Heterogeneous Catalysis and Catalytic Processes
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Module - 03
Lecture – 10

Good morning. In my last lecture, I was talking about BET Isotherm in multilayered adsorption on isotherm. So, let us continue the same today for the derivation or understanding the isotherm. So, I just said earlier also that Langmuir adsorption isotherm which is for the multi not for the multilayered adsorption or that a monolayer and BET is the explosion of Langmuir taking care of that multilayer adsorption.

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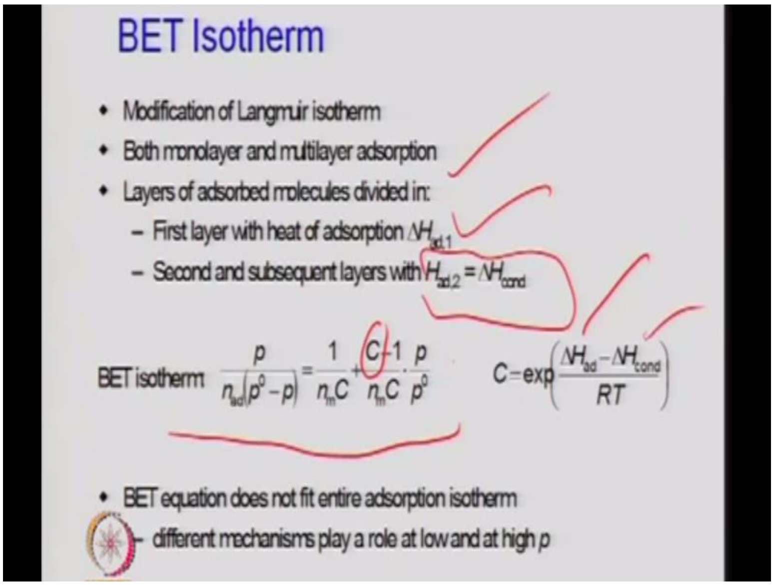

BET Isotherm

- Modification of Langmuir isotherm
- Both monolayer and multilayer adsorption
- Layers of adsorbed molecules divided in:
  - First layer with heat of adsorption $\Delta H_{ad,1}$
  - Second and subsequent layers with $H_{ad,2} = \Delta H_{cond}$

BET isotherm $\frac{p}{n_{ad}(p^0 - p)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} \cdot \frac{p}{p^0}$ $\quad C = \exp\left(\frac{\Delta H_{ad} - \Delta H_{cond}}{RT}\right)$

- BET equation does not fit entire adsorption isotherm
  - different mechanisms play a role at low and at high p

So, both monolayer and multilayer adsorption is possible in BET Isotherm and the adsorbed layers, when you look at in the Langmuir isotherm also we assume that the surface is uniform in BET also, the same assumption has been taken, the surface is uniform adsorption takes place. So, heat of adsorption for the first layer is same but, when you look at the multilayer it is nothing but, the condensation of the molecule.

So, Therefore, the heat of adsorption for the subsequent layer will be different then the heat of adsorption in the first layer. Because, first layer is on a gas molecule adsorbs on the surface of the solid but, in the second case the condensation is on the layer of the liquid which is already there on the surface. So that is basically heat of condensation of that gas molecule.

So, this is the difference heat of adsorption here and heat of adsorption for each subsequent layer, is taken as the heat of condensation. So, suppose this there is a big difference between deltas H adsorption and delta H desorption, this heat of condensation then it resembles to your Langmuir adsorption isotherm. So, term we will talk later because, here this C which is defined is a term related to heat of adsorption, on the first layer and condensation in the subsequent layer.

So, this is what the exponentially related term for the multilayer adsorption, where the heat of adsorption and heat of condensation in subsequent layer is different. So, overall derivation of BET Isotherm, we have talked last time and let us see the steps which takes place during the BET Isotherm.

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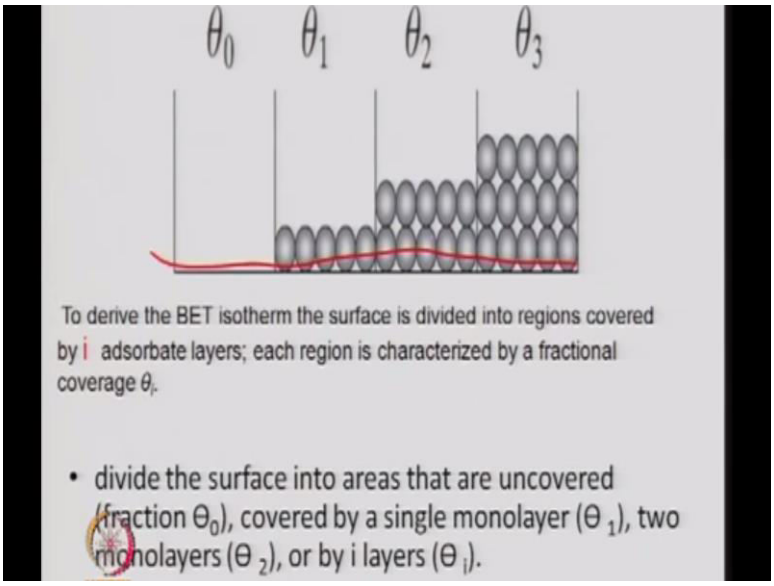

To derive the BET isotherm the surface is divided into regions covered by i adsorbate layers; each region is characterized by a fractional coverage θ_i.

- divide the surface into areas that are uncovered (fraction Θ_0), covered by a single monolayer (Θ_1), two monolayers (Θ_2), or by i layers (Θ_i).

So, we just talked at a model where we are assuming that each layer is formed so, this is the bare surface so, we are seeing the fraction of the bare surface theta 0 theta 1 is the fraction of the surface, where the monolayer is formed theta 2 is the fraction of the surface where 2 layers are formed and so on. So, this surface total surface of a solid is divided into areas that are uncovered theta 0, covered by a monolayer covered by 2 layers and that summation will be nothing. But, if I just add all these mono layers here, that is my surface area or your BET surface area or surface area of the solid surface. So, we are interested in determining this total number of molecules which adsorbs on the surface and the surface which is bare and then we can just add that.

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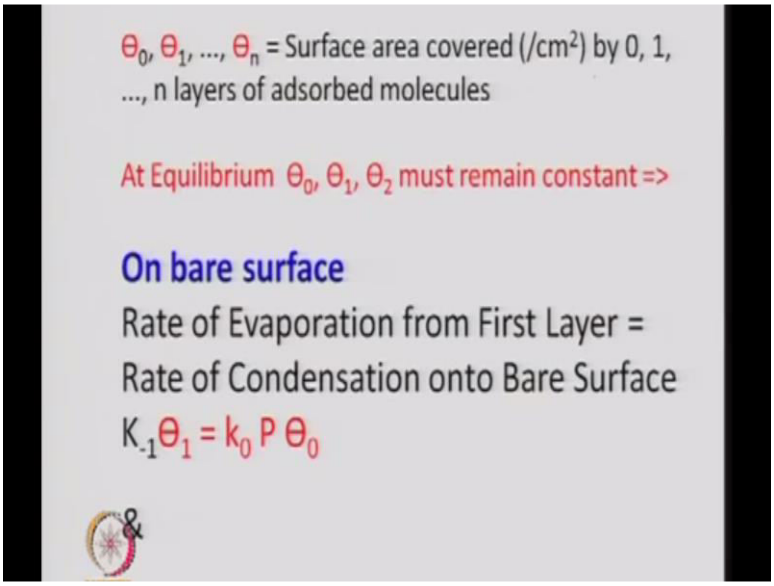

$\theta_0, \theta_1, \ldots, \theta_n$ = Surface area covered (/cm^2) by 0, 1, ..., n layers of adsorbed molecules

At Equilibrium $\theta_0, \theta_1, \theta_2$ must remain constant =>

On bare surface

Rate of Evaporation from First Layer = Rate of Condensation onto Bare Surface

$K_{-1}\theta_1 = k_0 P \theta_0$

So that, we have just discussed last time in terms of the fraction of the surface which is covered per unit area and isotherm when we are talking, we are talking at dynamic equilibrium between the later. So, when you have bare surface the first surface which is your bare surface here so, molecules are evaporating from there and adsorbing here.

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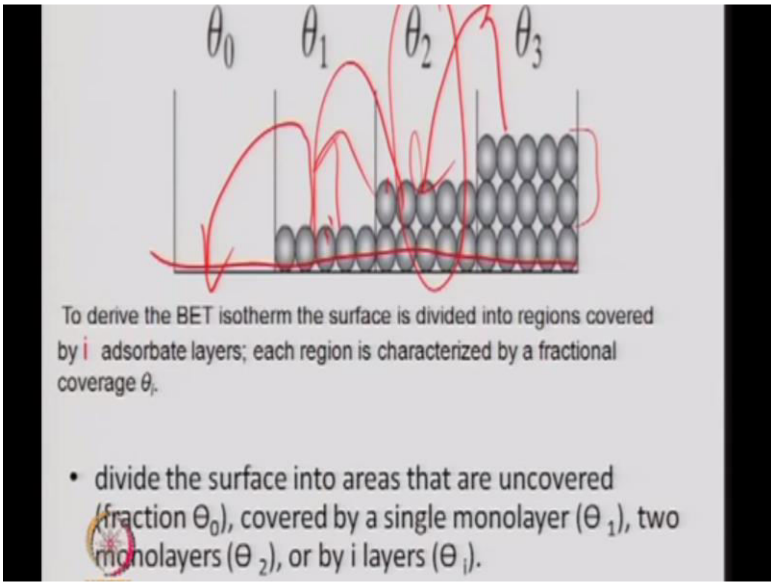

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So, when you have bare surface the first surface which is your bare surface here so, molecules are evaporating from there and adsorbing here. So, equilibrium when I say that rate of adsorption on the first layer or rate of adsorption on the second layer. So, when there is equilibrium adsorption equilibrium, the net rate of adsorption is 0. So, rate of adsorption will be equal to rate of desorption at that. So, when we are talking the BET Isotherm because, it is a multilayer so, there will be dynamic equilibrium among these layers.

So, for bare surface when I am talking, so whatever the molecule which absorbs here desorbs from here they will come and adsorb here. So, it means rate of adsorption on the bare surface which is proportional to the partial pressure, which proportional to the fraction of the sides vacant that will be nothing but, whatever the layers which are desorbing from this evaporation.

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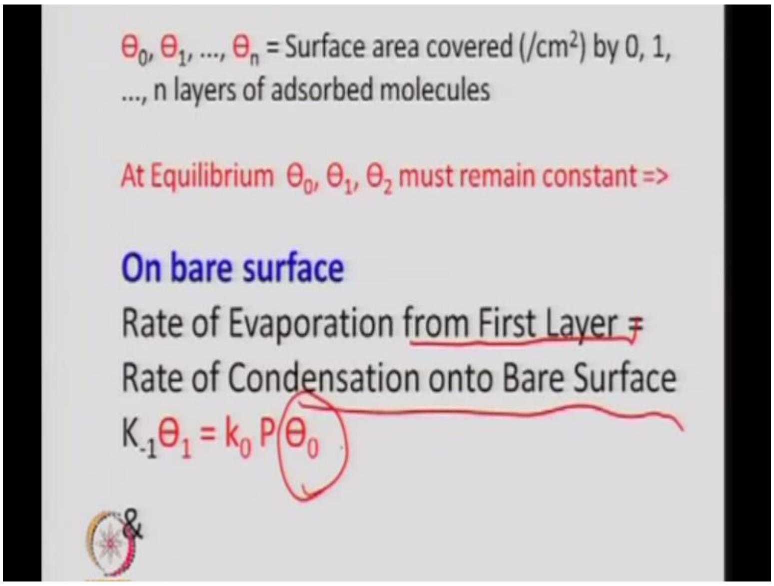

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On bare surface

Rate of Evaporation from First Layer =

Rate of Condensation onto Bare Surface

$K_{-1}\theta_1 = k_0 P \theta_0$

So, evaporation meaning is desorption and adsorption. When I am saying or I will say the condensation, condensation of the molecule same thing when I talk this layer which is the second layer. So, whatever the molecule evaporates from here, they will come here and adsorb and whatever the molecules which evaporates from here they will go there but, when I say in general equilibrium. So, whatever the rate of evaporation from there will be equal to the rate of adsorption on the lower layer. So, that is what the meaning of dynamic equilibrium and we have already made certain assumption that in this the delta

H is different. But, when the adsorption or desorption takes place from these layers the heat of adsorption is equal to heat of condensation of liquefaction.

So, this is for the bare surface which we were discussing last time also. So, rate of evaporation from first layer, which is first layer I am saying evaporation. So, this is desorption rate, so rate of desorption from first layer is nothing but, the fraction of the sides which are covered in 1 first layer. So, that is K minus 1 times theta 1 and that will be equal to rate of condensation on a bare surface.

So, rate of condensation means adsorption on that bare surface which will be proportional to the fraction of the sides which are available on the surface. So, bare sides' vacant sides and pressure of the gas partial pressure of the gas time's constant whatever the rate constant adsorption rate constant. So, this is for the bare surface or equilibrium on a bare surface and when you look at or the subsequent layers so this is for the first layer here so for first layer.

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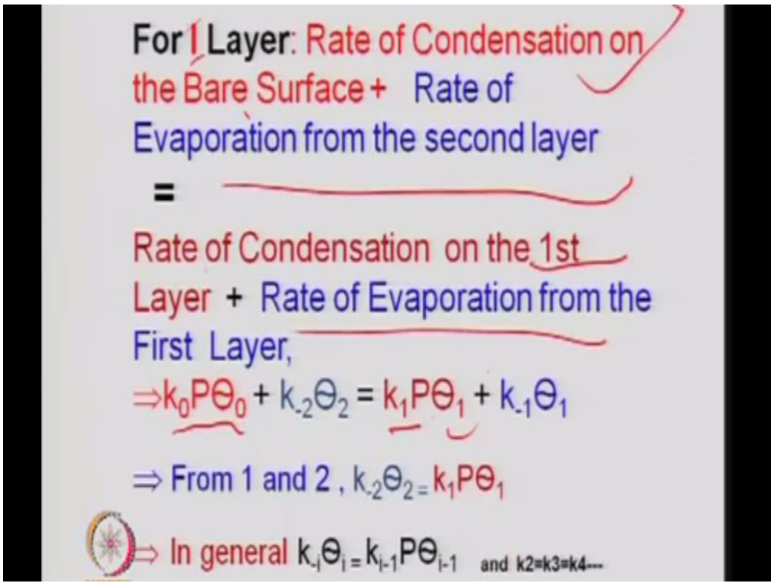

For 1 Layer: Rate of Condensation on the Bare Surface + Rate of Evaporation from the second layer

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Rate of Condensation on the 1st Layer + Rate of Evaporation from the First Layer,

$\Rightarrow k_0 P\Theta_0 + k_{-2}\Theta_2 = k_1 P\Theta_1 + k_{-1}\Theta_1$

$\Rightarrow$ From 1 and 2, $k_{-2}\Theta_2 = k_1 P\Theta_1$

$\Rightarrow$ In general $k_{-i}\Theta_i = k_{i-1} P\Theta_{i-1}$ and k2=k3=k4---

Now, we are talking the layer 2, from where the evaporation will take place and it will adsorb on the first layer and from first layer also evaporation will take place, which will go to 0 layers. So, that is what I said last time also that therefore, i-th layer we have to go with i minus 1 and i plus 1, from I plus 1 will be the evaporation and from on i-th layer there also there will be evaporation and it will go to the i minus 1 layer condensation. So, this is what the meaning of dynamic adsorption equilibrium.

So, rate by same equation what I said here that rate of condensation on the bare surface plus rate of your pressure from the second layer, will be equal to rate of condensation on the first layer, plus rate of your pressure from the first layer. So, for a first layer I am talking second layer. So, second layer will have some evaporation. So, evaporation from the second layer and when I talk a first layer from first layer also there is evaporation which is here and whatever the molecule which evaporates from the first layers them will go to a lower layer. So, they will come on the bare surface and this is the tau which is from second it will come to the first.

So, again adsorption equation means nothing but, K0 time's P time's theta 0 fraction of the side which is vacant, for the second layer again this will be that rate of evaporation when I am saying. So, will depend on the fraction of the sides which are covered, so K minus 2 times theta 2 because it is the evaporation desorption. Here again, condensation on the first layer. So, adsorption rate constant first layer rate constant times pressure times the theta 1; which is related to your because, on that layer the fraction is being adsorbed it is a multilayer. So, adsorption is possible that is what it is not Langmuir adsorption isotherm. So, even the sides are available theta 1which are nothing but, the adsorbed molecule

But, here the delta H or heat of adsorption is equal to heat of liquefaction, the last term which is here again rate of desorption from the first layer which is desorption rate constant times the fraction of the sides which are already covered. So, if you just look at this and this so, K minus 1 theta 1 is equal to k 0 p theta 0. So, your equilibrium relationship because these terms are equal, so, you have just k minus 2 theta 2 will be equal to k 1 P theta 1.

For we can generalize this equation now because this equation k minus 2 upon k 1 is equal to your simply E times theta 1 over theta 2. So, in general I can write for any i-th layer you will have k minus i theta i is equal to k i minus 1 P times theta i minus 1 and we assume that because the same surface. When we are talking above 0 layer the surface is similar. So, k 2, k 3, k 4, which are the rate constant for adsorption they are similar same.

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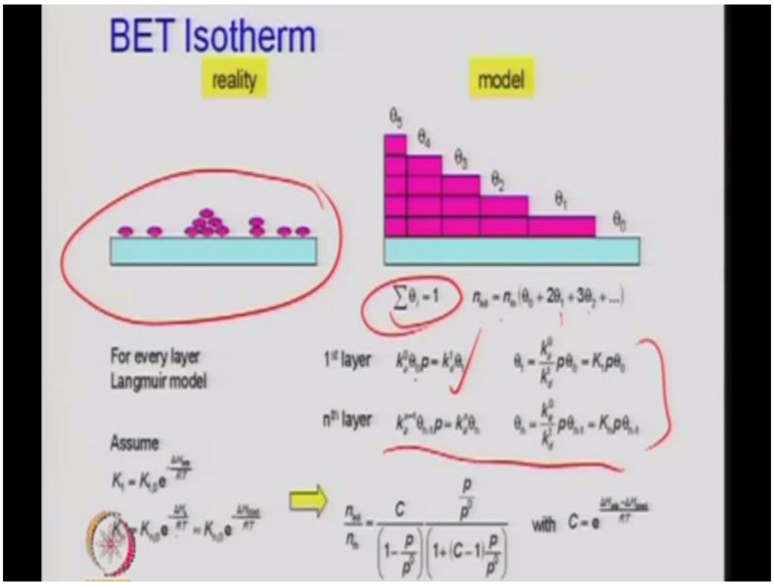

BET Isotherm

reality

model

$\sum \theta_i = 1$ $\quad n_{ad} = n_m(\theta_1 + 2\theta_2 + 3\theta_3 + \dots)$

For every layer Langmuir model

1st layer $\quad k_a^0 \theta_0 p = k_d^1 \theta_1 \quad \theta_1 = \frac{k_a^0}{k_d^1} p\theta_0 = K_1 p\theta_0$

nth layer $\quad k_a^{n-1} \theta_{n-1} p = k_d^n \theta_n \quad \theta_n = \frac{k_a^0}{k_d^1} p\theta_{n-1} = K_n p\theta_{n-1}$

Assume

$K_1 = K_{1,0} e^{\frac{\Delta H_{ads}}{RT}}$

$K_n = K_{n,0} e^{\frac{\Delta H_L}{RT}} = K_{n,0} e^{\frac{\Delta H_{liq}}{RT}}$

$$\Rightarrow \frac{n_{ad}}{n_m} = \frac{C \frac{p}{p^0}}{\left(1 - \frac{p}{p^0}\right)\left(1 + (C-1)\frac{p}{p^0}\right)} \quad \text{with } C = e^{\frac{\Delta H_{ads} - \Delta H_{liq}}{RT}}$$

The same thing has been shown in the different model, that what we have discussed is the rate is something like this. But, we have assumed that there are they are disciplined layers 1, layer 2 and layer second layer. But, in reality there may be some surface which is vacant. But, in total we are calculating the fraction of the surface, which is vacant and fraction of the surface which are covered by different layers, so, sigma of theta i because, it is a summation of the each monolayer. So, that will be 1 for it is total surface and number of molecule adsorbed if you want to calculate for a given concentration or given pressure that at saturation and n m is the when the monolayer forms.

So, in multilayer this can be more than n m in BET this when the monolayer forms this will become saturated or Langmuir it will become saturated. So, in BET it can be here when I add this i theta i when I just wrote yesterday, that can be cannot be 1 summation sigma of theta is 1. But, i theta is because 1 layer plus 2 layer 3 layer. So, that can be more than 1, same thing here so, number of molecule which are adsorbed is nothing. But, monolayer coverage times the layers which are the form. So, theta 0 is the vacant this is the 2 layers formed here they are 3 layers. So, this is nothing but, i times sigma of theta.

So, for first layer we have already seen now so, we have written the equation k adsorption times theta 0 timees p. So, this is rate of adsorption on bare surface and desorption is from the first layer. So, this same equation which we have seen before, so, we have developed a relationship like this and then you have this equation for any nth layer. So, we have already assumed that adsorption equilibrium constants k 1 for the first, bare surface that is k 1 0, it is for minus delta H adsorption, upon R T for subsequent, it is delta h 1 upon R T which is something equal to the heat of condensation.

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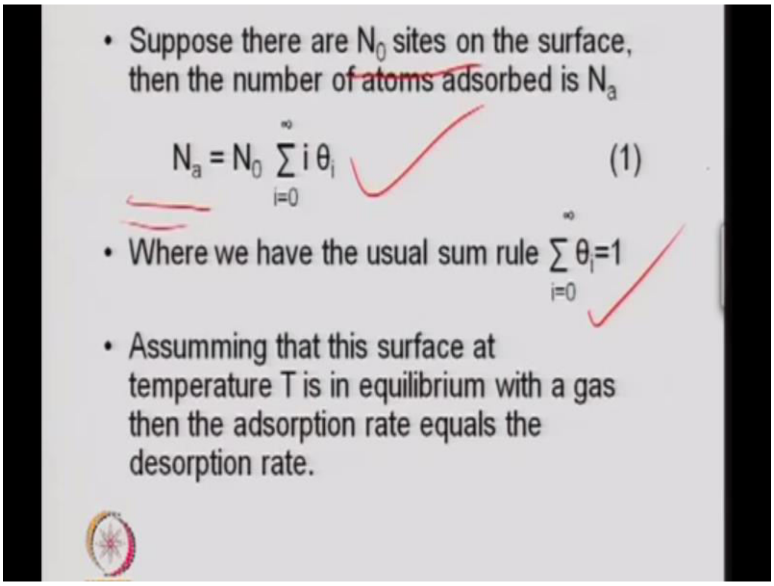

- Suppose there are N_0 sites on the surface, then the number of atoms adsorbed is N_a

$$N_a = N_0 \sum_{i=0}^{\infty} i\,\theta_i \qquad (1)$$

- Where we have the usual sum rule $\sum_{i=0}^{\infty} \theta_i = 1$
- Assumming that this surface at temperature T is in equilibrium with a gas then the adsorption rate equals the desorption rate.

So, the derivation if you look at that isotherm, which we are talking something like BET Isotherm you know now p upon V into p 0 minus p is equal to 1 upon V m C plus C minus 1 over V m C times p by p 0 this isotherm, which we have just seen here, just 1 similar to this 1 that is the same expression on written in a linear form. So, that is what we want to check or develop the expression something like this. So, quickly I will show you some salient points here.

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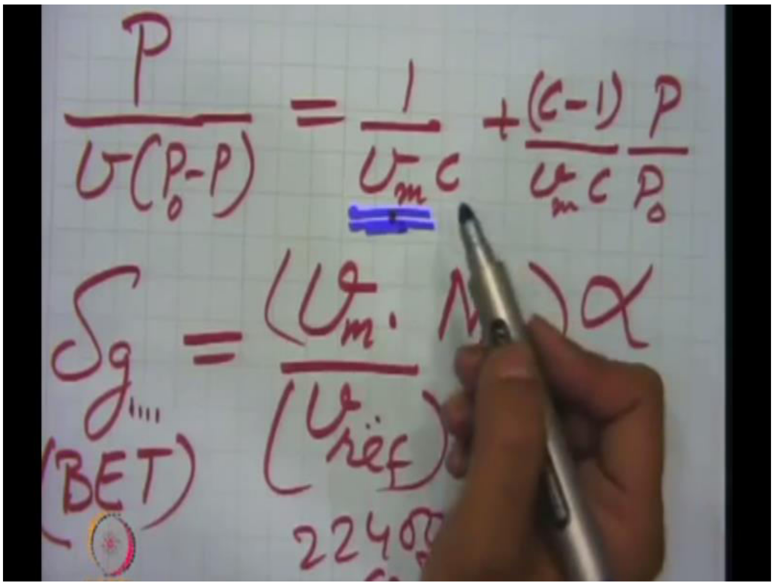

$$\frac{P}{v(P_0-P)} = \frac{1}{v_m c} + \frac{(c-1)}{v_m c}\frac{P}{P_0}$$

$$\underset{(BET)}{S_g} = \frac{(v_m \cdot N)}{(v_{ref})}\alpha$$

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So, what we are assuming here that there are total number of sides which are N0 on the surface. Which because, you are relating the number of gas molecule adsorb on the surface with whatever the surface which is covered because, we are saying the number of molecules it is known to us, then we can multiply it with the area of 1 molecule. So, that is what we have seen last time, that surface area will be Sg if I write BET surface area will be represented sometimes like this based on the isotherm is equal to simply if I know some volumes of the gas, which had been adsorbed when monolayer has formed and if I know some reference temperature or s t p, when this volume is known 1 gram molecule of the gas which is adsorbed at say s t p. So, this is 22400 centimeter cube per gram, mole of the gas per gram mole of the gas. So, this is basically that at this condition. Whatever, the condition V m is the number of molecules of gas adsorbed and you know that at standard condition this is the volume of the gas and this volume contains the Avogadro number.

So, how many molecules are available in this volume, that is calculated and if I just multiply with area 1 molecule which we have seen yesterday, alpha the area of 1 molecules here I said for liquid nitrogen molecules it has the area 16.2 in the square. So, that is your surface area total BET surface area and this is what we are looking from this isotherm.

So, the same thing here that our interest is that either you get this v m monolayer coverage or find out the N0 into v m that is at this which is number of molecule. Which are adsorbed on a surface basically when the monolayer forms? So, this is our interest and then if you look at here this is the total number of molecules of the gas when multi layers formed because, I just said that the formation is nothing but, a same monolayer but, ultimately we are calculating this V m.

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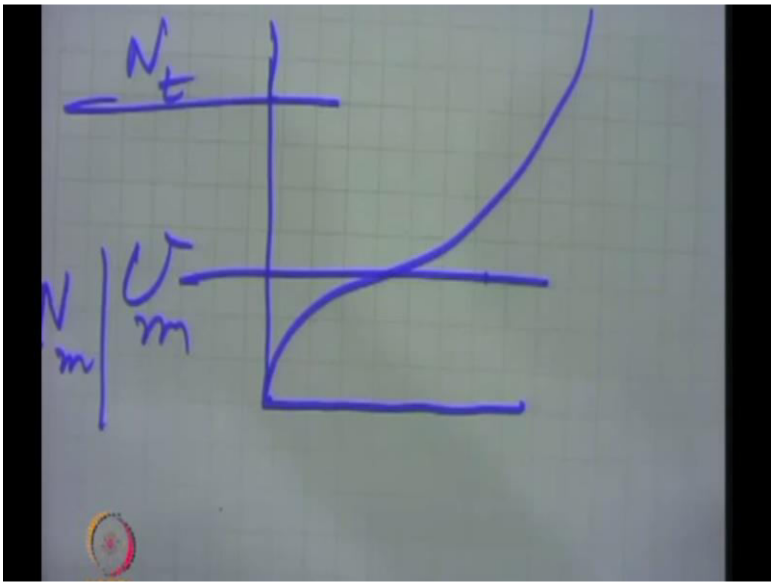

But, in B E T Isotherm this has gone like this. So, your monolayer is formed here. So, we are interested in finding out this V m or whatever N m number of molecules at this condition not this N t. But, since number of molecules are adsorbing at a multilayer. So, we have to calculate that total number of molecules and then co-relate it with the V m so, keeping that thing in mind. So, total number of molecule which comes on the surface or fraction, if I calculate or N 0 is the number of molecules multiplied by each number of layers. So, you can calculate the number of molecules of sides.

I am talking I am co-relating it with the number of sides on the surface. So, the number of atoms adsorbed is given by this. So, which can be used to calculate the surface area and this is known to you. That if you add the entire mono layer the summation will be 1 theta 0 plus, theta 1 plus, theta 2 that is going to be 1. Because, there we are talking only monolayer but, when we are talking theta 0 plus theta 1 plus 2 times theta, theta 2 plus 3 times theta 3 and so on. i theta i which I said that is not going to be 1.

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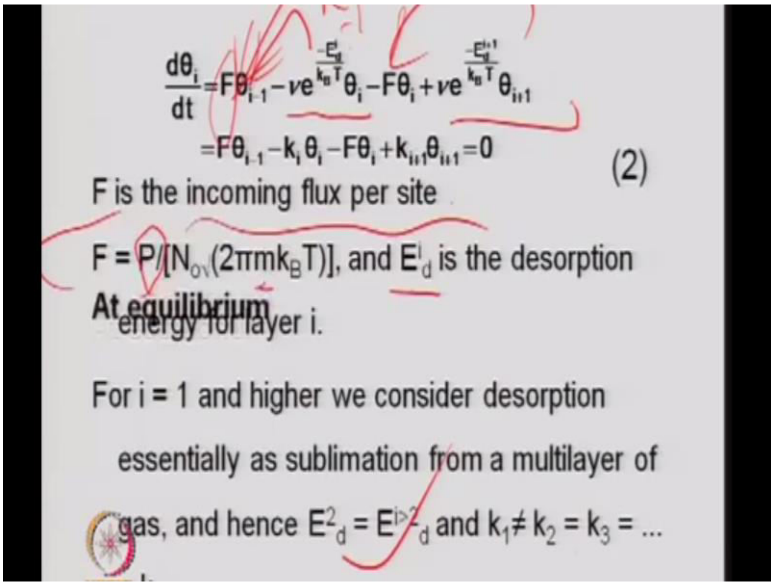

$$\frac{d\theta_i}{dt} = F\theta_{i-1} - \nu e^{\frac{-E_d^i}{k_B T}}\theta_i - F\theta_i + \nu e^{\frac{-E_d^{i+1}}{k_B T}}\theta_{i+1}$$

$$= F\theta_{i-1} - k_i\theta_i - F\theta_i + k_{i+1}\theta_{i+1} = 0 \qquad (2)$$

F is the incoming flux per site

$F = P/[N_{0}\sqrt{(2\pi m k_B T)}]$, and E^i_d is the desorption energy for layer i.

At equilibrium

For i = 1 and higher we consider desorption essentially as sublimation from a multilayer of gas, and hence $E^2_d = E^{i>2}_d$ and $k_1 \neq k_2 = k_3 = \ldots$

So, we have just assumed the dynamic equilibrium and then if have just used this basic kinetic theory of the gas, which is generally used because it is related to the sticking probability so, the same thing when I write this F it is something which is related to the flux, how many molecules of the gas which come to the surface and adsorb. So, number of molecule which is stakes on to the surface and adsorb which can be true for chemisorptions also, when you talk a chemical reaction or a chemical reactive gas like hydrogen and come on to the surface of the slide.

So, this is simply representing the incoming flux per site and related to your sticking probability. So, and this is defined by P upon N 0 times the square root of 2 phi m k B T . Where M is the molecular width mass of the atom you can say. So, per unit atom or molecule, kB is the Bergman constant, T is the temperature in degree Kelvin, p is the pressure of the gas and N 0 this is the probability of the gas, which is related to basically a pressure of the gas.

So, that is why instead of writing this when you write the rate of adsorption, you write the expression k 1 times p. So, that k 1 is related to this, the term which is other than pressure. So, constant for that adsorption which you write and that is related to something like collision theory you calculate that p exponential factor and then you correlate it.

So, and E i d we are talking adsorption because this temperature related parameter will come from the activation energy of the desorption layers what is the effect of temperature. So that, is a desorption so, E i d I am assuming that it is the energy for desorption. So, the same equation what we have write earlier now I am talking a dynamic equilibrium. So, at equilibrium for any layer d theta i by d T will be 0 because, when the there is an equilibrium. So, within that multilayer where there some molecules are evaporating, some are adsorbing but, there is no net gain or loss of these molecules.

So, for any i-th layer if I am talking something is coming from i plus 1 layer. But, in i plus 1 layer also something is coming from i plus 2 layers. So, it is balanced and in i-th layer something is evaporating from i-th layer and that is going to i minus 1 layer. So, these all terms which are written here so, first term if I look at here or F times theta i minus 1. So, I am writing equilibrium for i-th layer, on which something is evaporated from i-th layer and that has been adsorbed in i minus 1 layer. So, earlier we wrote this term something like k i minus 1 times p times, theta i minus 1 and the same term has been instead of writing that k i minus 1 times p we have written it in terms of F, where F is nothing but, the flux.

So, basically your this term is something like your k i minus 1. So that, is what the parameter which you are defining is written in terms of flux and this is your desorption term now because the molecules are desorbing from i-the layer, so, you wrote it k minus i theta i. So, k minus i means desorption rate constant and that will be depending on the activation energy for desorption. Because, it is a function of temperature, so and new is the frequency factor just like in your r n s equation so, new times u to power E d upon k d T times theta i.

So, this is the term which is relating to the effect of temperature also on desorption. So, this is now the first term which is rate of condensation on i minus 1 layer. This is rate of desorption from i-th layer, this is F theta i that is the adsorption on the, i-th layers so, where from i plus 1 layer. So, rate of evaporation from or desorption from the i plus 1 layer, that has come to this layer and what about the desorption from here has come here into this and this is the meaning of dynamic equilibrium and at equilibrium, there is no net change so this term is 0.

So, you can you can now simplify this equation because, we have certain assumption now that for first layer the activation energy is different for bare surface. But, for subsequent layer the activation energy of each layer is same. So, Ed activation energy for desorption for subsequent layer, when i is greater than 1, than it is same just like heat of adsorption. We have used and k 1 is not equal to k 2 but, k 2, k 3, k 4 and they are equal for the multilayer. Because, it is same kind of molecule which is adsorbing on the surface you can see here, because we have already assumed now E d is same.

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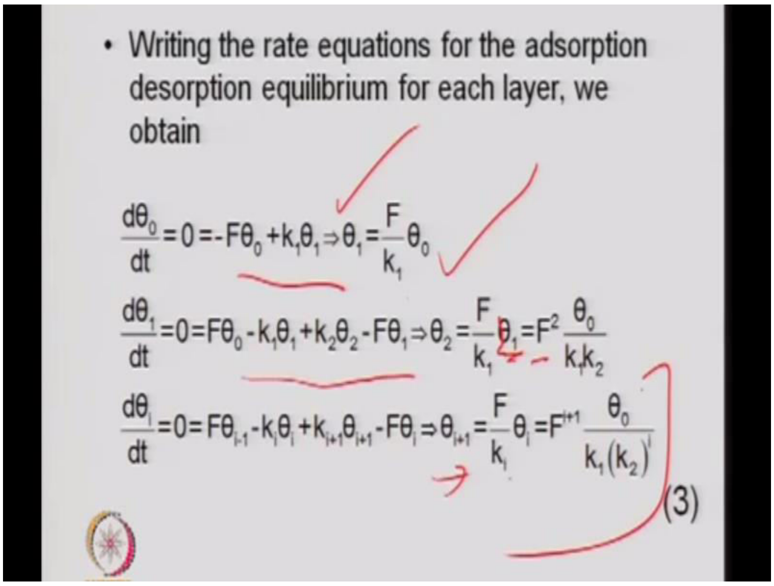

- Writing the rate equations for the adsorption desorption equilibrium for each layer, we obtain

$$\frac{d\theta_0}{dt}=0=-F\theta_0+k_1\theta_1\Rightarrow\theta_1=\frac{F}{k_1}\theta_0$$

$$\frac{d\theta_1}{dt}=0=F\theta_0-k_1\theta_1+k_2\theta_2-F\theta_1\Rightarrow\theta_2=\frac{F}{k_1}\theta_1=F^2\frac{\theta_0}{k_1k_2}$$

$$\frac{d\theta_i}{dt}=0=F\theta_{i-1}-k_i\theta_i+k_{i+1}\theta_{i+1}-F\theta_i\Rightarrow\theta_{i+1}=\frac{F}{k_i}\theta_i=F^{i+1}\frac{\theta_0}{k_1(k_2)^i}\qquad(3)$$

So, 1 can simplify the expressions which I have just written. So, B theta by 0 by dt for the bare surface. So, rate of adsorption on the bare surface will be equal to rate of desorption from the first layer so that is the equation here and so, theta 1 can be correlate. So, basic idea is that we are trying to find out because theta 1 plus, theta 2 plus so, on theta n is to be known. So, theta 1 is equal to F by k 1 times theta 0, for first layer if you write now the same equation because you have already calculated here theta 1. So, you can very easily simplify this equation, so theta 2 comes out to be F by k 1 times theta 1 and when you substitute this theta 1.

So, this becomes F square times theta 0 divided by k 1 k 2 and so on. So, you can have for any i-th layer this theta i plus 1 is equal to F by k i times theta i and that can be substituted in terms of theta i. So, it becomes F i plus 1 times theta 0 divided by k 1 times k 2 to the power i. So, this is a generalized form of equation for i-th layer. So, now what

I mean to say you has determined theta 1, theta 2, and theta 3 and so on. But, still this to be written in terms of theta 0, so theta 0 has to be find out because once theta 0 is known then each term can be calculated and then you can find out sigma of theta i or i theta i.

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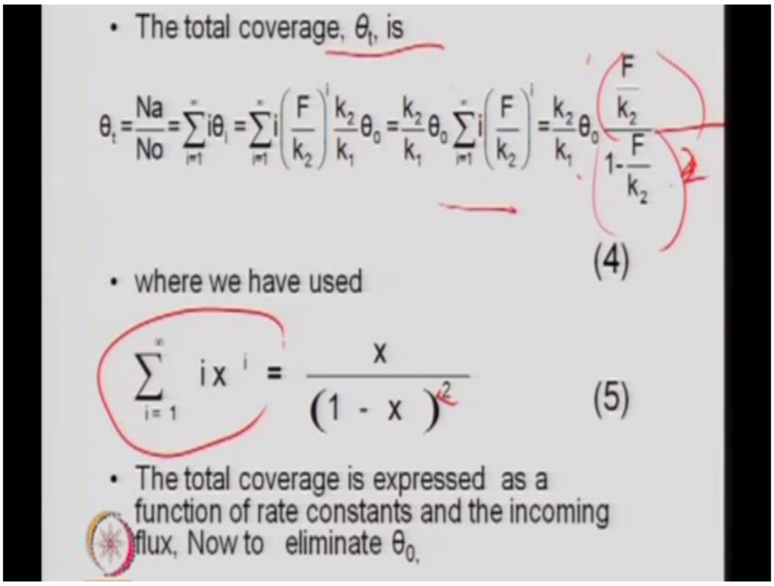

- The total coverage, θ_t, is

$$\theta_t = \frac{Na}{No} = \sum_{i=1}^{\infty} i\theta_i = \sum_{i=1}^{\infty} i\left(\frac{F}{k_2}\right)^i \frac{k_2}{k_1}\theta_0 = \frac{k_2}{k_1}\theta_0 \sum_{i=1}^{\infty} i\left(\frac{F}{k_2}\right)^i = \frac{k_2}{k_1}\theta_0 \frac{\frac{F}{k_2}}{\left(1-\frac{F}{k_2}\right)^2} \qquad (4)$$

- where we have used

$$\sum_{i=1}^{\infty} i x^i = \frac{x}{(1-x)^2} \qquad (5)$$

- The total coverage is expressed as a function of rate constants and the incoming flux, Now to eliminate θ_0.

So, for theta i we just co-relate that total coverage or theta 0 calculation. So, total coverage theta t which we are defining now fraction N a divided by N 0. So, total number of molecule adsorbed and N 0 is the molecule when it is monolayer V m. So, that is nothing but, sigma of i theta i first layer, second layer, third layer so on, add all these layers because, these are the molecules which have been adsorbed on the surface.

So, you can this is a kind of mathematical equation now. So, k 2 by k 1 times theta 0 sigma i 1 2 infinite i F by k 2 to the power i. You must have d1 this kind of solutions here sigma i 1 to infinite i x i is equal to x over 1 minus x whole square. Simple mathematics, you have to just add it to the infinite series and expression. So that, is what the idea here we have just divided the term or separated the term in terms of k2 by k1 theta 0 and rest of the term I have been taken in terms of i 1 to infinite i x which is F by k 2 to the power i so, just this is your F by k2 is your x.

So, you can very easily k2 by k1 times theta 0 F by k2 this is your x divided by 1 minus x whole square so this is 1 minus F by k2 whole square. So, this is just the mathematical expression which can be solved, I think this is 1 over 1 minus x. So, I will just check it and say 1 over 1 minus x solution of this x over 1 minus x not x square. So, that will be F by k 2 1 minus F over k2.

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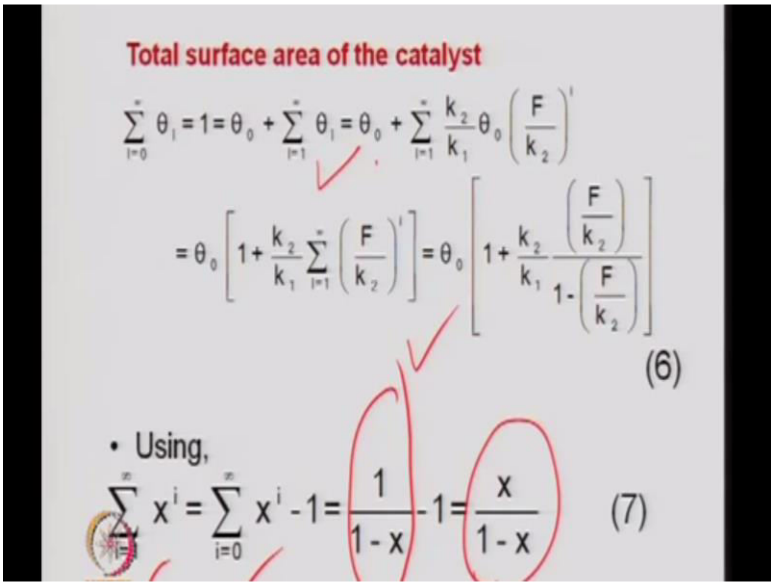

Total surface area of the catalyst

$$\sum_{i=0}^{\infty}\theta_i = 1 = \theta_0 + \sum_{i=1}^{\infty}\theta_i = \theta_0 + \sum_{i=1}^{\infty}\frac{k_2}{k_1}\theta_0\left(\frac{F}{k_2}\right)^i$$

$$= \theta_0\left[1+\frac{k_2}{k_1}\sum_{i=1}^{\infty}\left(\frac{F}{k_2}\right)^i\right] = \theta_0\left[1+\frac{k_2}{k_1}\frac{\left(\frac{F}{k_2}\right)}{1-\left(\frac{F}{k_2}\right)}\right] \qquad (6)$$

- Using,

$$\sum_{i=1}^{\infty}x^i = \sum_{i=0}^{\infty}x^i - 1 = \frac{1}{1-x} - 1 = \frac{x}{1-x} \qquad (7)$$

So, the same expression here, if you look at now sigma of theta i the first term was i theta i and this is sigma of theta i that is addition over a monolayer so, here again theta 0 bare surface plus, the fractions which are already covered. So, i is equal to 1 to infinite theta i and that can be rewritten as theta 0 plus i is equal to 1 to infinite theta i is nothing but, k 2 by k 1 theta 0, F by k2 to the power i which is again based on this expression if you have already d1 before also, i is equal to 1 to infinite x i can be rewritten i 0 to infinite x i minus1 because, the first when it is 0 it is just 1.

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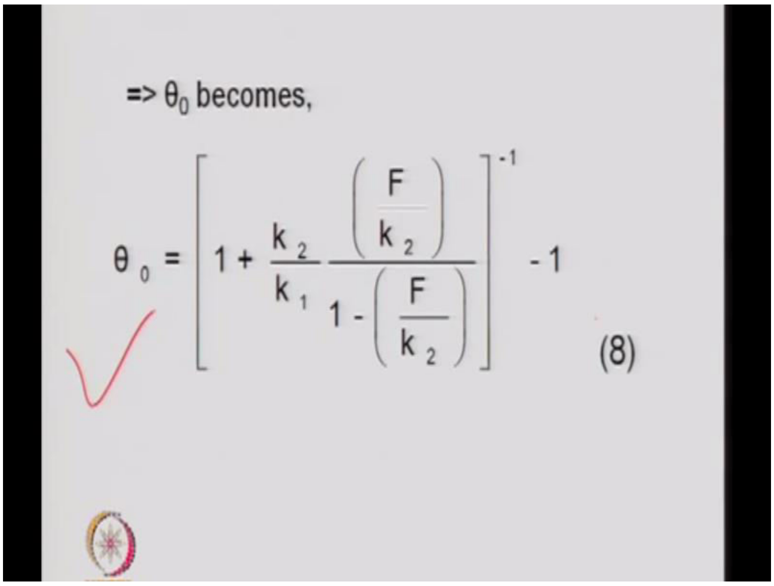

=> θ_0 becomes,

$$\theta_0 = \left[1 + \frac{k_2}{k_1}\frac{\left(\frac{F}{k_2}\right)}{1 - \left(\frac{F}{k_2}\right)}\right]^{-1} - 1 \qquad (8)$$

So, we can write i 0 to infinite and this i 0 to infinite x i is equal to 1 over 1 minus x 0 to infinite x to the power i is nothing but, 1 over 1 minus x, this summation over a series for infinite series you can check it and minus 1. So, that is already there so, this gives you x over 1 minus x. So, it means over x is this F by k2 o, this expression becomes theta 0 times 1 plus this whole term k2 by k1 and summation over this which is now F by k2 which is this x over 1 minus F by k2.

So, you can very easily simplify the expression, which is given over a series up to infinite series and you can simplify it and this is the expression. So, once these 2 are known so, theta 0 is known now because this is your theta 0 which is summation. So, we can very easily write theta 0 which is equal to 1 plus k 2 by k 1, F by k 2 divided by 1 minus F by k 2 to the power minus 1 minus 1. So, this expression for theta 0 which we need to calculate from here that has been calculated in terms of theta i. Because, this expression we had already defined here in terms of theta. So, once theta 0 is known then you can go back to your original expression that theta T was written in terms of theta 0.

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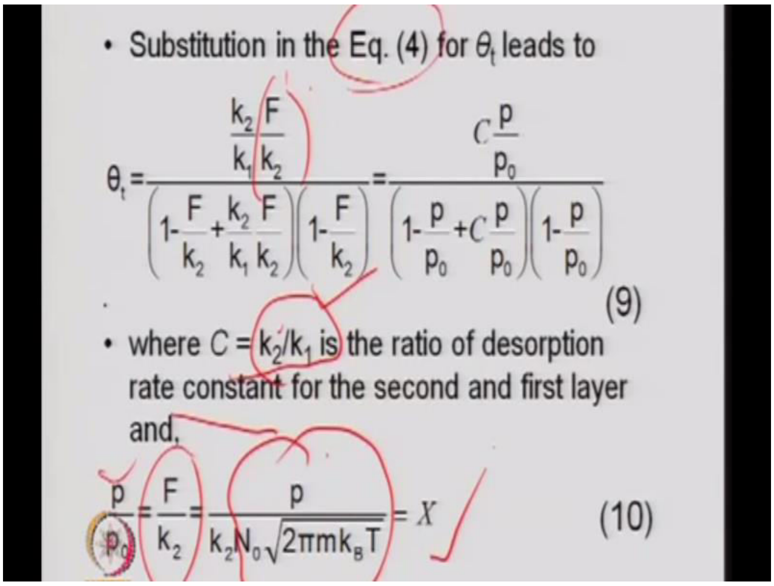

- Substitution in the Eq. (4) for θ_t leads to

$$\theta_t = \frac{\frac{k_2}{k_1}\frac{F}{k_2}}{\left(1-\frac{F}{k_2}+\frac{k_2}{k_1}\frac{F}{k_2}\right)\left(1-\frac{F}{k_2}\right)} = \frac{C\frac{p}{p_0}}{\left(1-\frac{p}{p_0}+C\frac{p}{p_0}\right)\left(1-\frac{p}{p_0}\right)} \qquad (9)$$

- where $C = k_2/k_1$ is the ratio of desorption rate constant for the second and first layer and,

$$\frac{p}{p_0} = \frac{F}{k_2} = \frac{p}{k_2 N_0\sqrt{2\pi m k_B T}} = X \qquad (10)$$

So, this is the expression for theta T so that, was our original equation 4. So, theta T can be calculated now because theta 0 has been substituted. So, k 2 by k 1 times F by k 2 this term divide by 1 minus by k 2 plus k 2 by k1 F by k2 and this whole term in bracket multiplied by 1 minus F by k 2. So, this F I told you is related to pressure and C is the term which we have co-related earlier in terms of exponential of heat of adsorption in the first layer, minus heat of condensation or liquefaction for the subsequent layer and that were related to the activation energy for that subsequent adsorption and activation energy for the desorption.

So, basically this k 2 by k 1, k 2 is for the second layer, k 1 is for the first layer where the adsorption is taking place which I said first layer and then subsequent layer. It is k 2, k 3, k 4 something like that. so that, is the ratio of desorption rate constant for the second layer to the first layer. So, that means the C which we are writing expentially this you can see from here. Because, C we have this already we have defined it in terms of exponential powers here.

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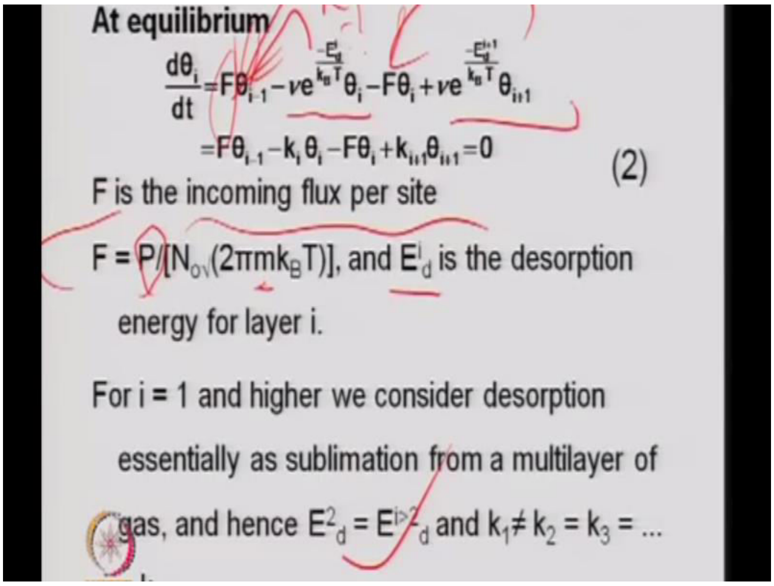

At equilibrium

$$\frac{d\theta_i}{dt} = F\theta_{i-1} - \nu e^{\frac{-E_d^i}{k_B T}}\theta_i - F\theta_i + \nu e^{\frac{-E_d^{i+1}}{k_B T}}\theta_{i+1}$$

$$= F\theta_{i-1} - k_i\theta_i - F\theta_i + k_{i+1}\theta_{i+1} = 0 \qquad (2)$$

F is the incoming flux per site

$F = P/[N_0\sqrt{(2\pi m k_B T)}]$, and E^i_d is the desorption energy for layer i.

For i = 1 and higher we consider desorption essentially as sublimation from a multilayer of gas, and hence $E^2_d = E^{i>2}_d$ and $k_1 \neq k_2 = k_3 = \ldots$

So, these 2 terms which we are talking in terms of desorption in the first layer i is equal to 0.When I am saying bare surface and then for the first layer if you are writing 0 and first because for subsequent layers it is same. So, this C is basically for a bare surface and the subsequent layers so, heterogeneous surface and where the homogenous where the liquid molecule, is already available on the surface and the gas molecule comes and adsorbs. So, this is basically related to enthalpy or activation energy for desorption and the adsorption. So, you can and F we have already defined in terms of the probability of striking that is flux so that, is related to pressure so, F by k 2 is basically p by p 0.

So, we have co-related that F which is already in terms of p divided by N 0 under root 2 phi m k B T. So, if I write F by k 2 so that, can be correlated in terms of pressure because in 1 way, I am writing it is k rate constant for adsorption times p times theta i. So that, k1 times p is your term which is F. So, we can correlate it in terms of the rate constant and that is for the multi layers that is homogenous surface and your flux which comes to that surface number of molecules, which comes to that surface number of molecules which comes in stakes to the surface. So, F divided by k 2 and that whole term we have called now x a constant, just to simply the expression.

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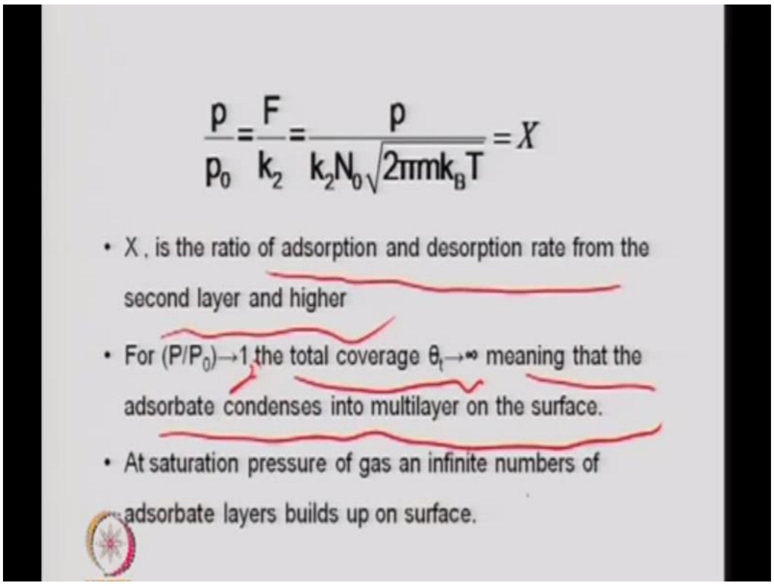

$$\frac{p}{p_0}=\frac{F}{k_2}=\frac{p}{k_2N_0\sqrt{2\pi m k_B T}}=X$$

- X, is the ratio of adsorption and desorption rate from the second layer and higher
- For $(P/P_0)\rightarrow 1$ the total coverage $\theta_t \rightarrow \infty$ meaning that the adsorbate condenses into multilayer on the surface.
- At saturation pressure of gas an infinite numbers of adsorbate layers builds up on surface.

Now, if you just write it in form of p by p0 which you have f by k2 that I have already discussed that is your x. So, your equation which we are taking x is the ratio of adsorption and desorption rate from the second layer and higher. So, how many molecules adsorbed and how many molecules desorbed for subsequent layer. So, you can find out and co-relate it because p 0 is the saturation pressure and p is the pressure so, at saturation no further adsorption takes place.

So, when p by p0 which is to 1 then your total coverage theta T up to infinite that I have said that the layers are completed or this is nothing but, at this is the point where condensation is starred and the capillary condensation phenomena, which we are discussing for nitrogen adsorption desorption isotherm. So, pores are totally filled when pores are filled nothing can be adsorbed now. So, it means the bet isotherm validity it up to a certain ratio of p by p 0 because, after that the capillary condensation phenomena starts and then isotherm is no more valid correct. So, this is what the adsorbate condenses into the multilayer on the surface. So, a capillary condensation phenomenon starts in micro pore. So, at saturation pressure of gas an infinite number of adsorbate layers built up on the surface.

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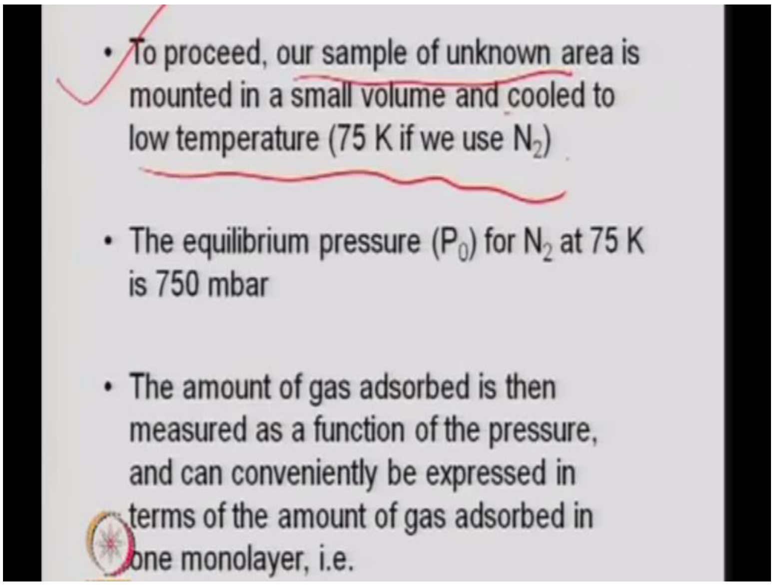

- To proceed, our sample of unknown area is mounted in a small volume and cooled to low temperature (75 K if we use N_2)
- The equilibrium pressure (P_0) for N_2 at 75 K is 750 mbar
- The amount of gas adsorbed is then measured as a function of the pressure, and can conveniently be expressed in terms of the amount of gas adsorbed in one monolayer, i.e.

So, now how to use this isotherm because now we have discussed this isotherm the derivation of this isotherm and the meaning of C, which is related to the adsorption and desorption activation energy or heat of adsorption on the bare surface and heat of condensation on the subsequent surface. So, these parameters can be determined experimentally, also and by using the isotherm equation so, when you do that so, when because now our interest is to find out the surface area of the solid catalyst.

So, to precede for any unknown sample the given mass we have to put in a small volume and cooled to a lower temperature something like 75 Kelvin for nitrogen. So, generally 77 Kelvin or 75 Kelvin is the condensation temperature of nitrogen. So, what you have to do in the specified chamber; like what you call BET operators. So, you put a given mass of catalyst and over that you allow the nitrogen gas in presence of some may be helium also or nitrogen itself that is passed through the sample and you has to calibrate the system first. So, helium can be used for that and then you place a flask which contains liquid nitrogen and that will allow the gas to adsorb.

And then you measure through a detector the volume of the gas which is adsorbed, as a function of pressure you need not to go to p 0 values. So, you can define the points so, p by p0 value and then you can find out the number of molecule, adsorbed and then you can use this isotherm because this is nothing but, a linear form of isotherm, where we are just plotting P upon v into p0 minus p versus p by p0 so, this will be a straight line. So, the meaning is that if I have this isotherm.

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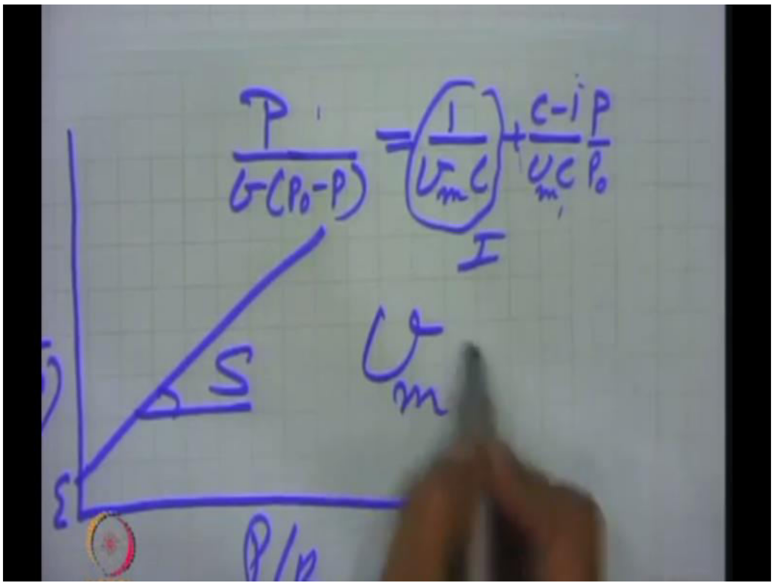

So, we have a linear form of this equation now which I can write here again. So, P upon V into p0 minus p the same isotherm what we have derived here is in the linearzed form. So, I am just writing it again here this form of isotherm this is your BET isotherm, where when we write it in terms of fraction. So, a plot of this p upon V into p0 minus p is equal to 1 upon V m C plus c minus 1 upon V m C into p by p0. So, a plot of this that is P upon V into p0 minus p versus p by p0 will be a straight line like this.

So, this can be the linear form or non-linear form can also be used by using the software's regression technique, you can use the non-linear regression technique or linear regression method and you can find out the parameter. Because, this is your interception of this is your interception i and this is your slope S, c minus v upon c m because this is times p by p0 here.

So, this c minus 1 upon V m C is your slope. So, from these 2 you can find out the surface area or V m value because, first we have to find out V m. So, this can be used to determine the surface area. So, same thing has been discussed here that you allowed the gas to adsorb and then measure the volume of the gas adsorbed as a function of partial pressure or pressure of the gas. So, at when there is an equilibrium that is p0 which will at temperature 75 Kelvin the pressure is roughly 750 mile bar. That is the saturation pressure of nitrogen. So, amount of gas adsorbed, either in terms of number of molecule or volume is then measured as a function of pressure and can conveniently be expressed in terms of amount of gas adsorbed in 1 monolayer. So, we are interested in having a monolayer V m or n m which is given here now.

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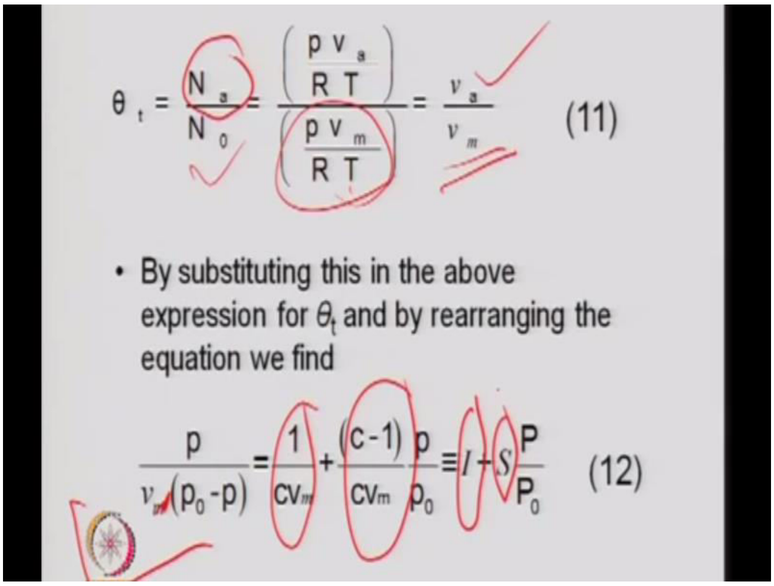

$$\theta_t = \frac{N_a}{N_0} = \frac{\left(\frac{p\,v_a}{R\,T}\right)}{\left(\frac{p\,v_m}{R\,T}\right)} = \frac{v_a}{v_m} \qquad (11)$$

- By substituting this in the above expression for θ_t and by rearranging the equation we find

$$\frac{p}{v_a(p_0-p)} = \frac{1}{cV_m} + \frac{(c-1)}{cV_m}\frac{p}{p_0} \equiv I + S\frac{P}{P_0} \qquad (12)$$

So, this is the number of molecules of the gas total number of molecule of gas which adsorb on the surface and this is when the monolayer forms. So, this is something related to V m which I have written here and this is the volume which is adsorbed for the total number of layers, which are i theta i sigma in that layers. So, basically you know p v is equal to N R T so, we are applying that law here. So, number of molecule p v is equal to N R T so, N has been calculated same thing for N has been calculated at monolayer. So, this gives you v upon V m which I just said before.

So, by substituting this in your equation which we have derived earlier for theta T and just rearrange that. So, you have the expression like this p upon V into p0 minus p. So, basically this is your V naught V m is equal to 1 upon V m C plus C minus 1 upon C V m p by p 0 which I just said and so, this is your interception. So, I called it I and this is your slope so I called it S. So, this can be used to determine the surface area of a solid.

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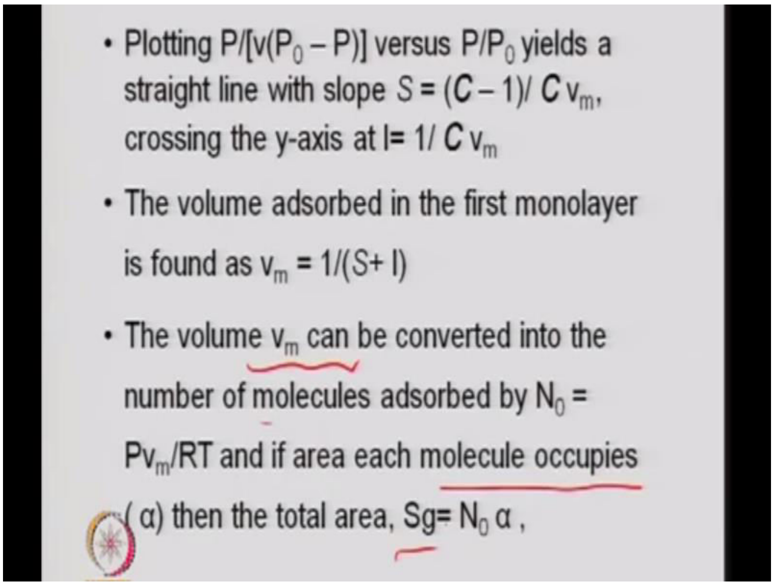

- Plotting $P/[v(P_0 - P)]$ versus P/P_0 yields a straight line with slope $S = (C - 1)/ C v_m$, crossing the y-axis at $I = 1/ C v_m$
- The volume adsorbed in the first monolayer is found as $v_m = 1/(S + I)$
- The volume v_m can be converted into the number of molecules adsorbed by $N_0 = Pv_m/RT$ and if area each molecule occupies (α) then the total area, $Sg = N_0 \alpha$,

So, plotting P over V into P0 minus P versus P by P0 will give you a straight line with the slope of S which is C minus 1 upon C V m and interception I 1 upon V m C. So, you can very easily solve these 2 equations and you can find out V m is equal to 1 upon slope plus interception I plus S. And once that is known the volume of V m that is this, can be converted into number of molecules adsorbed by N0 which is equal to P into V m upon RT, as I before also and if the area of 1 molecule is known then your BET surface area is nothing. But, N0 times alpha area of 1 molecule multiplied by the number of molecule in the monolayer.

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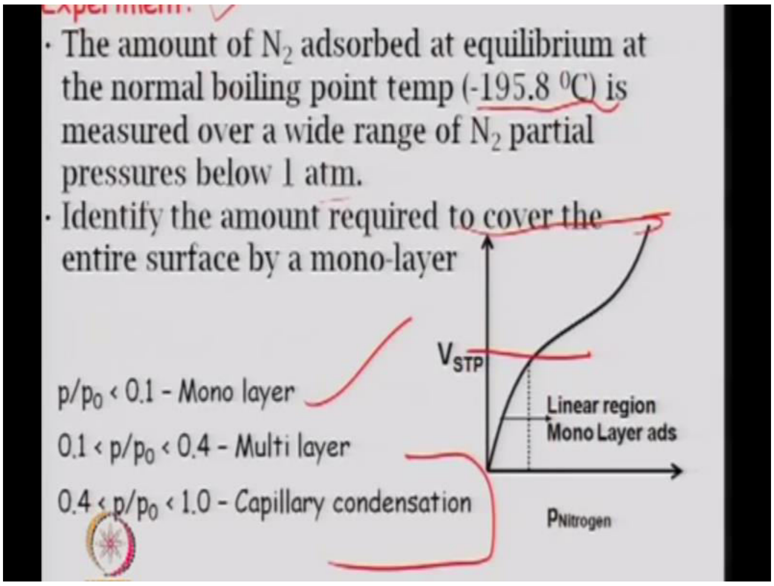

- The amount of N_2 adsorbed at equilibrium at the normal boiling point temp (-195.8 °C) is measured over a wide range of N_2 partial pressures below 1 atm.
- Identify the amount required to cover the entire surface by a mono-layer

$p/p_0 < 0.1$ - Mono layer

$0.1 < p/p_0 < 0.4$ - Multi layer

$0.4 < p/p_0 < 1.0$ - Capillary condensation

So, this is what the data how to use that data because, as I said if you had used the Langmuir adsorption isotherm, it will show a monolayer here because it does not talk about multilayer adsorption. So, Langmuir isotherm will talk about V m value here. But, BET actually the V m is 0. So, your Langmuir adsorption isotherm if you calculate the surface area from that it will always be higher than your BET surface area, because BET Isotherm has removed those multilayer molecule, or multi layers in compared to the Langmuir. But, when it is a chemisorptions, chemical adsorption then both these areas will be equal because that time though no further chemisorptions is possible.

So, basically when you take the data when generate the data for this determination of surface area of a catalyst, then same thing can be extended for pore size distribution also by nitrogen adsorption desorption method, which is your capillary condensation. So, you have to just consider the normal boiling temperature that in nitrogen. Generally, adsorbs at this as I said 77 Kelvin minus 196 degree centigrade or 77 Kelvin is measured over a wide range of partial pressure which is below 1 for saturation 750, what I said before also millimeter of mercury.

So, identify the amount required to cover the entire surface by the monolayer. So, this is a monolayer. So, generally p by p 0 less than 0.1 is a monolayer and when p by p 0 reached from 0.1 to 0.4 a multilayer starts and beyond 0.4 it becomes a capillary condensation. So, we need not to when we have to determine the surface area, we need not to go to this range, when you have to determine the capillary condensation of pore size distribution then you have to desorb it also. Desorption isotherm has to be used then you have to fill the pore or saturate the pore first. So, this generally up to 0.3 you can generate the data for this isotherm to check or just 0.1 is also sufficient. So, how many data points are required, that you have to check on a priory and 1 can use this isotherm very easily for determination of surface area.

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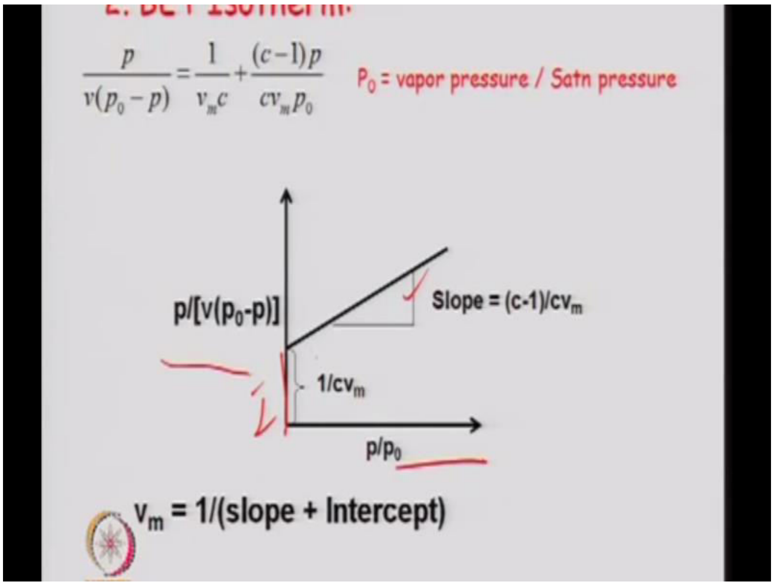

$$\frac{p}{v(p_0-p)}=\frac{1}{v_m c}+\frac{(c-1)p}{c v_m p_0}$$

P_0 = vapor pressure / Satn pressure

V_m = 1/(slope + Intercept)

So, Langmuir Isotherm as I said it is something like the theta is equal to K p upon 1 plus K p. So, if you just linear zed this theta is your v by v m volume of gas adsorbed divided by monolayer coverage. So, p upon v is equal to 1 upon K v m plus p upon v m. So, a plot of this p upon v versus p is a straight line and you can find out monolayer. But, for physical adsorption this value will be higher so, not very light BET Isotherm, we have already discussed now.

So, p upon v into v 0 minus p is equal to 1 upon V m C plus C minus 1 upon C V m as p by p0 where p0 is the vapor pressure or saturation pressure. So, p upon v upon divided by p upon v divided by p 0 minus p versus p by p 0 gives you a straight line. Find out this slope and find out interception and solve it, then once that V m is known because, from this graph you get the v m.

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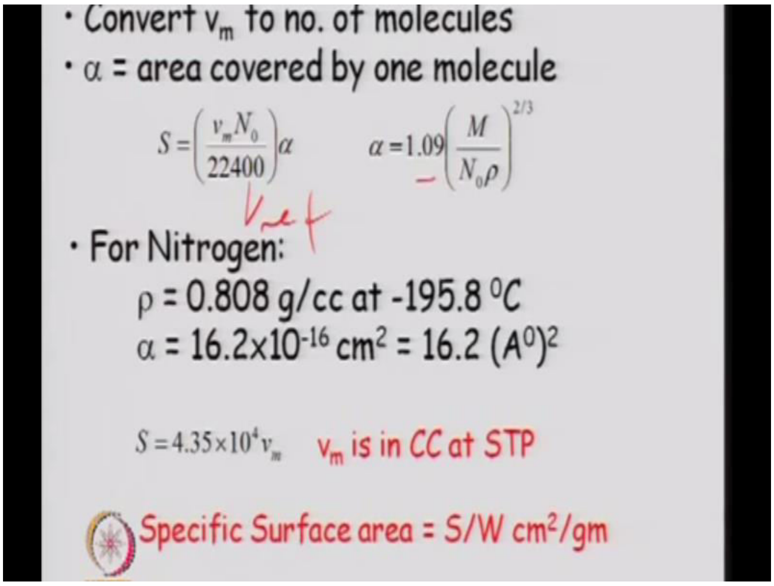

- Convert v_m to no. of molecules
- α = area covered by one molecule

$$S = \left(\frac{v_m N_0}{22400}\right)\alpha \qquad \alpha = 1.09\left(\frac{M}{N_0 \rho}\right)^{2/3}$$

- For Nitrogen:

$\rho = 0.808$ g/cc at $-195.8\ ^0C$
$\alpha = 16.2 \times 10^{-16}\ cm^2 = 16.2\ (A^0)^2$

$S = 4.35 \times 10^4 v_m$ V_m is in CC at STP

Specific Surface area = S/W cm^2/gm

So, then you can calculate because, alpha is the area covered by 1 molecule as I said before. So, surface area is v m times N 0 divided by 22400 which is your V reference basically into alpha area covered by 1 molecule. So, alpha I discussed yesterday is the projected area phi r square. Where a r is the radius of the molecule. So, nitrogen which adsorbing on the surface so, that is F times I told a packing factor. So, basically that is 1.09 so, it becomes 1.09 times M by N0, rho to the power 2 by 3, where m is the molecule weight of the gas, N 0 is the Avogadro number and rho is the density of the liquid nitrogen or density of the gas at adsorption condition.

So, remember this is the density of the liquid nitrogen because the condensation is for liquid nitrogen or density of the nitrogen at 77 Kelvin. So, this value is written here 0.808 gram per centimeter cube of layer that condensation temperature of nitrogen gas molecule and alpha it gives you roughly 16.2 square which can be used. So, you can very easily find out the surface area that will be forgiven mass so, divided by mass of the catalyst.

So, we call that specific surface area. So, these are some of the data if you look at from literature, lot of literature is available for different kind of solid material and you can use them. So, silica gel roughly has the average pore diameter of 10 nanometer and surface area roughly 200 meter square per gram at different, if you have different treated silica gel, it can have surface area 6 mean diameter 6 nanometer and surface 400. So, different kind of area may be available from the same solid material, depending upon the catalyst preparation, centering, ageing temperature. You can have the variety same thing for gamma alumina say surface area roughly 150 and it can be 500 also, pore size 10 nanometer average and 5 nano meter smaller the pores.

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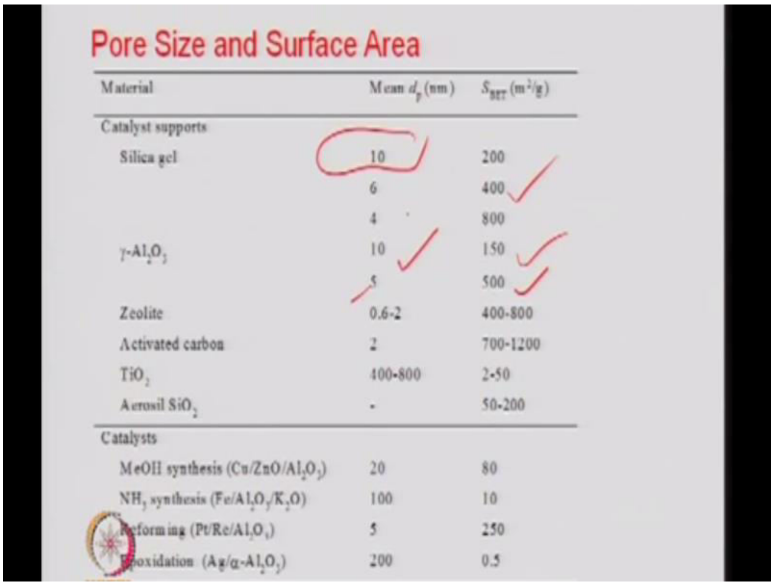

Pore Size and Surface Area

Material	Mean d_p (nm)	S_{BET} (m^2/g)
Catalyst supports		
Silica gel	10	200
	6	400
	4	800
γ-Al_2O_3	10	150
	5	500
Zeolite	0.6-2	400-800
Activated carbon	2	700-1200
TiO_2	400-800	2-50
Aerosil SiO_2	-	50-200
Catalysts		
MeOH synthesis ($Cu/ZnO/Al_2O_3$)	20	80
NH_3 synthesis ($Fe/Al_2O_3/K_2O$)	100	10
Reforming ($Pt/Re/Al_2O_3$)	5	250
Epoxidation (Ag/α-Al_2O_3)	200	0.5

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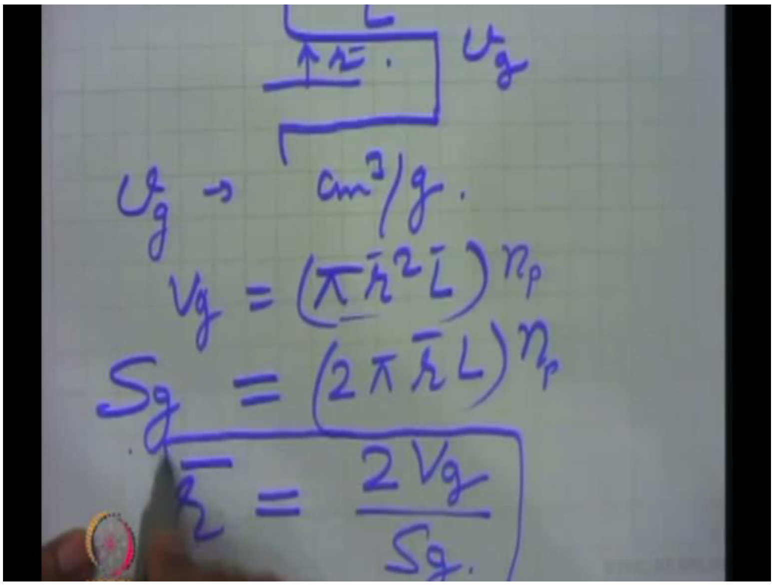

$$v_g \rightarrow cm^3/g.$$

$$V_g = (\pi \bar{r}^2 \bar{L}) n_p$$

$$S_g = (2 \pi \bar{r} L) n_p$$

$$\boxed{\bar{r} = \frac{2 V_g}{S_g}.}$$

So, pore size is related to surface area, if you just look at the cylindrical geometrical pore straight cylindrical, if I say if radius is r and pore volume is V g. So, V g generally I said pore volume. So, V g unit is generally defined centimeter cube per gram of the catalyst.

So, basically what is V g? So, V g if I talk a cylinder of this pore length average pore length L bar average radius r bar. So, total pore volume so, average pore radius I am talking so, that is simply pi r square into L something like this average and I will say r bar and times the whatever because, this is the pore volume. So, times the number of pore this is for 1 pore. So, average pore radius has been defined average pore length has been defined and if there are n numbers of pores, you can write it like this.

What is S g? S g is the surface area of the catalyst. So, surface area is not the external it is not suppose if I say a solid pellet and this is not that radius or surface area of that solid. It is the area because of these pores cylindrical pores. So, if they we have already defined so, surface area is basically for a cylinder 2 phi r bar L so that, will become 2 phi r bar L for 1 pore and the n number of pores so it is like this. So, I can very easily develop a relationship between these 2 that if you just divide these 2 expressions. So, you will have average pore radius r bar is equal to 2 times V g divided by S g. So, this can be used 2 determine the average pore size. So, smaller the capillary so, there may be larger number of pores in the same solid so, micro porous material, ratio porous material, so like that.

So, this is generally used to determine the average pore size of a catalyst for a given mass. So, same thing for Zeolite you know Zeolites are the smaller pores. So, 0.6 nanometer can be the average pore size or diameter and the area can be between 400 and 800 BET square per gram. So, same thing Activated carbon you can see it can have the area up to 1200 BET Square per gram.

So, different metals, so different catalyst can be used for methanol synthesis, copper zinc oxide on alumina catalyst have been tested; ammonia synthesis, iron alumina and potassium oxide is promoter have been tested. There forming platinum range alumina has been used or is being used also same thing for a epoxidation in petro chemical industry the ethylene oxidation. Resins formation so still what ways catalyst are used on alpha alumina. So, different catalyst can be used who have been tested for different process and the surface area and the pore size or pore size distribution is strongly depends on the pore geometry, catalyst preparation, raw materials ageing, drying is very crucial.

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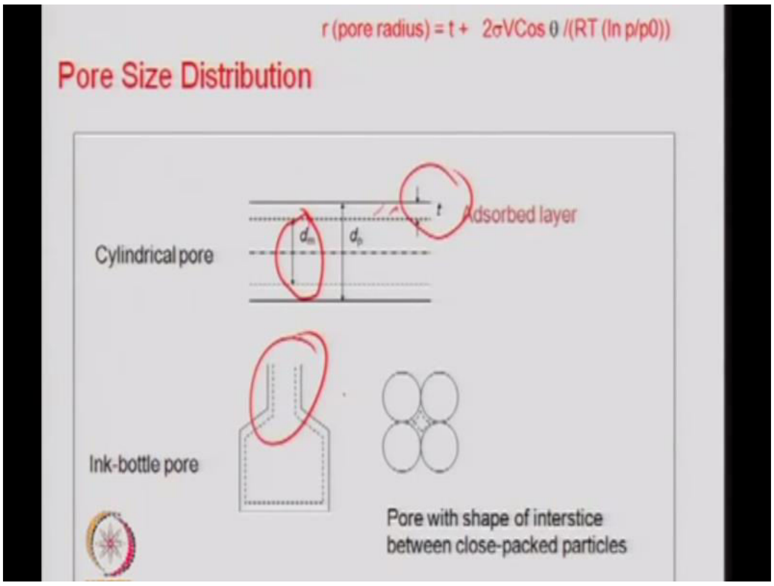

r (pore radius) = t + $2\sigma V \cos\theta / (RT (\ln p/p0))$

Pore Size Distribution

Pore with shape of interstice between close-packed particles

So, we have already discussed this thing last time also but, since the condensation phenomena takes place and based on that we determine the pore size distribution; that is capillary condensation when you have nitrogen adsorption desorption method. So, basically it is a BET method, again now only thing that you are going towards saturation or you are applying higher pressure and then calculating. So, your T plots method which generally used to find out the thickness and same thing. The adsorption desorption which is used for pore size distribution and volume of the pore and same thing for the mercury penetration method approach is based on surface tension effect.

But, the same fundamental thing pressure is applied in then we calculate delta v. So, in the case of nitrogen, when we talk we have this term adsorbed layer thickness. So, we have to find out this also, a t plot is to be d1 where this can be plotted as a function of size of the pore, pore size and you can find out the surface area also from the slope. So, this is to be compared with a non-porous material then only you can do that because in non-porous material there would not be any pores.

So, only this thickness of the adsorbed layer will come so that is why yesterday we are talking 0.305 nanometer, So that, is at for nitrogen that is 1 monolayer formed that t m will be there. So, to how many layers are formed, you can very you can calculate and correlate it with the adsorbed layer thickness. That will be required when you find out the pore size distribution because your capillary condensation will give you or Kelvin equation gives the radius which is beyond that t value.

So, this is what you get from the Kelvin equation or condensation method. This is already adsorbed layer this is an adsorbed layer. So, this plus t so, t has to be determined so, as I said wheeler's model can be used for finding out and this thickness maybe a function of pressure. Adsorbed layer thickness relates to the pressure and hysteresis. Again you can get the idea about the type of pore their complex nature because, the adsorption, desorption hysteresis which you get because of these kind of ink bottle effect here. They maybe kind of ageing it are a slit type pore. So, you will have a different kind of adsorption desorption hysteresis in these kind of pores, a pores are straight cylindrical you would not get any hysteresis.

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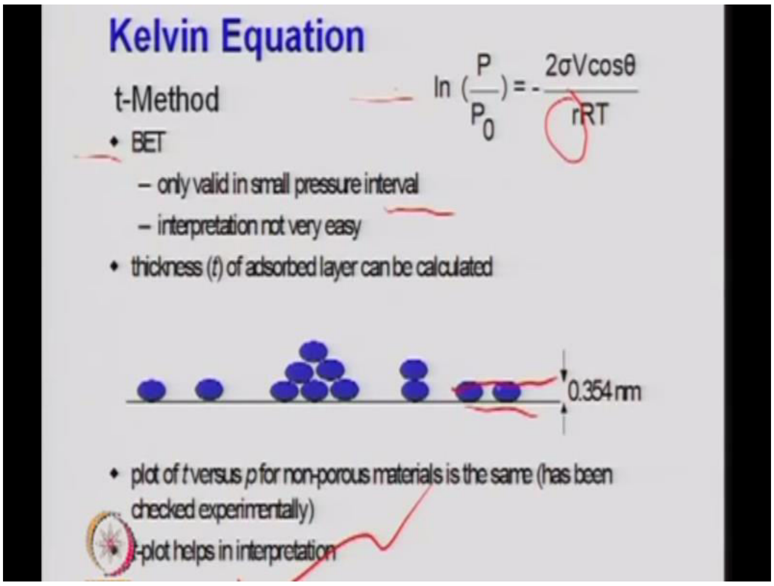

Kelvin Equation

$$\ln\left(\frac{P}{P_0}\right) = -\frac{2\sigma V\cos\theta}{rRT}$$

t-Method

- BET
  - only valid in small pressure interval
  - interpretation not very easy
- thickness (t) of adsorbed layer can be calculated

- plot of t versus p for non-porous materials is the same (has been checked experimentally)
- t-plot helps in interpretation

So, this we have discussed last time at this either Kelvin equation, which relates the vapor pressure required to condense the pore the nitrogen gas in a capillary. So, pressure is related with the radius of that capillary here. So, r sigma we have talked surface tension of the nitrogen v is the volume or the molecule of the gas liquid nitrogen and theta is the contact angle, which was taken 0. Because, it is a wets the surface nitrogen wets the surface.

So, t method which is BET only valid for small pressure intervals so, only you have to look at the pressure differentials. So, very narrow range pressure differentials p and then go p plus delta p in a small range point 0 1 variation whatever the pressure so that, is very important. So, thickness of the adsorbed layer can be calculated and this is for the 1 layer what I have stopping for nitrogen roughly 0.354 nanometer t m. But, you have to calculate the multilayer thickness so that can be determined.

So, plot of thickness versus pressure for a non-porous material is the same and that has have been. So, when you are in that has been done in this and check the experimentally. Then when you plot the thickness versus pressure for a non porous material nothing will condense in the capillary there are no capillary. So, only it will be thickness of the layer adsorbed layer or t m monolayer, so that can be used to calculate the t m value this for a non-porous material. So, 2 plots can give you the idea how to interpret or check the complex nature of the pore by looking at this data.

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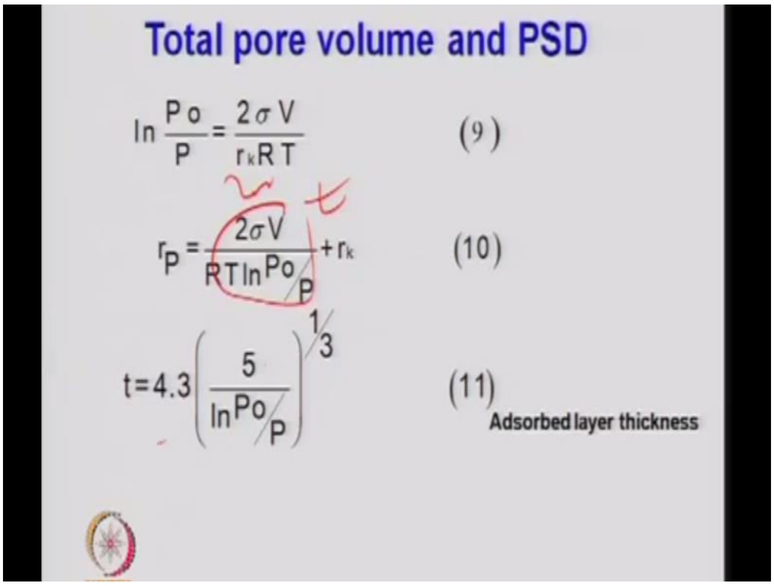

Total pore volume and PSD

$$\ln\frac{P_o}{P} = \frac{2\sigma V}{r_k RT} \quad (9)$$

t

$$r_p = \frac{2\sigma V}{RT\ln P_o/P} + r_k \quad (10)$$

$$t = 4.3\left(\frac{5}{\ln P_o/P}\right)^{1/3} \quad (11)$$

Adsorbed layer thickness

So, the pore volume pore size distribution PSD so that, is again important when you look at because 1 thing is that you can determine the average pore size. But, that is not a correct way of representing the pore size when you have a dispersed pore or different type of pores. So, 1 pore or some pores may have a diameter of say 50 nanometer and other pores are of a diameter of say 500 nanometer you cannot compare these your results were entirely different. So, you have to just look at the distribution that what fraction of the pore or what fraction of the pores has this much volume and what is the pore size distribution same thing for the second, if they are a wide variation in the pore size.

So, Kelvin equation is this now I have written here r k because this will give you the Kelvin radius. So, and this is to be added in the find out the total pores so that, is some integral coalition which is to be used to find out t. So, I can write it t here r k plus t thickness of that layer, adsorbed layer. So that is your radius of the pore where this thickness can be determined by this.

So, thickness is a function of pressure as you have seen here. So, this roughly comes 4 0.3 it is the same equation; so 0.43 times 5 divided by l n o p0 by p to the power 1 by 3 because, last time I told n is 3. So, wheelers this is basically wheeler's model so, we can find out the thickness of the adsorbed layer. Now, if you nowadays the software's are available if you just have the instrument then these are already available in the software, where you have to just generate the data in terms of pressure as a function of volume adsorbed and then the software calculates all these things and it gives you the data but, we have to see here that how these data have been generated.

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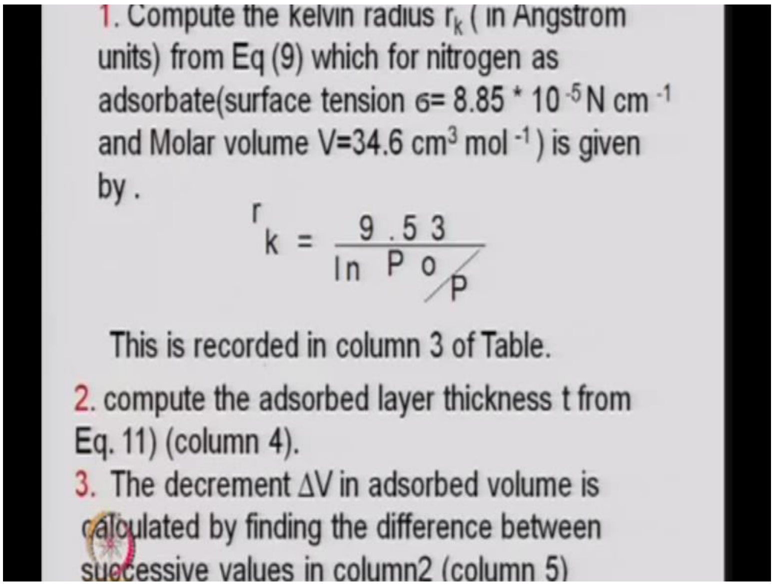

1. Compute the kelvin radius r_k (in Angstrom units) from Eq (9) which for nitrogen as adsorbate(surface tension $\sigma = 8.85 * 10^{-5}$ N cm^{-1} and Molar volume V=34.6 cm^3 mol^{-1}) is given by .

$$r_k = \frac{9.53}{\ln P_o/P}$$

This is recorded in column 3 of Table.

2. compute the adsorbed layer thickness t from Eq. 11) (column 4).
3. The decrement ΔV in adsorbed volume is calculated by finding the difference between successive values in column2 (column 5)

So, just I am looking certain steps or briefly I will or quickly I will just go to these steps which are generally used to give a complete characterization of the catalyst. This is something like what different kind of solids a plot something like this.

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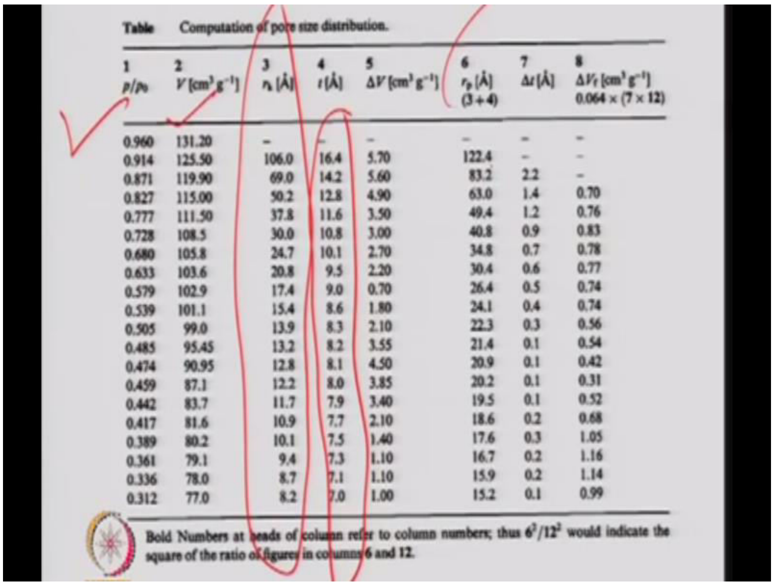

Table Computation of pore size distribution.

1 p/p_0	2 V [cm^3 g^{-1}]	3 r_k [Å]	4 t [Å]	5 ΔV [cm^3 g^{-1}]	6 r_p [Å] (3+4)	7 Δt [Å]	8 ΔV_t [cm^3 g^{-1}] 0.064 × (7 × 12)
0.960	131.20	–	–	–	–	–	–
0.914	125.50	106.0	16.4	5.70	122.4	–	–
0.871	119.90	69.0	14.2	5.60	83.2	2.2	–
0.827	115.00	50.2	12.8	4.90	63.0	1.4	0.70
0.777	111.50	37.8	11.6	3.50	49.4	1.2	0.76
0.728	108.5	30.0	10.8	3.00	40.8	0.9	0.83
0.680	105.8	24.7	10.1	2.70	34.8	0.7	0.78
0.633	103.6	20.8	9.5	2.20	30.4	0.6	0.77
0.579	102.9	17.4	9.0	0.70	26.4	0.5	0.74
0.539	101.1	15.4	8.6	1.80	24.1	0.4	0.74
0.505	99.0	13.9	8.3	2.10	22.3	0.3	0.56
0.485	95.45	13.2	8.2	3.55	21.4	0.1	0.54
0.474	90.95	12.8	8.1	4.50	20.9	0.1	0.42
0.459	87.1	12.2	8.0	3.85	20.2	0.1	0.31
0.442	83.7	11.7	7.9	3.40	19.5	0.1	0.52
0.417	81.6	10.9	7.7	2.10	18.6	0.2	0.68
0.389	80.2	10.1	7.5	1.40	17.6	0.3	1.05
0.361	79.1	9.4	7.3	1.10	16.7	0.2	1.16
0.336	78.0	8.7	7.1	1.10	15.9	0.2	1.14
0.312	77.0	8.2	7.0	1.00	15.2	0.1	0.99

Bold Numbers at heads of column refer to column numbers; thus $6^2/12^2$ would indicate the square of the ratio of figures in columns 6 and 12.

So, the data which is generally used raw data will be something like P by P 0 versus pressure and then we have to calculate this Kelvin radius and then thickness of the adsorbed layer which is also a function of pressure. So, you can see that this thickness of the adsorbed layer may vary from 16 point 4 to 7 in angstrom unit.

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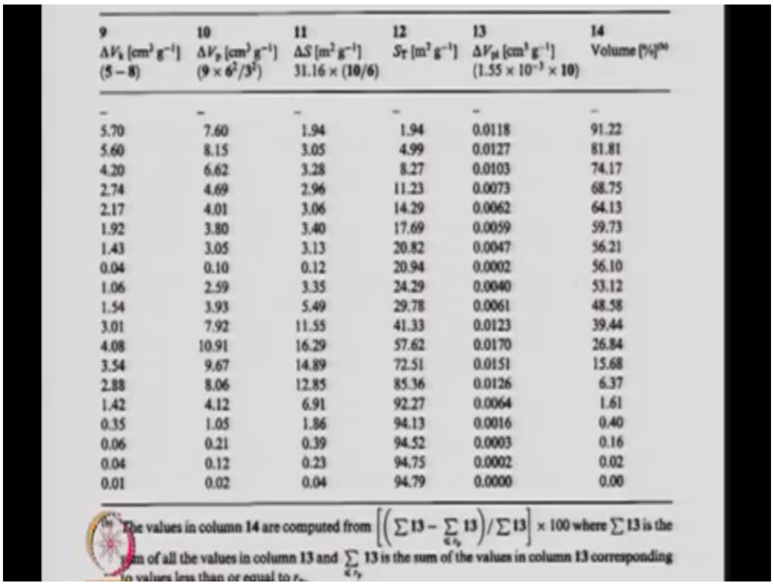

9 ΔV_k [cm^3 g^{-1}] (5 − 8)	10 ΔV_p [cm^3 g^{-1}] (9 × $6^2/3^2$)	11 ΔS [m^2 g^{-1}] 31.16 × (10/6)	12 S_T [m^2 g^{-1}]	13 ΔV_{pl} [cm^3 g^{-1}] (1.55 × 10^{-3} × 10)	14 Volume (%)$^{(a)}$
–	–	–	–	–	–
5.70	7.60	1.94	1.94	0.0118	91.22
5.60	8.15	3.05	4.99	0.0127	81.81
4.20	6.62	3.28	8.27	0.0103	74.17
2.74	4.69	2.96	11.23	0.0073	68.75
2.17	4.01	3.06	14.29	0.0062	64.13
1.92	3.80	3.40	17.69	0.0059	59.73
1.43	3.05	3.13	20.82	0.0047	56.21
0.04	0.10	0.12	20.94	0.0002	56.10
1.06	2.59	3.35	24.29	0.0040	53.12
1.54	3.93	5.49	29.78	0.0061	48.58
3.01	7.92	11.55	41.33	0.0123	39.44
4.08	10.91	16.29	57.62	0.0170	26.84
3.54	9.67	14.89	72.51	0.0151	15.68
2.88	8.06	12.85	85.36	0.0126	6.37
1.42	4.12	6.91	92.27	0.0064	1.61
0.35	1.05	1.86	94.13	0.0016	0.40
0.06	0.21	0.39	94.52	0.0003	0.16
0.04	0.12	0.23	94.75	0.0002	0.02
0.01	0.02	0.04	94.79	0.0000	0.00

(a) The values in column 14 are computed from $\left[\left(\sum 13 - \sum_{\leq r_p} 13\right)/\sum 13\right] \times 100$ where $\sum 13$ is the sum of all the values in column 13 and $\sum_{\leq r_p} 13$ is the sum of the values in column 13 corresponding to values less than or equal to r_p.

So, there when the pressure varies then thickness may also vary and then you calculate the difference in volume, that delta v for an incremental pressure p what is the additional volume which have been adsorbed. When you have changed the pressure from p to plus delta p and then you calculate the pore radius r k plus t. Then you calculate; what is the additional thickness of the layer which has been increased rather between 2 successive pressure changes and then you calculate.

So, many things are required here, if you look at when you look a complete characterization. So, which can be a t plot it can be a Barrett Joyner and Halinda plot. The different kind of software's or packets or so, it is available to determine these. So, the salient points which I am talking here to find out this. So, I just have written certain steps.

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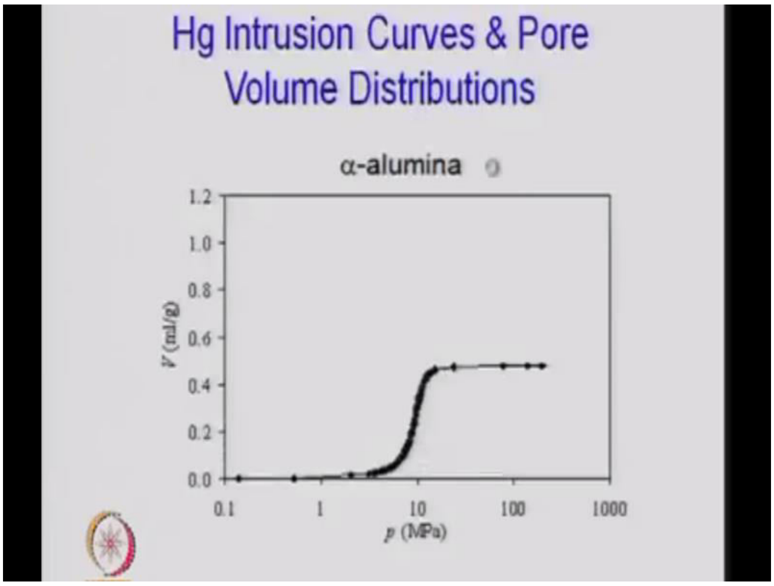

Hg Intrusion Curves & Pore Volume Distributions

So, first thing is that calculating the Kelvin equation r k. So, compute Kelvin radius in the unit of angstrom and that equation. We have already talked this 1 Kelvin radius. So, which for nitrogen as an adsorb ate surface tension of nitrogen is 8.85 into 10 to power 5 minus 5 Newton per centimeter molar volume of nitrogen, we talked yesterday also roughly 35 centimeter cube per gram mole. So, r k is then roughly 9.53 divided by l n of P0 by P.

So, this is the same equation 9 which have been now simplified after substituting the parameters sigma has been substituted r is the gas constant; t is the temperature in Kelvin. So, 1 can very easily find out this r k Kelvin radius. But, different pressure of the gas you have different Kelvin radius. So, this is given in table 3 as I shown and we will just look at that. So, Kelvin once you have the data in terms of P by P 0 versus p.

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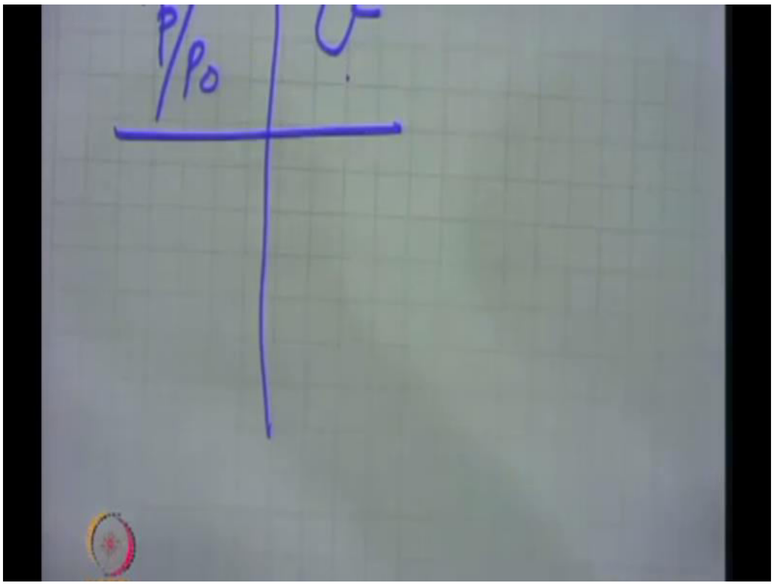

So, your data is something like a different pressure you is generating P by P0 data then recording in terms of volume of the gas adsorbed at a given condition of temperature. So, you are generating these data and then once this because you're P0 is known now saturation pressure is known P is known. So, you very easily find out what we did the Kelvin radius of that condition.

So, the first one, then what this is known then find out the adsorbed layer thickness t again from this equation because, both terms are known P is known P0 is known saturation pressure. So, thickness can be calculated and once thickness is known you can find out, because you have already measured the volume at given pressure P and P plus delta P what is the additional increase in volume. So, delta v can be calculated. So, volume adsorbed is calculated by difference between the successive values in column 2. So, I will just discuss this next time. So, I stop here and we will continue it next time.