processes happening simultaneously the surface area S 1 does not change and not only that all the four processes taken together does not change the overall concentration or the overall pressure. So, hence this process 1 and 4 which increase. So, 1 which is you know adsorption onto the bare surface and 4 which is desorption from the second layer both of these process increase S 1 the coverage of the first layer or the amount of the first layer that is present whereas, step 2 and 3 reduces the the surface area of the first layer. So, I will try to reemphasize this once again in this case it is not possible to balance or it is not you know sensible to balance the overall rate of adsorption and the overall rate of desorption instead the layer the first layer which is formed from these four processes is essentially conserved.



Subtracting Eq. (1) from Eq. (2)

$$k_{des}^{(2)} S_2 e^{-E_2/RT} = k_{ad}^{(2)} S_1 P \quad ----- \quad ③$$

Generic form:

$$k_{des}^{(i+1)} S_{i+1} e^{-\frac{E_{i+1}}{RT}} = k_{ad}^{(i+1)} S_i P$$

where $i = 1,2,3 \ldots \infty$

$$V_{total} = V_0 \sum_{i=1}^{\infty} i S_i = V_0 (S_0 + 1 \times S_1 + 2 \times S_2 + ----)$$

$$\theta = \frac{V_{tot}}{V_{mon}} = \frac{\sum_{i=1}^{\infty} i S_i}{\sum_{i=1}^{\infty} S_i}$$

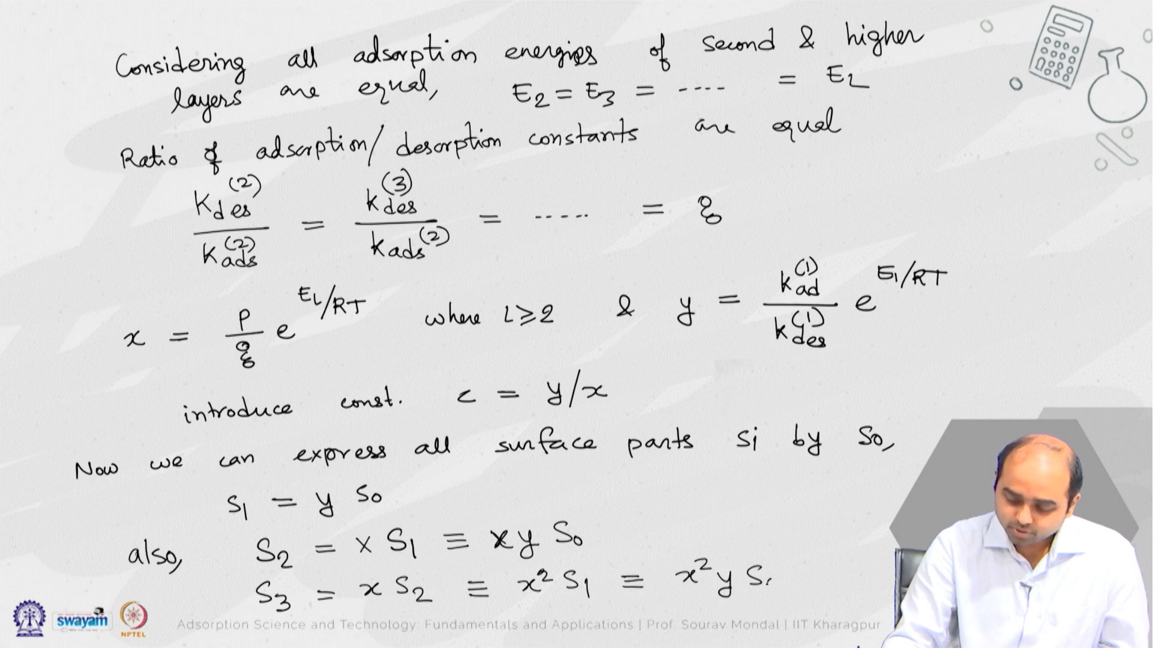
So, the total surface area of the first layer should remain constant by these four by the action of these four process. So, essentially this means the first layer is created by adsorption on the bare surface as well as desorption from the second layer also creates the formation of the first layer. So, both of these two should equal to the process of desorption of first layer and the, I mean desorption from first surface and adsorption over first layer. I mean desorption from first surface of course, removes the first surface and sorry adsorption over first surface creates second layer. So, both of these process step 2 and step 3 essentially reduces the amount of first layer or the surface area of first layer.

Whereas step 1 and step 4 increases the formation of the first layer and that is where we are making this equality. Now, from here we move forward to some you know algebraic steps and we try to develop some more you know correlations and finally, see with the help of the mathematical transformations how do we arrive at the final equation of the BET. Now, generally the the equations that we have obtained here referring to as this as equation 1 and this as equation 2 if you substitute or if you subtract this equation 1 from equation true we immediately get this. So, this can be related as equation 3 here and following this scheme you can easily realize that it is possible to connect the surface area of the i plus 1 layer with the previous layer. So, if I write the generic form such a correlation can be easily perceived.

So, where I could be equal to 1, 2, 3 all the way up to infinity because there is a possibility of having infinite number of layers. Now, let us revisit that picture of the formation of the multi layers over the adsorbent using different types of molecule. This is just a description of you know one layer two layers and three layer formation I have designated different colour to the different layers depending on how many number of layers are formed by these individual you know particles. So, the surface covered by the black or the blue or the you know this red can be differently mentioned. So, or this is like the part surface area of the different layers.

So, the total volume in this case can be represented as v 0 summation of i into s i where this i can be from 1 to infinity. So, this suggest that the total volume occupied by these individual molecules can be designated with respect to the surface area coverage for each case multiplied with the number of layers and multiply with this you know constant V 0 which is nothing, but the you know a constant that helps to convert the surface area to the volume. So, this is like the specific volume per surface area part. So, V 0 can be referred to as the specific volume per surface area part. So, here we can consider like for black i is equal to 1 for red i is equal to 3 and for blue i is equal to 2 assuming that only 3 layers are forming in this case.

Now, the fractional coverage of this you know adsorbed amount or the ratio is very important in this case. So, the by ratio I mean the ratio of the total volume with respect to a perfect monolayer. So, let us call this ratio as theta or a different you know notation as the ratio of the total volume with respect to the volume of a perfect completely monolayer V m I mean this is nothing but the coverage ratio is not it the total volume by the monolayer volume can be represented as this where you only considered one layer coverage and this ratio is definitely greater than 1 because here you are considering the you know multilayer coverage altogether, sorry this layer is always less than 1 because you are only considering the monolayer formation in the denominator. Now, we consider the assumptions that all the adsorption energies of the. Now considering that all adsorption energies which is nothing but the sort of activation energies that we are talking about are second and higher layers are equal.



Considering all adsorption energies of second & higher layers are equal, $E_2 = E_3 = \cdots = E_L$

Ratio of adsorption/desorption constants are equal

$$\frac{K_{des}^{(2)}}{K_{ads}^{(2)}} = \frac{k_{des}^{(3)}}{k_{ads}^{(2)}} = \cdots = g$$

$$x = \frac{p}{g} e^{E_L/RT} \quad \text{where } L \geq 2 \quad \& \quad y = \frac{k_{ad}^{(1)}}{k_{des}^{(1)}} e^{E_1/RT}$$

introduce const. $c = y/x$

Now we can express all surface parts s_i by S_0,

$$s_1 = y\, S_0$$

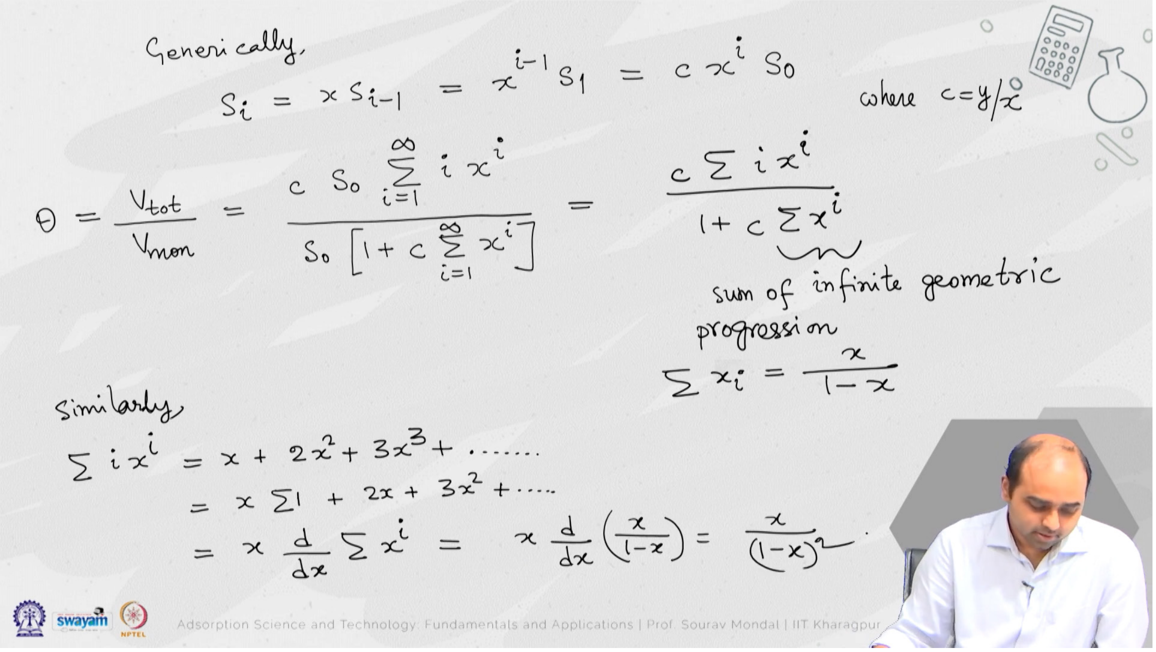
also, $S_2 = x S_1 \equiv x y S_0$

$$S_3 = x S_2 \equiv x^2 S_1 \equiv x^2 y S_0$$

So, which means this E 1 E 2 sorry starting from E 2 E 3 these are all set to a constant value let us call that as E L. Also the ratio of adsorption ratio of adsorption to desorption constant from second layer onwards this is also set to equal. Let us call this value as G and this is treated for I mean this is very much realistic assumptions for you know ideal systems. Note that the first layer is treated differently because its rate constants as well as the adsorption energy is largely different from those of the higher layers that is why we treat the first layer slightly different. Now, we define these two constants x as p by g e to the power you know e l by r t where of course, l is greater than equal to 2 and we define this y is equal to this is for the first layer. Now also introduce another constant as c which is nothing but y by x.

So, now we can express all surface parts S 1 or let us say S i in terms of S 0 as something like this. So, I can write my S 1 as equal to y into S 0. So, this is possible from this expression 3 or expression you know this 4 you can see that entire thing is actually captured within this y itself. So, I can write y s 1 as equal to y into s 0 also from second layer onwards I can write s 2 as x into S 1 now S 1 can again be written as y into S 0. So, this is equal to x y into S 0.

I hope it is understood. Similarly, S 3 can be written down as x into S 2 which is equal to x square S 1 and which is equal to x square y into S 0. So, generically we can write for any you know i, s i is equal to x into x s of i minus 1 which is equal to x to the power i minus 1 into s 1 and this is equal to c into x i now into s 0 where c is equal to y by x. Now, with this idea we can define our this ratio of the v total with respect to the v monolayer. as c into s 0 summation of i into x to the power i where i 1 to infinity divided by s 0 1 plus c into summation of x to the power i from y to infinity. This is exactly following the formulation that we have already described here for this two purpose.



Generically,

$$S_i = x S_{i-1} = x^{i-1} S_1 = c x^i S_0 \qquad \text{where } c = y/x$$

$$\Theta = \frac{V_{tot}}{V_{mon}} = \frac{c S_0 \sum_{i=1}^{\infty} i x^i}{S_0 \left[1 + c \sum_{i=1}^{\infty} x^i\right]} = \frac{c \sum i x^i}{1 + c \underbrace{\sum x^i}_{\text{sum of infinite geometric progression}}}$$

$$\sum x_i = \frac{x}{1-x}$$

Similarly

$$\sum i x^i = x + 2x^2 + 3x^3 + \ldots\ldots$$

$$= x \sum 1 + 2x + 3x^2 + \ldots$$

$$= x \frac{d}{dx} \sum x^i = x \frac{d}{dx}\left(\frac{x}{1-x}\right) = \frac{x}{(1-x)^2}$$

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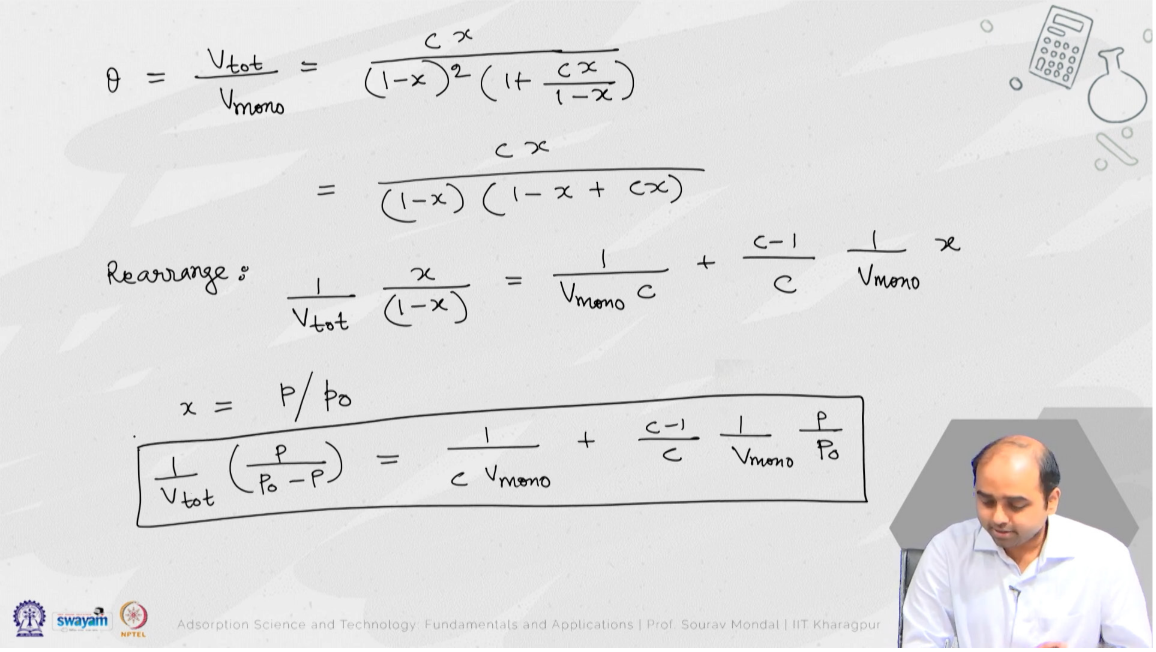
So, we are only representing the ith state or all the states with respect to s 0 and representing terms of x. So, this is nothing, but equal to c into summation of x i summation of x i. So, in the denominator we have a in the you know this summation of the infinite geometric progression . So, this this quantity this is an infinite sum of infinite geometric progression So, which means that summation of x i is equal to x by 1 minus x. Similarly, with some algebraic manipulations we can also write i of i xi as equal to x plus 2 x square plus 3 x cube sorry it is i and so on. So which can be rewritten as x summation of 1 plus 2x plus 3x square and this can be written x d dx of summation of x to the power i or in other words this is x into d dx of the infinite series of x 1 minus x and this is nothing but x pi 1 minus x whole square. So, with this we can frame the fractional coverage theta as c x divided by 1 minus x whole square and also we have 1 minus c x by

1 minus x. So, on doing some algebraic manipulation this equation can take I mean this expression can take this shape of 1 minus x 1 minus x plus c x. Now, you can of course, rearrange this expression in terms of 1 by V total to give the classical expression of the BET isotherm.



$$\theta = \frac{V_{tot}}{V_{mono}} = \frac{c x}{(1-x)^2 \left(1 + \frac{c x}{1-x}\right)}$$

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

Rearrange :

$$\frac{1}{V_{tot}} \frac{x}{(1-x)} = \frac{1}{V_{mono}\, c} + \frac{c-1}{c} \frac{1}{V_{mono}} x$$

$$x = P/P_0$$

$$\boxed{\frac{1}{V_{tot}} \left(\frac{P}{P_0 - P}\right) = \frac{1}{c\, V_{mono}} + \frac{c-1}{c} \frac{1}{V_{mono}} \frac{P}{P_0}}$$

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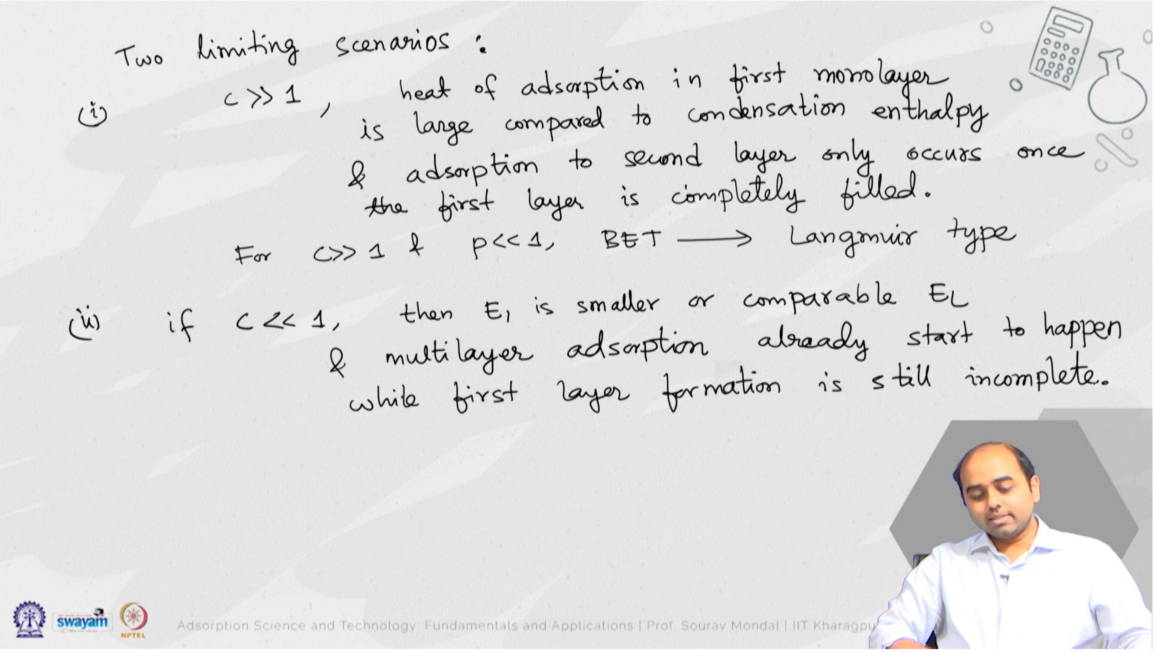
We arrive at this expression. Now x can be substituted by the fact that the volume V total must become infinity for P is equal to P0 and since the monolayer volume is finite x has to be equal to 1 for this case. Otherwise x can be represented as P by P0 and since both P and P0 are measurable quantities we can eliminate this x and write this expression in the form of P and P0. Thus this equation takes the famous form of the BET that we are all used to as like this. So, this is the famous you know BET isotherm equation that we have derived considering the multilayer adsorption profile and in this case considering monolayer to each of these multilayer systems. Now, there are two limiting cases which can be distinguished here and it is important to understand them.

So, one is when the constant C is much much larger than 1, the heat of adsorption of the very first monolayer, the heat of adsorption in first monolayer is large compared to the condensation in enthalpy. And adsorption onto the second layer only occurs, and adsorption to second layer only occurs once the first layer is filled is completely filled I would say. So, for C much much larger than 1 and P much much smaller than 1, BET isotherm you know switches to the Langmuir mode . This can also be understood physically as well as from the equation of the BET isotherm . Conversely if C is small then E 1 is smaller or comparable to EL or the other energies of the other layer and a multilayer adsorption in that case a multilayer adsorption already start to happen while the first layer formation is still is still incomplete.



Two limiting scenarios :

(i) $c >> 1$, heat of adsorption in first monolayer is large compared to condensation enthalpy & adsorption to second layer only occurs once the first layer is completely filled.

For $c >> 1$ & $p << 1$, BET $\longrightarrow$ Langmuir type

(ii) if $c << 1$, then E_1 is smaller or comparable E_L & multilayer adsorption already start to happen while first layer formation is still incomplete.

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So, these are the two limiting situations which normally one encounters in this I mean you can easily identify in this BET particularly the second case which suggest that if E 1 is smaller are comparable to EL then it is possible that the you know multiple layer starts to form even though the first layer is still not formed properly and this is typically the scenario of type 3 mode of this adsorption profile which we have already discussed. Nevertheless, these are the this is the you know background of the BET isotherm and you have seen that how this equation framework is actually developed in this case and this helps us to understand the assumptions as well as the different you know consideration that is made within this scenario. I hope all of you found this lecture useful as well as the understanding from this will greatly help in the BET operation particularly for people who are working with you know measurements of BET equipment and how does the background actually is evolved and what are the necessary assumptions behind it. Thank you and I hope all of you like this lecture.