Heterogeneous Catalysis and Catalytic Processes
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Module - 03
Lecture – 09

In my last lecture, I was talking about textual properties of the catalyst and we were talking about the adsorption isotherm.

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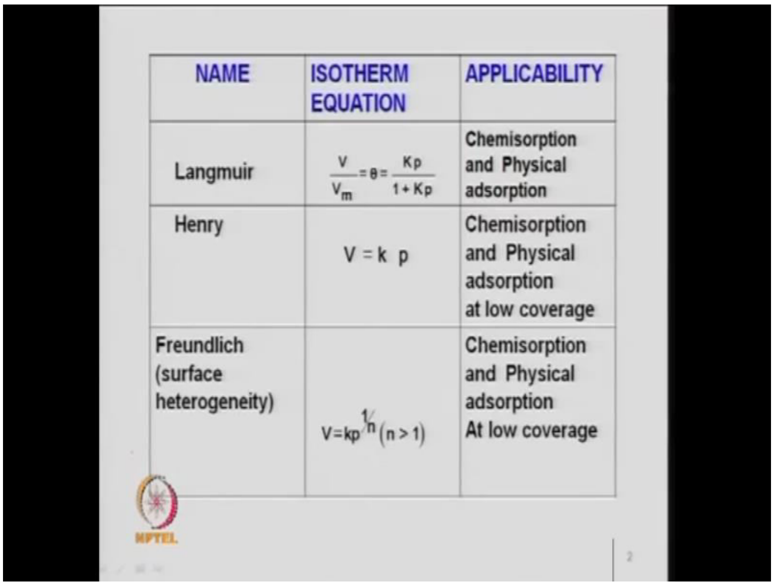

NAME	ISOTHERM EQUATION	APPLICABILITY
Langmuir	$\frac{V}{V_m} = \theta = \frac{Kp}{1+Kp}$	Chemisorption and Physical adsorption
Henry	$V = k\ p$	Chemisorption and Physical adsorption at low coverage
Freundlich (surface heterogeneity)	$V = kp^{1/n} \ (n > 1)$	Chemisorption and Physical adsorption At low coverage

So, we have seen the different adsorption isotherm Langmuir adsorption isotherm, which is based on basically chemisorptions principle, because the there are several assumptions of Langmuir adsorption isotherm, which makes it fit for the chemical adsorption, when the surface monolayer forms no further adsorption will take place. So, there are several other isotherms also, because the Langmuir adsorption isotherm this states that, heat of adsorption is independent of surface coverage, this is not true in all cases. So, heat of adsorption, generally decrease with surface coverage. So, how does it decrease? It might decrease langmuirically there are different assumptions.

So, but, in general, when the adsorption takes place then, the heat of adsorption decreases. So, for subsequent layers if you look at, it is just like a condensation of the molecule, that is nothing but, the latent heat of condensation so that will be lower than the first layer adsorption, because the first layer is the heterogenic, the gas molecule adsorbs on the surface. So, accordingly there are several isotherms, which have been derived or developed. So, I have just taken here few isotherms.

So, Langmuir adsorption isotherm which is basically, chemisorptions. So, most of the time, it talks a monolayer surface, the Henry isotherm which takes care of the heat of adsorption, which decrease exponentially. So, basically this is just related to that. The volume of the gas, which is adsorbed, is proportional to pressure and the second term k, which will take care of the adsorption in terms of activation energy of heat of adsorption for the different layers. Freundlich isotherm, which talks on surface heterogeneity, because in homogeny the Langmuir isotherm it is stated that the surface is uniform everywhere. So, the gas molecule can come and adsorb on the each surface. It is freundlich isotherm and it is logarithmically with surface coverage.

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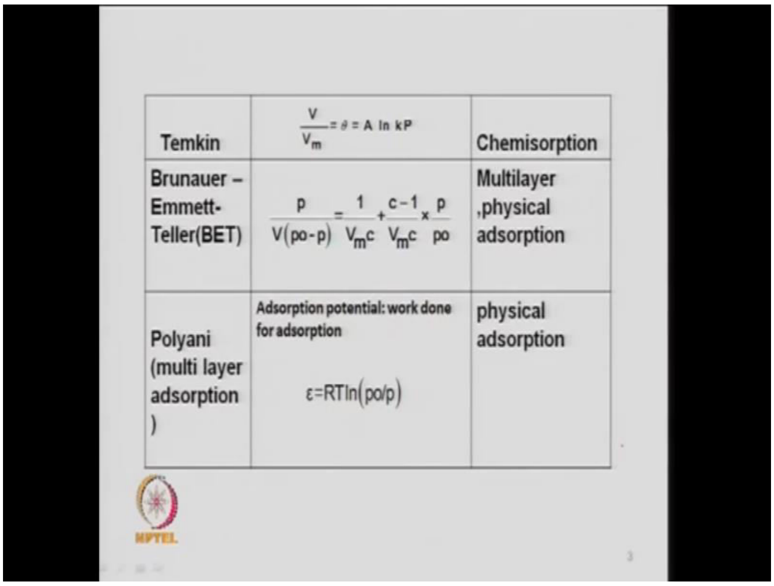

Temkin	$\frac{V}{V_m} = \theta = A \ln kP$	Chemisorption
Brunauer – Emmett-Teller(BET)	$\frac{p}{V(po-p)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} \times \frac{p}{po}$	Multilayer ,physical adsorption
Polyani (multi layer adsorption)	Adsorption potential: work done for adsorption $\varepsilon = RT \ln(po/p)$	physical adsorption

So, and accordingly the fraction volume, the fraction of the gas adsorbed. So, v is the volume adsorbed and v m is the volume, when the monolayer adsorbed theta is the fractional coverage and that can be related some log of theta is p so that parameter is a and k, these are the adsorption parameters and these can be determined. The BET isotherm is the one of the most important isotherm for determining the surface area of the porous material. So, and we will talk on that more, because this talks on multilayer physical adsorption. So, basically the Langmuir adsorption isotherm has certain restrictions but, when you look at a b e t isotherm, it has taken care most of those assumptions. So, surface coverage what we say that, the when there is adsorption it can be a multilayer Langmuir suggests. It is just a monolayer heat of adsorption varies with surface coverage and there may be, when you say that, the surface it covers a molecules have come to the surface. So, the subsequent molecules, which come to the surface and adsorb, there are dependent on the action of the surface, which is already covered.

So, all these assumptions, which were considered in the Langmuir and may not be correct they have been corrected or incorporated in the BET isotherm known as Brunauer Emmett and teller isotherm. The another one, which is known as polyani isotherm, again in multi layer adsorption and this is basically, related them to the force of attraction sometimes be defined epsilon but, this force of attraction, which is related to adsorption potential or energy required for adsorption, because it will depend on distance if the gas molecule are away from the surface of the solid. The force of attraction is poor, when they are closer then, adsorption will be faster.

So, based on that they have calculated the fraction adsorption or adsorption potential, which is related to the word done for a gas molecule and related that is nothing but, related to the force of attraction. So, the layers may form when you look at the gas molecules, which comes to the surface and when they are far away there, the work that is the energy required will be higher or force of attraction is low in that case. So, basically it is used for physical adsorption but, not very common.

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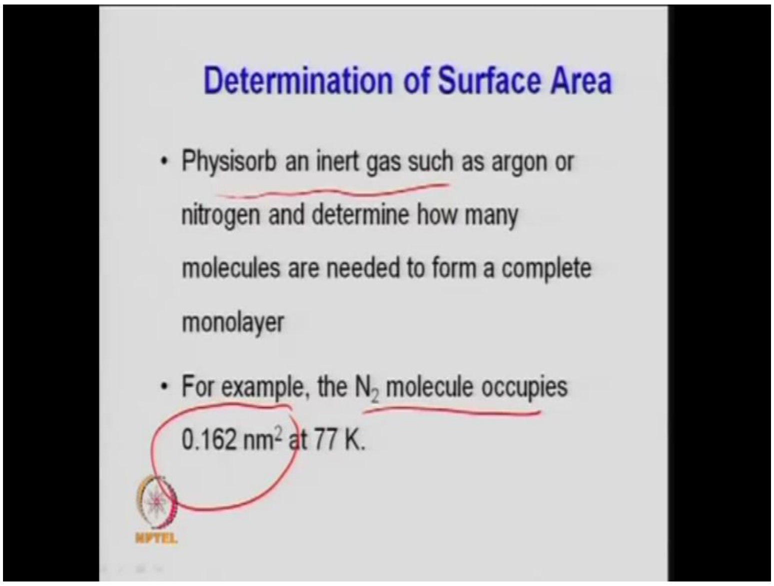

Determination of Surface Area

- Physisorb an inert gas such as argon or nitrogen and determine how many molecules are needed to form a complete monolayer
- For example, the N_2 molecule occupies 0.162 nm^2 at 77 K.

So, how to determine the surface area so that is again important, the physical adsorption, when I am saying it is multi layer adsorption. The molecules are adsorbing on the surface of the solids. So, logically if you look at the conceptually from the kinetic theory, also that how many gas molecule adsorbs on the surface of a solid if you are able to measure those volume or volume of the gas and equate it with the number of molecules and then calculate assuming that, they are covering the surface uniformly and then, that can be correlated if you know the area of one molecule correlated with some projected area and then, you can determine the surface. So, basically as I said, it is a physical adsorption and condensation of the molecule. So, the gas molecule, which adsorbs on the surface the area of one molecule, is known. So, how many molecules are adsorbing on the surface. So, multiply with that, you can find out the total surface area of a solid material.

So, this phenomenon thing, we are using and most of the time we use the nitrogen as an adsorbent gas which is inert gas under normal condition or most of the condition. So, the fundamental thing here, if you look at you physisorb an inert gas which may be argon, which may be nitrogen but, the carbon dioxide have also been used, oxygen can also be used and determine how many molecules are needed to form a complete monolayer and just for example, if you look at the nitrogen molecule, it occupies 16.2 angstrom square or 0.162 nano meter square.

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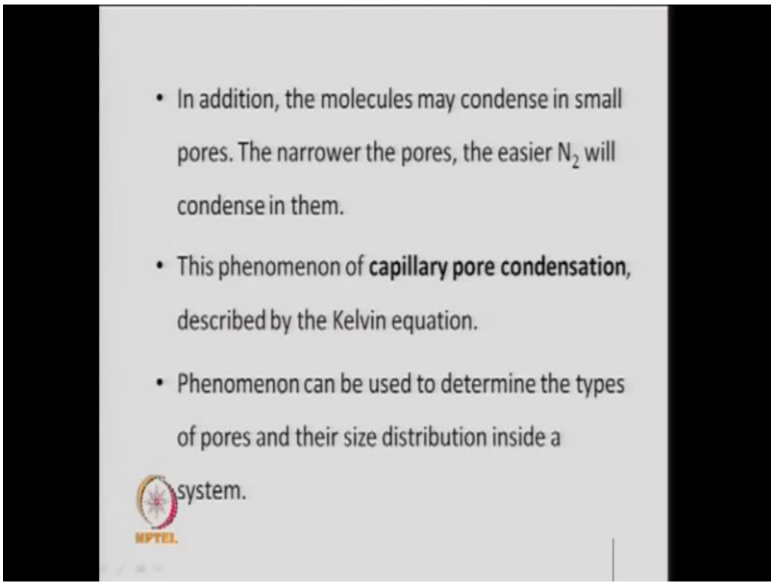

- In addition, the molecules may condense in small pores. The narrower the pores, the easier N_2 will condense in them.
- This phenomenon of **capillary pore condensation**, described by the Kelvin equation.
- Phenomenon can be used to determine the types of pores and their size distribution inside a system.

So, area of one nitrogen molecule is roughly 16.2 angstrom square or 0.162 nano meter square, which is the adsorption temperature or condensation temperature of nitrogen is 77 Kelvin. So, how many molecules of the liquid nitrogen, which comes on the surface and adsorb? So, you can calculate and correlate it with the surface area and when you look at pore size distribution.

So, we were talking about the Kelvin equation yesterday, which is related to the vapor pressure and the pore radius to fill a pore and then, chemisorptions takes place when, the pores are totally filled. So, how much pressure is released and accordingly you can find out the adsorb layer thickness and the radius of that capillary condensation phenomena, what we discussed last time. So, basically what I am saying, the molecules come on to the surface and they condense physical adsorption.

So, you have kept that temperature, which is equivalent to the condensation temperature of the gas. So, they will come and adsorb. So, narrower the pore easier will be for nitrogen to adsorb, because in the lower pore the vapor pressure will be low. So, they will easily condense. So, this is phenomenon what you call capillary condensation but, it is valid only in the small pores, because capillary phenomenon is valid only in micro pores or to some extent meso pores or to may be 50 angstrom you can use this.

So, this phenomenon is known as capillary pore condensation phenomena, which we had discussed yesterday and we can calculate the adsorbed thickness also and we can find out pore size distribution also and also by looking at the adsorption desorption isotherm, you can have idea about the geometry of the pore also, whether they are close from one end or they are open from both end or they is ink bottle effect, narrower from the top and then wider for us types. So, we call the desorption hysteresis, which you get that gives you the idea about the shape or geometry of the pore so t hat, information can be obtained. So, this phenomenon can be used to determine the types of pores and their size distribution for a given solid catalyst.

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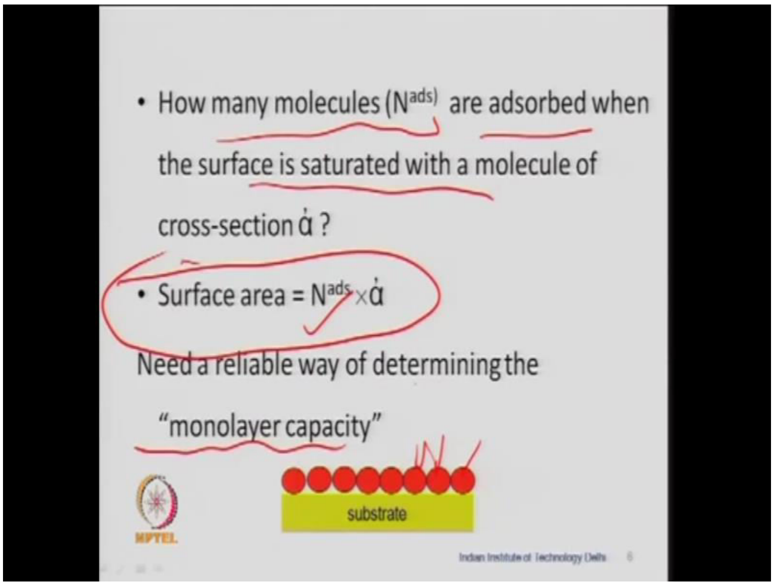

- How many molecules (N^{ads}) are adsorbed when the surface is saturated with a molecule of cross-section $\dot{\alpha}$?
- Surface area = $N^{ads} \times \dot{\alpha}$

Need a reliable way of determining the "monolayer capacity"

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So, the same thing which I discussed is that, how many molecules which I am saying adsorbed molecules are adsorbed, when the surface is saturated with a molecule of an area alpha. So, alpha is your cross section area of one molecule projected area. So, logically if I say a molecule, which has radius r. So, sterical which we assume psi is simply pi r square, projected area, note the area of the sphere.

So, projected area when, you look at the molecule comes and that is adsorbed over the surface. So, this area we are correlating with the property and r can be found out, this is the radius. So, one of molecule. So, if you know the molecular weight of that gas, one gram mole of the gas and molecular weight of that gas is known and N 0, which is Avogadro number most of the time. So, this is roughly 6.02 into 10 to the power 23. That is one gram mole of the gas contains, this much number of the atoms. So, I am talking in terms of atoms of the nitrogen alright or molecules.

So, gas molecules one gram of the molecule of the gas at normal condition will have 6.02 into 10 to the power 23. So, if you know this. So, I can find out that, what is the mass of one atom or one molecule, one molecule of nitrogen will have M by N 0. So, this is the mass of one molecule and you know that, this mass of the one molecule, because you are assuming it is spherical in shape. So, this will be equal to 4 by 3 pi r cube into the density of the nitrogen liquid density. So, you can very easily find out r from this equation. So, r can be calculated and this r can be substituted in this equation and you can find out.

So, basically I can if you just do that. So, your alpha will be roughly some factors, which is here times M divide by N 0, which is Avogadro number times density M to the power two-third. So, this fundamental thing, which is here written that alpha is the area covered, because I am saying it is a projected area is simply nothing but, that in one gram mole of the gas the molecular weight is there.

So, mass is there divide by N 0 find the mass of one molecule, equate it with density and the volume and then, you can find out the radius of one molecule and that is related to your pi r square surface area of one molecule. So, if there is N number of molecules adsorbed on the surface. So, this multiplied by alpha and by alpha is your surface area for the given mass.

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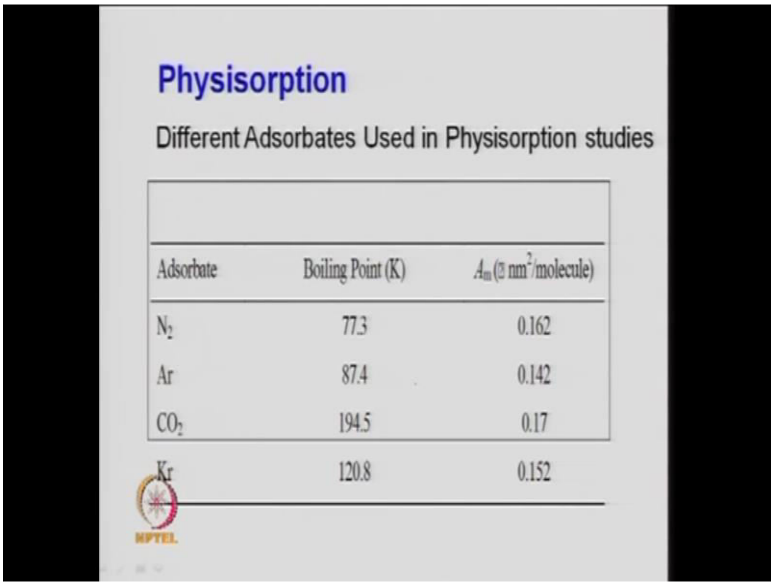

Physisorption

Different Adsorbates Used in Physisorption studies

Adsorbate	Boiling Point (K)	A_m (□ nm^2/molecule)
N_2	77.3	0.162
Ar	87.4	0.142
CO_2	194.5	0.17
Kr	120.8	0.152

So, this phenomenon has been used here, which is written here the surface area of the catalysts. So, alpha is the area covered by one molecule. So, the same number what I said for nitrogen, it is 16.2 angstrom square and N is calculated from your isotherm. So, you need a reliable way to determine this adsorption capacity or monolayer capacity. So, this is what we are talking here a substrate, the gas molecules are adsorbed here and you can just find out the number of molecules and then you can find out the surface area, which is your BET surface area or by Langmuir surface area any surface area whatever, the isotherm which have been used.

So, any gas can be used as I said. So, nitrogen which is more common 77 Kelvin is the boiling point and area of one molecule of nitrogen in nano meter square is your 16.2 angstrom square or in nano meter square 0.162 nano meter square. So, argon again point one four two nano meter square per molecule. So, these are the values of alpha, which can be written A m or alpha and carbon dioxide. It is 0.17 again in nano meter square krypton 0.152. So, any gas can be used for adsorption.

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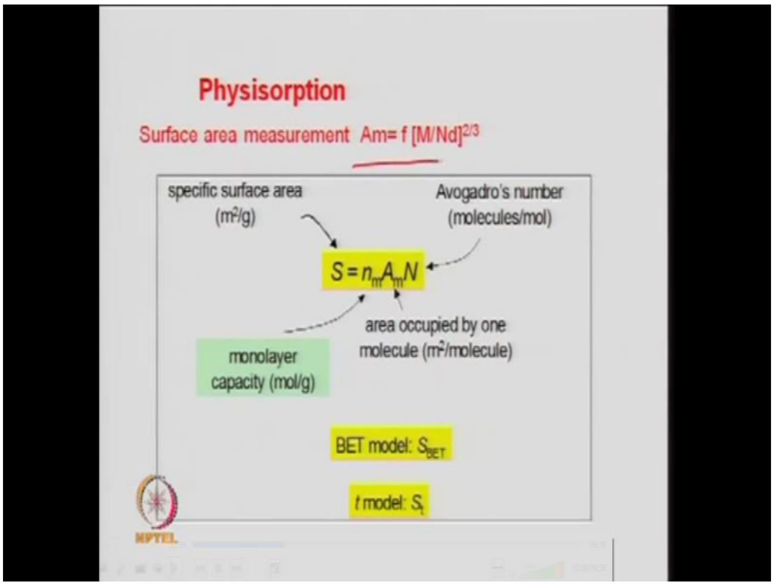

Physisorption

Surface area measurement $A_m = f\,[M/Nd]^{2/3}$

specific surface area (m^2/g)

Avogadro's number (molecules/mol)

$S = n_m A_m N$

monolayer capacity (mol/g)

area occupied by one molecule (m^2/molecule)

BET model: S_{BET}

t model: S_t

So, this is written here, also M by N 0 rho. So, this is d is the density or you write rho. So, M by N 0 rho to the power two-third and equator factor, which may be roughly 1.09. So, if you calculate from that, whatever pi and other factors. So, this is what the number of molecules area covered by one molecule, which you say sometime it is written here alpha. So, it is the A m your alpha. So, N is Avogadro number which is 6.02 into 10 to the power 23. So, BET model or T model. So, by using the different models, you can find out this, you can find out adsorb layer thickness and that is what, the nitrogen adsorption desorption isotherm you can find out the pore size distribution and thickness of the adsorb layer, what you call t plot.

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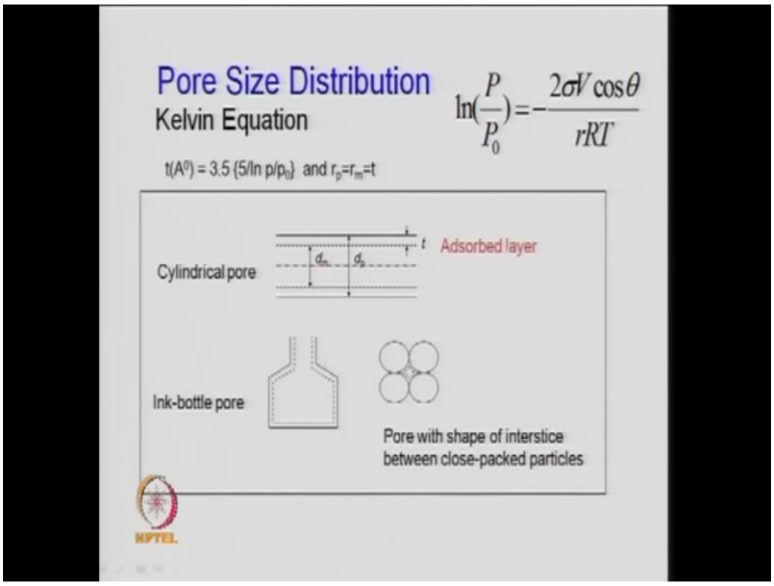

Pore Size Distribution

Kelvin Equation

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

$t(A^0) = 3.5\,\{5/\ln p/p_0\}$ and $r_p = r_m = t$

This capillary condensation phenomena, which we are talking and the pore size distribution, generally that is determined as I discussed last time, based on mercury presentation method and the nitrogen adsorption desorption method. So, mercury presentation method based on surface tension effect where as nitrogen adsorptions desorption method is based on your Kelvin equation. Vapor pressure is related to the pore radius.

So, when you are applying the pressure on the gas to fast the adsorb layer thickness, it will form on the surface of the solid in a pore and then, when the if you still keep on increasing the pressure then, the condensation will take place and pores will fill, when you release the pressure then the pores will start vacating. So, larger pore will vacate first and then, the smaller ones and so on and so forth.

So, while filling the larger pore will fill first and then, smaller so that phenomenon can be used or phenomenon can be used to find out or to correlate the pressure variation delta p, as a function of the pore radius or delta v pore volume, which can be correlated with the pore radius. So, you can find out the pore size distribution and the average pore size.

So, this Kelvin equation is related to the vapor pressure. So, log of P by P 0 is equal to minus 2 sigma V cos theta upon r into RT like this. So, r is the radius of the capillary, sigma is the surface tension. So, sometime I write gamma also, surface tension V is the volume of the liquid nitrogen, which is adsorbed on the surface can be correlated with the gaseous molecules, theta is for because nitrogen wets most of the surface. So, theta is 0. So, cos theta will be 1 in most of the cases. So, this can be used for determination or of this radius r.

So, generally we are interested in finding out this pore size, which is here written in terms of diameter. So, r is related to simply 2 sigma V cos theta divide by R T l n of P by P 0. So, negative sign. So, generally when, we write P 0.P it will become a positive sign. So, very easily you can find out, you can correlate the pressure with radius but, as I said earlier that since some of the nitrogen is already adsorbed on the surface.

So, this will not be available for condensation capillary condensation, because that is adsorbing layer thickness. So, the first thing is that you have to find out, what is the thickness of the adsorb layer and. So, basically your Kelvin equation will give you a minus T see this is shown here, this one so what? I just if I explain it here.

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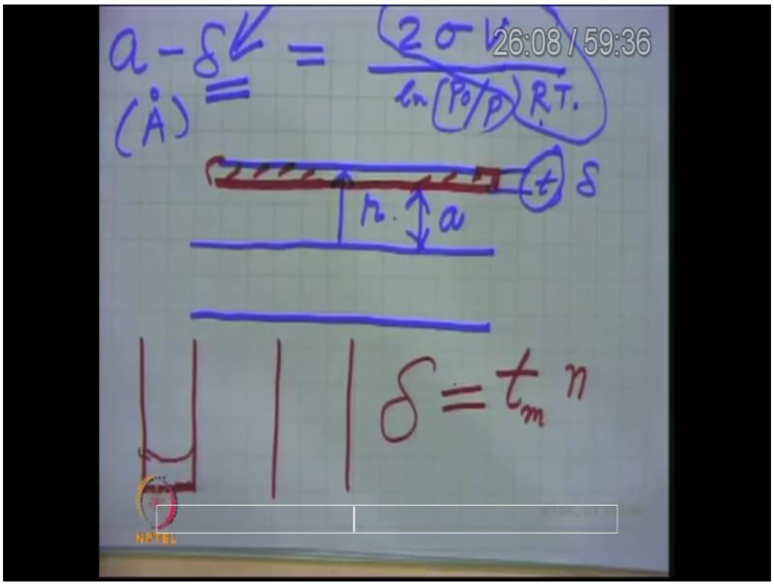

So, in any pore, which has a radius r, or sometime I write a also, there is when the gas comes, first it will adsorb on the surface, this is your adsorb layer thickness. So, the first thing is that you have to find out, what is this t? What you call or sometimes, we write delta also adsorb layer thickness. So, your capillary condensation or Kelvin equation is giving you this value. So, I will write it a say here fine. So, this is a, you get from this capillary condensation equation.

So, this delta or t you have to find out separately and you can find out this by using the same material in non porous condition. So, when you have a non porous condition though pores are available. So, this will just give you. So, pores are not finding of no condensation, only t will be obtained. It can be a multi layer. So, find out a mono layer thickness and multiplied by the number of layers so that is the thickness of the adsorbed layer.

So, monolayer thickness say one nitrogen is roughly 3.5 angstrom, which are known already and. So, one can find out this adsorbed layer thickness. So, basically now my Kelvin equation is giving you the value a minus delta or r minus t by t s and that can be written in terms of 2 sigma or I will write it now, 2 sigma V, because cos theta is roughly 1 divide by l n of P 0 by P times R T, because sigma is known for nitrogen surface tension, V is the volume of the gas adsorbed that is also known like for one gram molecule if you take at normal condition 77 Kelvin. So, that is volume of the liquid nitrogen.

So, I will just talk on this value R is the gas constant, T is the temperature Kelvin. So, everything is basically a parameter, which is a constant. So, this comes roughly say in some book you will see 9.52 most of the books only. You will see 7.87. So, this unit will become in angstrom and then it can be written some constant divide by l n of P 0 by P. Now, I can very easily find out, because delta you have to calculate from the integral correlation or vieler’s model, what I said that? it is just nothing but, the same equation derivation based on this equation but, some l n of P 0 by P to the power minus 1 by n where, n you may have 1,2, 3 like that. So, one can find out, I mean to say delta can be calculated from integral correlation and then, you get a minus delta from Kelvin equation and then, calculate a which is whatever, this plus delta but, delta is your adsorb layer thickness.

So, this, which is written here, that I have shown here are d m in terms of diameter and d p, which is the pore diameter half of this is your radius and this is your adsorbed layer thickness you have to find out t that is thickness of the adsorbed layer and calculate the radius from the nitrogen adsorption desorption method based on capillary condensation which is your Kelvin equation and then your actual pore size will be delta plus whatever you get from the Kelvin equation and that will be your pore size distribution.

So, when you have a hysteresis like adsorption, desorption, hysteresis the pores are like this see. So, this is what by ink bottle effect as I said. So, when the adsorption desorption condensation phenomena takes place though. So, this will fill first and then, this will and then, when you dissolve it. So, the operation takes place first on this surface. So, this operation may require even a lower pressure. So, you get a kind of hysteresis adsorption hysteresis.

So, because of the variation in pressure if the pores are of similar size or if the pores are just like this straight cylindrical closed at one end. So, it will make some kind of spherical surface here. So, surface will go like this. So, meniscus will be spherical here. Now, when the pores are straight cylindrical closed for one end you would not get any hysteresis, because whatever the isotherm for adsorption pressure there will not be any variation in pressure.

But when, you have pores which is open from both end you will have a variation, there will be a kind of hysteresis, because the pressure variation pressure will vary, when you have the pores are saturated and when you release the pressure. Now, at lower pressure larger volume, it desorbs or a smaller pressure is required to evacuate that pore and same thing happens in this kind of that is where, that is ink bottle type or the pores are narrower from the neck and then, wider is foroids type also where, they are spherical in shape from the lower end but, then narrower from the top. So, you will ink bottle or for these kinds of structures you will have the hysteresis in your isotherm.So, what I mean to say by understanding this nitrogen adsorption, desorption, isotherm you can get the idea about the pore structure.

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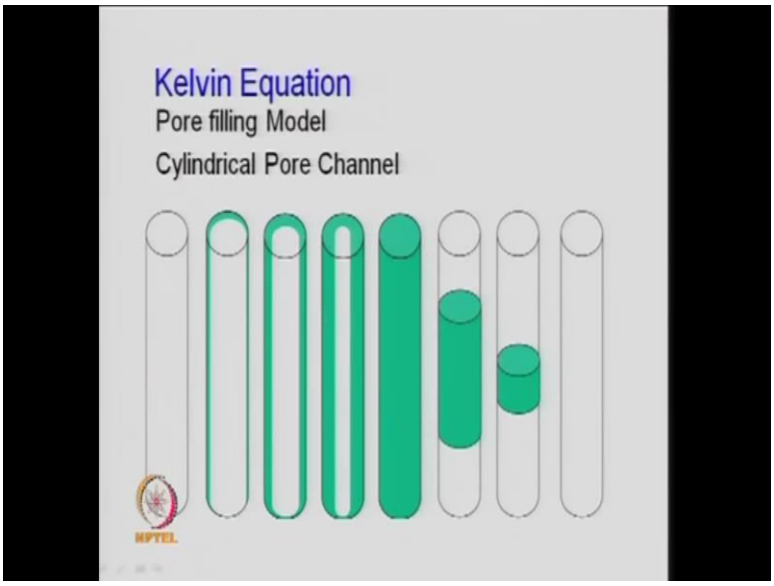

Kelvin Equation

Pore filling Model

Cylindrical Pore Channel

So, this is what, shown here in this Kelvin equation pour filling model. So, first, this layer forms and this layer thickness increase and then so on. Now, condensation starts and finally, the pore get filled and this will happen, when the vapor partial pressure at saturation P 0 and now you have started removing or releasing the pressure. So, larger pore will get empty first and finally, your structure will go like this and the pore gets saturated. So, in this, because just these are open from both sides you would not get any hysteresis.

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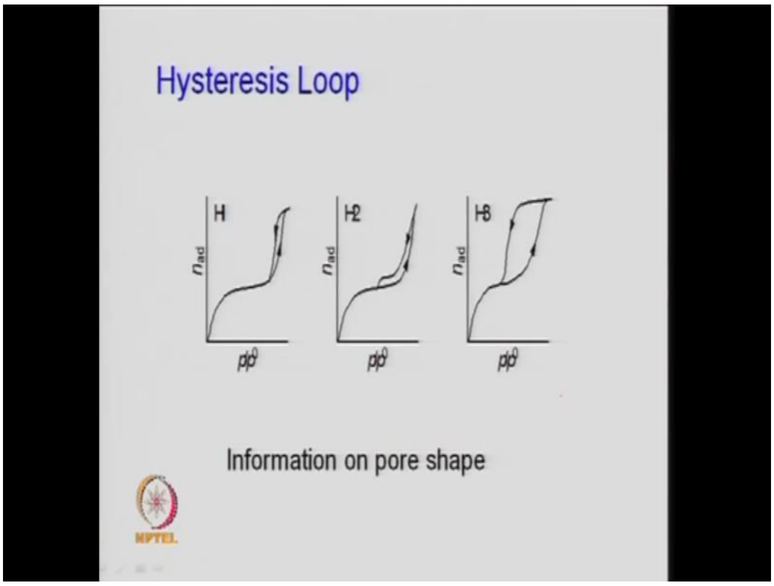

Hysteresis Loop

Information on pore shape

So, this is what say, the hysteresis type of hysteresis. So, depending upon the complex geometry of the pore lower end no hysteresis will be obtained virtually. So, this simply saying that, at this pressure, when adsorption the volume is this but, when it is desorbing a larger volume can be desorbed over the same pressure or the basic idea is that, when you desorb it and there is a kind of hysteresis. So, at lower pressure the more volume can be desorbed. So, you can get the information about the pore shape by doing this adsorption, desorption and isotherm using nitrogen.

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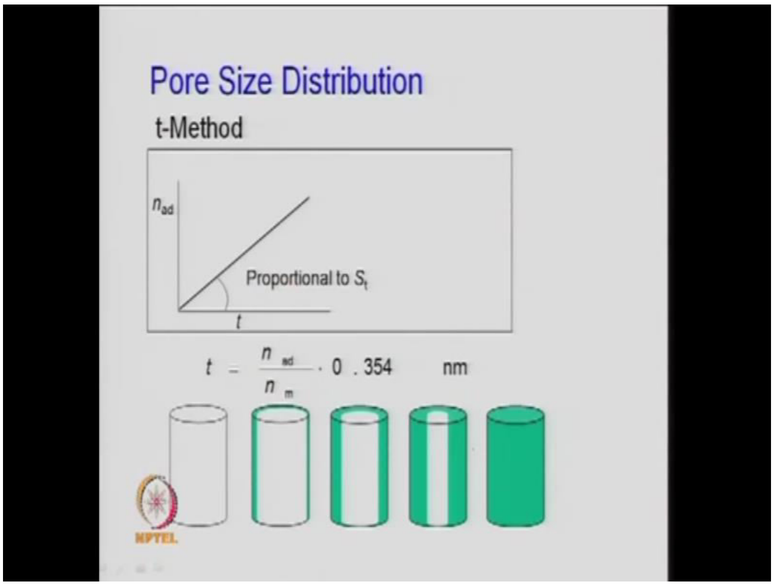

Pore Size Distribution

t-Method

$$t = \frac{n_{ad}}{n_m} \cdot 0.354 \text{ nm}$$

So, t-method, what I said is done generally this but, I am talking in this equation is 0.354, which is written here or 3.54 when, I write in terms of angstrom unit so that is the value of this one mono layer thickness, when the surface is adsorbed. So, it forms a monolayer but, there can be multilayer. So, whatever number of layers multiplied by thickness of one mono layer is your adsorbed layer thickness delta.

So, delta is basically or this t or delta is nothing but, t m times whatever the numbers of the layers for adsorbents, the gas molecules, which adsorbs on the surface, it can be multi layer adsorption. So, mono layer thickness for nitrogen is 0.354 nano meter. So, by using this t plot t you can find out this value of delta and in other words, what I said that Euler's equation that can be used for determining which is simply lower if you look at that equation.

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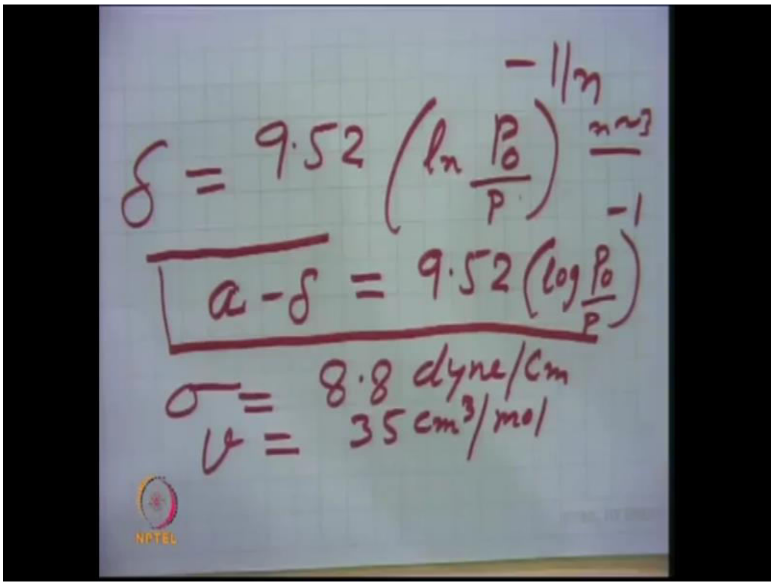

$$\delta = 9.52 \left(\ln \frac{P_0}{P}\right)^{-1/n} \quad \underline{n \sim 3}$$

$$\boxed{a - \delta = 9.52 \left(\log \frac{P_0}{P}\right)^{-1}}$$

$\sigma = 8.8$ dyne/cm

$v = 35\ \text{cm}^3/\text{mol}$

So, in the Euler equation, this delta is given by in angstrom unit 9.52 times l n of P 0 by P to the power minus 1 by n that n may be any number. So, most of the time, this n is taken 1. So, it comes in that way your equation becomes something like if I write n minus a minus delta. So, this gives you 9.52 times log of P 0 by P to the power minus 1. So, delta is calculated from this for this n is roughly 3 and then, you substitute it in your equation which is written here earlier a minus delta and substitute.

So, this value which I am writing here 2 sigma V divided by r t so that is roughly 9.52. So, you can very easily write this value, because sigma is roughly, you can calculate that sigma is roughly 8.8 for nitrogen in the unit of dyne per centimeter. This is the value of surface tension and volume v for adsorbed nitrogen is 35 centimeter cube per mole. I have given that later in my slides also. So, 35 cube centimeter cube per mole, which is the volume of liquid nitrogen adsorbed at this condition. So, by using this equation at gas condition, you can convert it or you know the density of liquid nitrogen then, you can calculate from that also. So, these are some values you can calculate based on that.

So, finally, what I mean to say that this equation is used to determine this, the value of a, a is equal to 9.52 log of P 0 by P to the power minus 1 plus delta and delta will be calculated from this equation, because it also varies with pressure and where, n is roughly 3 approximately 3. So, you can carry n calculate this pore size distribution or another method is that, this one where you can directly calculate by using the mono layer thickness and. So, this is the thickness of the adsorbed layer. So, n adsorption divide by n which I am writing mono layer is related to this equation which is here, P 0 by P, because it will change with pressure. So, you have to calculate that.

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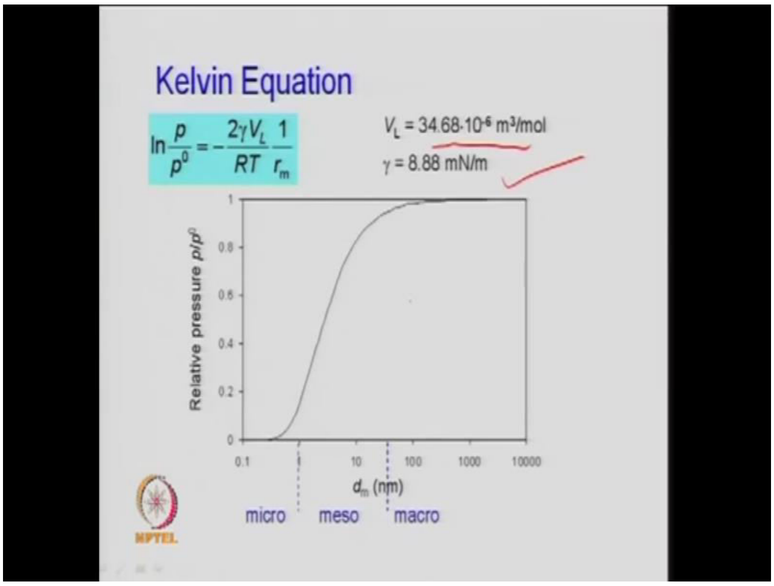

Kelvin Equation

$$\ln\frac{p}{p^0} = -\frac{2\gamma V_L}{RT}\frac{1}{r_m}$$

$V_L = 34.68 \cdot 10^{-6}\ \mathrm{m^3/mol}$

$\gamma = 8.88\ \mathrm{mN/m}$

So, this is the same calculation. So, I have written here in terms of gamma mille Newton per meter and volume is adsorbed, which is for liquid 34.68 into 10 to the power minus 6 meter cube per mole. So, roughly 35 in this and centimeter cube per mole and. So, P by P 0, if you look at in terms of diameter, your curve will go like this for micro pore, meso pore and micro pore. So, this is a based on Kelvin equation, you can find out the radius of the capillary. So, this is now the elative pressure as a function of pressure P by 0, you can have a plot. So, you can see that, the distribution of the pores. So, micro pore and meso pore capillary, same thing can be plotted in terms of the nitrogen adsorption, desorption, isotherm at I talked yesterday for the mercury penetration method, that I can just simply write here, that delta V upon d of log a where, a is the radius.

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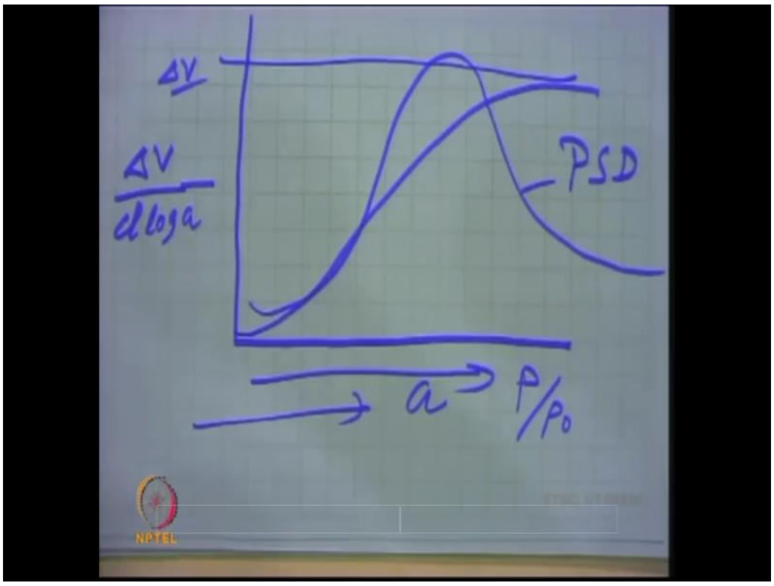

So, and or you can plot delta V upon delta a also and that will give you as a function of radius pore radius and that will be a cumulative pore size distribution. So, mercury penetration method, which is used for larger pore nitrogen adsorption desorption method, which is for smaller pore. So, you can have a similar pore size distribution trend what you look at here. So, this is for basically micro and a meso and you club it with the mercury penetration method, you will have total pore size.

So, basically if I look at a cumulative plot, that is volume versus pressure, I will have a similar cumulative for the micro pore and meso pore so that, can be a plot which will be just increasing and like this so that will be as a function of pressure also, if I look at pressure here or this will be P by P 0 this side and this side. It is the total cumulative volume. So, delta V, which I am saying for definition. So, total will be your V g for the micro pore and meso pore. So, similar trend, which you have seen yesterday, can be obtained or similar curve can be obtained for the pore size distribution. So, this one is known as pore size distribution plot P S D by using nitrogen adsorption, which is simply delta V upon delta a radius versus pressure or a radius, because both are interrelated.

So, my radius is basically, increasing in this side, pressure increasing in this side, because larger pressure smaller pores will fill, smaller pressure larger pore will get fill first. Now, when you look at chemisorptions isotherm see, Langmuir isotherm can be used for physical adsorption but, surface area which you get from Langmuir adsorption isotherm will be higher compared to B E T, because Langmuir isotherm does not take care of multi layer adsorption.

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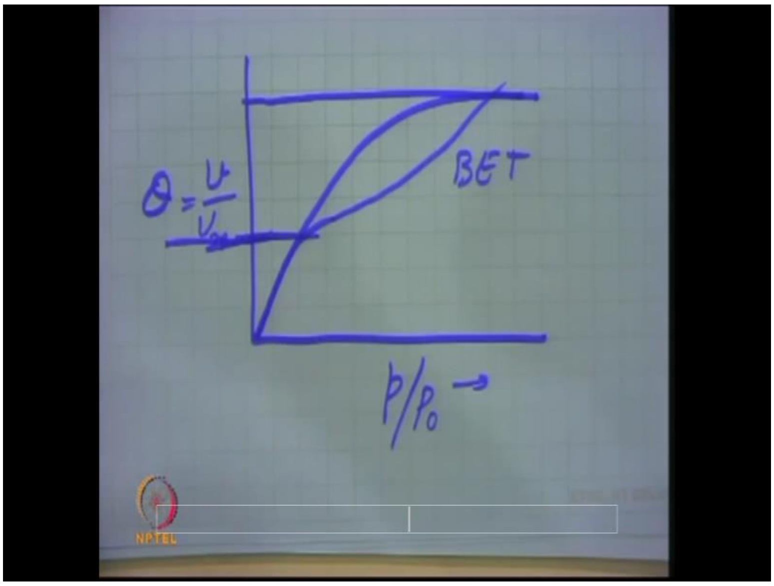

So, as I discussed in your isotherm that, this Langmuir adsorption isotherm gives you a curve like this, here you have theta fractional coverage and here you have just as a function of P or P by P 0. So, this is what something like V by V m in Langmuir but, what will happen, because surface is completely covered no further adsorption but, B E T according to B E T, this may happen somewhere here and then, it goes multilayer adsorption. So, this is your B E T. So, B E T can have the fractional surface coverage one here but, Langmuir says, the coverage is here. So, this is the difference, because the isotherm has not taken care of the multilayer physical adsorption. So, when it is physical adsorption a condensation of gas molecule more and more layers may form.

So, but, if look at the theory, the fractional of the surface coverage which can be written in terms of mass or can be written in terms of the volume of the gas adsorbed either way.

So, x is divided by x m. So, x m is the mass of the gas adsorbed at saturation and x is the mass of the gas adsorbed before saturation. So, isotherm we discussed last time that when, there is a equilibrium at equilibrium, the rate of adsorption is equal to rate of desorption.

So, K times p times 1 minus theta, because adsorption is proportional to the partial pressure of the gas and proportional to the fraction of the sites, which are vacant and desorption is proportional to the fraction of the sites, which is already covered and that gives you the isotherm something like theta, which is v by v m or x by x m is equal to k p divide by 1 plus k p where, k is the adsorption equilibrium constant. So, this can be used to find out the same graph, that is your this versus p will be a line like this but, you can line arise the equation to find out the parameter of the isotherm. So, like this.

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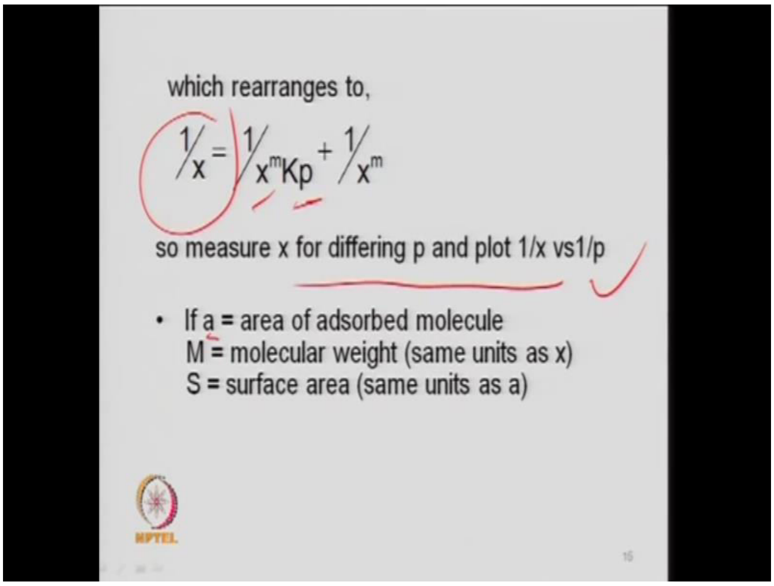

which rearranges to,

$$\frac{1}{x} = \frac{1}{x^m K p} + \frac{1}{x^m}$$

so measure x for differing p and plot 1/x vs1/p

- If a = area of adsorbed molecule
  M = molecular weight (same units as x)
  S = surface area (same units as a)

This is the linear form of the Langmuir adsorption isotherm to find out the parameter but, one can use the non-linear regression method also and directly find out the software tools are available. So, directly one can regress, the data and parameters can be determined. So, but, if you look at the this linear regression method, you can measure the x at different plot and you plot a graph of y 1 upon x as a function of pressure which is 1 upon P and you can find out the total molecular coverage at monolayer x m. The mass of the molecules adsorbed, when there is a monolayer x m, which is written earlier v m volume of the monolayer for a given mass of the solid or per gram of the solid. So, if you know the area alpha, which is written here a. So, alpha is the area of the adsorbed molecule, one molecule M is the molecular weight of that and S is the surface area.

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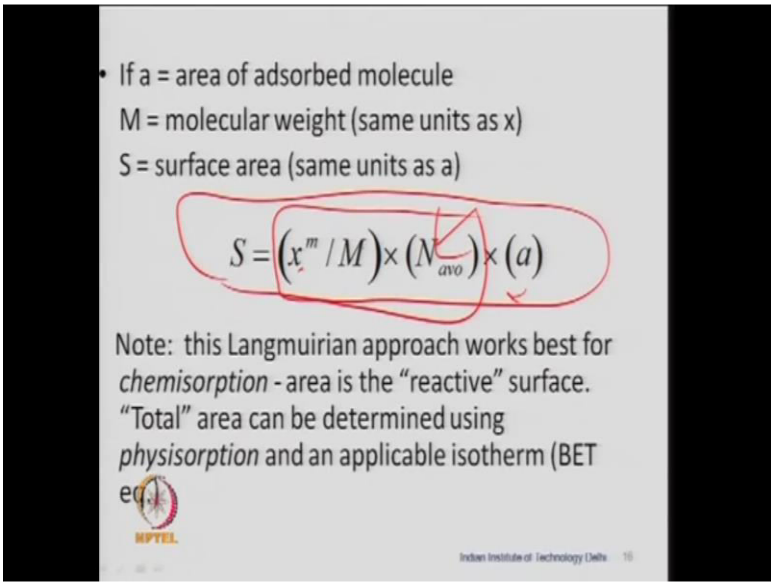

- If a = area of adsorbed molecule
  M = molecular weight (same units as x)
  S = surface area (same units as a)

$$S = \left(x^m / M\right) \times \left(N_{avo}\right) \times (a)$$

Note: this Langmuirian approach works best for *chemisorption* - area is the "reactive" surface. "Total" area can be determined using *physisorption* and an applicable isotherm (BET eq.)

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So, your surface area, which is your B E T surface area, is nothing but, as I said the number of molecules, which adsorb on the surface multiplied by area of one molecule. So, how to find number of molecules if v m is the monolayer coverage, you know that, at standard condition one gram mole of the mole of the gas will have some reference volume, which is which may be 22,400 centimeter cube per gram mole. So, 22.4liter.

So, you can very easily calculate at a given condition, how many molecules of the gas have been adsorbed on the surface. So, this is calculated here. So, either you write in terms of v m or in terms of x m unit is same, the method is same. So, this is nothing but, the number of one gram mole of the gas will have this much number of molecules. Avogadro number 6.02 into 10 to the power 23 for one gram mole. So, in this much gram mole, how many molecules are available. So, this is nothing but, the total number of molecules, which are adsorbed and this is the area of one molecule alpha 16.2 angstrom square say for nitrogen. So, this multiplied by area of one molecule is your total surface area. So, whether the B E T or Langmuir the principle is same.

So, you can find out here, v m also you can use it in terms of v m over v reference. So, molecule adsorbed divide by at reference condition, which is 22.4 liter times number of molecule. So, either you write in terms of mass or you write in terms of molecule. So, when it is in terms of volume, it will be v reference, because one gram mole of the gas has a mass of molecular weight or that same gram mole has 22.4 liter or I will say that v reference at one atmosphere that is 0.1 ampere mega Pascal. So, this can be calculated. So, this is just the Langmuir adsorption isotherm for calculating the surface area, which is written now here that.

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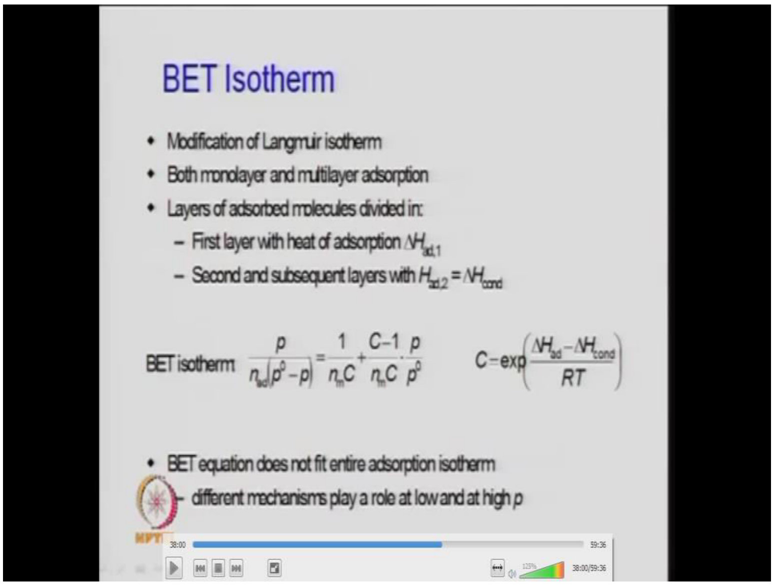

BET Isotherm

- 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, as I said that, Langmuir adsorption isotherm can be used to determine the surface area but, basically that is for a monolayer coverage, when there is a chemisorptions that may be correct but, for heterogeneous, because it is not considering the heat of adsorption with surface coverage, it does not consider the most important is that, it says that it is a monolayer coverage whereas, the B E T says, that it is a multilayer coverage there may be a formation of the multilayer, when the surface when there is a condensation of the. So, taking care of that the B E T modified isotherm.

So, B E T isotherm is a modification of the Langmuir adsorption isotherm, we say that, there is a monolayer as well as multilayer adsorption and the layers of adsorbed molecules can be divided in first unit. So, where it will be the adsorption of a gas molecule on a surface of the solid heterogeneous but, on the subsequent layer there will be the adsorption of a gas molecule on another molecule, which is already adsorbed on the surface. So, this is what you have. So, heat of adsorption is different latent heat of condensation or vaporization, when the molecule is coming and sitting over the same molecule, the water like condensation of the water.

So, in a subsequent layer this heat of adsorption is same for multi layers but, for first layer, it is whatever the adsorption heat of adsorption in subsequent layer. It is the heat of condensation of the molecule. So, this difference was not taken care in the Langmuir in that it was same. So, heat of adsorption but, you are saying that, it decrease with surface coverage has been taken care here. So, isotherm we have seen, I will just talk on that derivation of this, which is P upon v into P 0 minus P in terms of volume, if you write or P upon number of molecule adsorbed either way, you can write per unit mass also you can write per unit volume, you can write per unit gram mole but, bases should be same, unit should be consistent, the either way can be written.

So, as of now you are talking P upon V into P 0 minus P is equal to one upon v m c, that v m will be mono layer is equal to c minus one upon v m c times P by P 0. So, v m and n are inter related I told you then n is the number of gram mole equals adsorbed molecules number of molecules of the gas which are adsorbed gram moles or whatever and v m when I say it is the volume of the gas which is adsorbed even can convert them. C is the term which is related to heat of adsorption and heat of condensation in equisection.

So, which is exponent of heat of adsorption delta h minus heat of condensation divide by r t. So, this is the addition term in the case of the b e t isotherm. So, you can very easily linearism this equation and you can find out the v m mono layer coverage in either case we are trying to find out the mono layer coverage volume and then we are correlating it with the number of molecules of the gas which is adsorbed and that is correlated with the surface area of the solid material. So, B E T isotherm has also some assumption Langmuir has some advantage B but, the disadvantage was that, it had certain assumption, which may not be true for the physical adsorption for chemisorptions adsorption. The Langmuir isotherm fits back but, physical adsorption there may be some problem in that.

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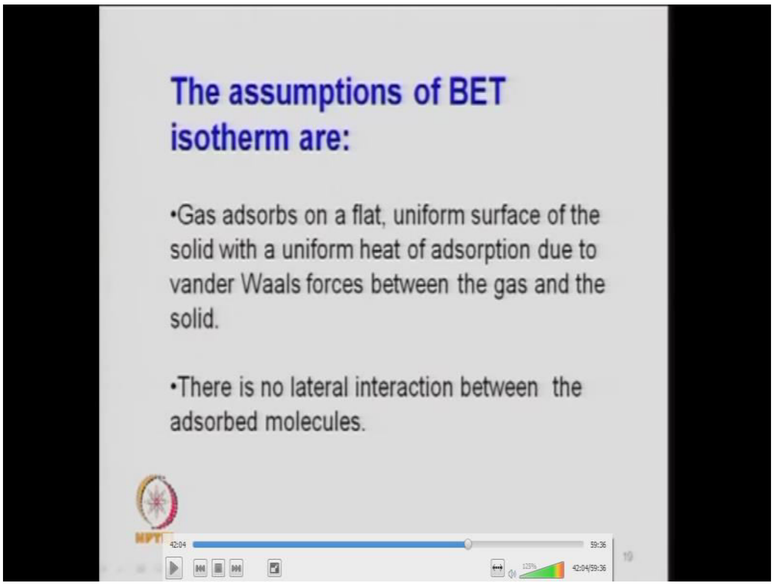

The assumptions of BET isotherm are:

- Gas adsorbs on a flat, uniform surface of the solid with a uniform heat of adsorption due to vander Waals forces between the gas and the solid.
- There is no lateral interaction between the adsorbed molecules.

So, you have to take care of that. So, in that, the B E T has over this corrected or taken care of those assumption but, still there are some assumption, which say that, the gas adsorbs on a flat uniform surface of the solid with uniform heat of adsorption due to Vander Waals force between the gas and the solid, because this is a physical adsorption. So, which is related to the Vander Waals force. So, in adsorbed layer first layer, when I am saying the heat of adsorption is same for all there is no lateral interaction between the adsorbed molecules so that is another assumption, that is the molecules, which adsorbs and second molecule adsorb then, no interaction.

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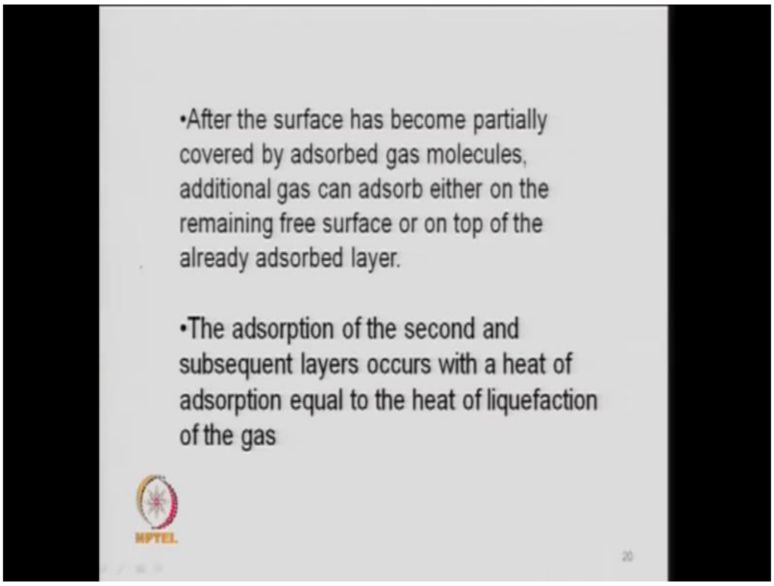

- After the surface has become partially covered by adsorbed gas molecules, additional gas can adsorb either on the remaining free surface or on top of the already adsorbed layer.
- The adsorption of the second and subsequent layers occurs with a heat of adsorption equal to the heat of liquefaction of the gas

So, there is no chemical reaction basically, so that is why multilayer physical adsorption and after the surface has become partially covered by adsorbed gas molecule. The additional gas can absorb either on the remaining free surface or on top of the already adsorbed layer. So, B E T is a multi layer adsorption. So, one molecule it adsorbs then, other can also come on to that and the remaining surface may be bare.

So, this is one assumption here, the adsorption of the second and subsequent layers occur with the heat of adsorption equal to heat of liquefaction so that is in subsequent layer. It is nothing but, the condensation of the molecule latent heat of condensation or latent heat of vaporization, when you take talk absorption. It is nothing but, the condensation. So, on subsequent layers it is nothing but, the heat of condensation of the gas molecule on the surface.

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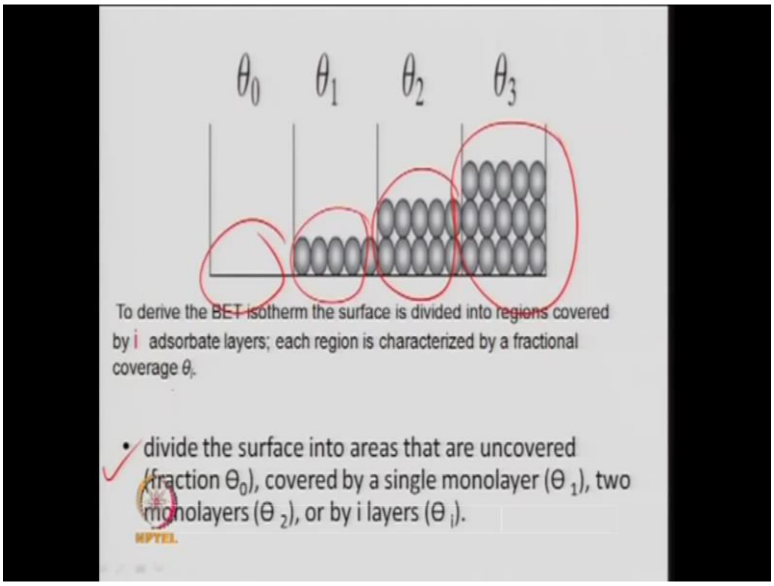

To derive the BET isotherm the surface is divided into regions covered by i adsorbate layers; each region is characterized by a fractional coverage θ_i.

- 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, this is just a fiction of the isotherm of the B E T for derivation but, practically if you look at the actual situation this is not but, to have a model we are just assuming that, this is the bare surface then, this is the surface where, the one layer is formed, this is surface where the 2 layer has been, 2 layers has been formed and this is the surface for 3 layers has been formed and so on. This can go to infinite.

So, it is just a model. So, this is what, we have written or discussed here, that to derive the B E T isotherm, the surface is divided into regions covered by i adsorbed layers or several adsorbed layers and each region is characterized by a fractional coverage theta i.

So, theta 0 is the bare surface, theta 1 is the fraction of the surface, which is covered by 1 layer, theta 2 is the fraction of the surface, which is covered by 2 layers and so on. So, this is what best and divide the surface into area, that are uncovered that is fraction 0 covered by a single layer theta 1 covered by 2 layers theta 2 or theta i. So, mathematically you can represent it.

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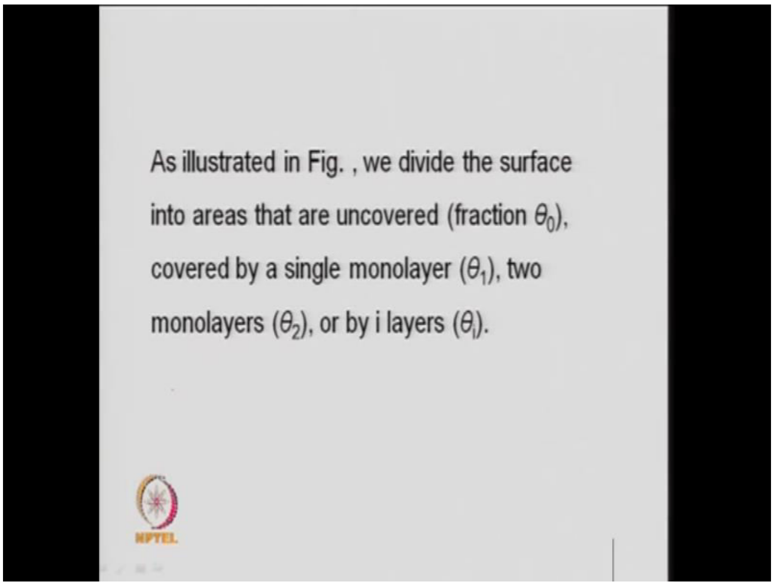

As illustrated in Fig. , we divide the surface into areas that are uncovered (fraction θ_0), covered by a single monolayer (θ_1), two monolayers (θ_2), or by i layers (θ_i).

So, this is what is written here, that area that is uncovered, covered by layer 1, 2 monolayer's and so on. So, we are assuming here, suppose the total number of sites are n 0 on the surface and the atoms which, adsorb which is n a. So, what we are doing here, that n by n 0 is your fraction, total fraction.

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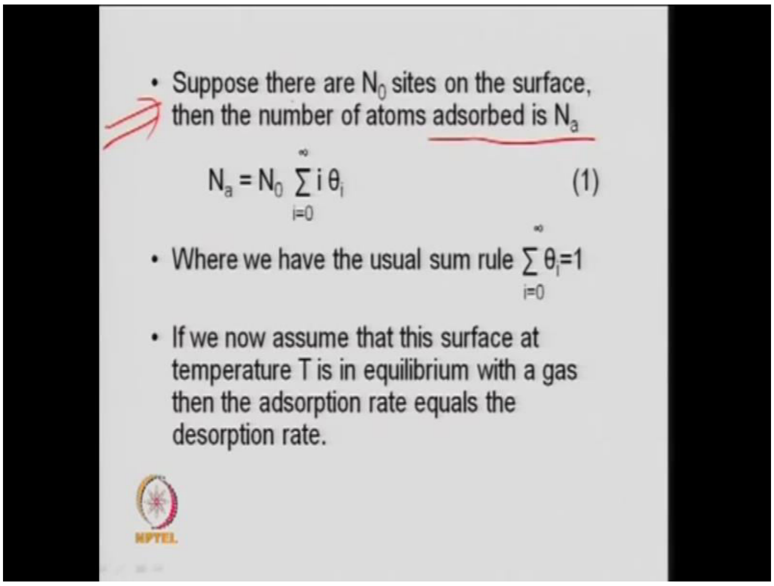

- Suppose there are N_0 sites on the surface, then the number of atoms adsorbed is N_a

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

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

So, this is multilayer remember, this is to a monolayer, in monolayer your sigma of all theta s 1 but, here why we write i theta i, because we are just calculating total fractions. So, see first layer i 0, this is theta 0. So, i 1 this is theta 1 layer is 2, this is 2 times theta 2, three times theta 3 so on. So, theta 1, theta 2, theta 3 which I am saying, it is the covered in each monolayer. So, those theta 0, theta 1 theta 2 if I write that will be 1 but, when I write total layers, where 2 layers are formed, 3 layers are formed, which fraction is not 1, because this is nothing but, the total number of molecules, which have been adsorbed on the surface for a multilayer coverage, not the monolayer but, using this information, because it is related to your sticking probability. These molecules are comes on to the surface and they adsorb. So, what is the sticking probability or what is the rate of adsorption on the surface will depend on that sticking coefficient also, adsorption and sticking phenomena.

So, what I mean to say here that n 0, which is the number of sites on the surface total number of sites. I am saying and the number of adsorbed atoms which is N a. So, N a by N zero, I am talking a is nothing but, a fraction of a sites which are adsorbed. So, this is equal to whatever nothing but, or N which is nothing but, the number of sites multiplied by the fraction of the sites which are covered and that is nothing but, i 0 to infinite i theta i, which is remember it is the total layers, not the monolayer property.

So that is why, we are writing it i theta i, because we are adding all these numbers. Now, here, this molecule plus this molecules and so on. Where, theta 0, theta 1, theta 2 is this and so on and this indicate this is 1, because this is the fraction of each monolayer. Now, vacant site plus where, the one layer has formed, second layer is theta 2, 3 layer is this but, total number of molecules if I calculate, that is nothing but, the layers which have a two layers, three layers, n layers, where it can be infinite number of layers also till saturation. So that is important that, the total number of layers are i 1 to 0 to infinite, i theta I, total number of molecules which come on to the surface in terms of the fraction if I write. But, i talk in the monolayer, it is sigma of all those.

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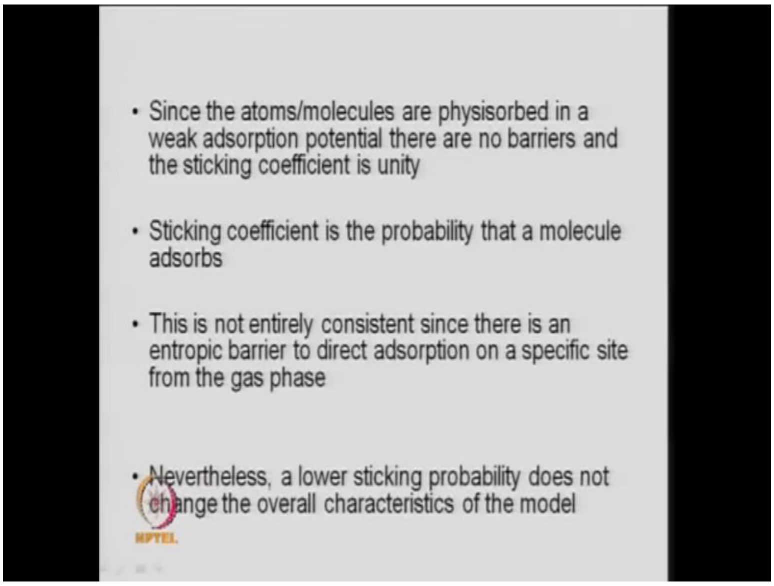

- Since the atoms/molecules are physisorbed in a weak adsorption potential there are no barriers and the sticking coefficient is unity
- Sticking coefficient is the probability that a molecule adsorbs
- This is not entirely consistent since there is an entropic barrier to direct adsorption on a specific site from the gas phase
- Nevertheless, a lower sticking probability does not change the overall characteristics of the model

So, this is what, I was talking sticking, because atoms and molecules are physisorbed in a weak adsorption potential, because it is a kind of Vander Waals's adsorption. It is a weak adsorption and there are no barriers and the sticking coefficient is unity when, there are no barriers but, generally sticking coefficient, when we are talking it is nothing. The probability is that a molecule adsorbs. So, in the case of chemisorptions this is very important, because the number of molecules they come and they are adsorbing on the specific sides, they are colliding among the molecules and then adsorb on the surface. So, we talk in terms of sticking probability but, here because it is a just a physical adsorption. So, a sticking probability may not differ much. So, but, even then it is related to your boards man equations or P upon 2 pi m where, the you have the boards man constant and the pressure of the gas temperature. So, it is a kind of nothing but, the something related to the kinetic theory of the gas. The molecule, which come and they are adsorbing and because of they are adsorbing, because there is coordination between the gas molecules so that is important.

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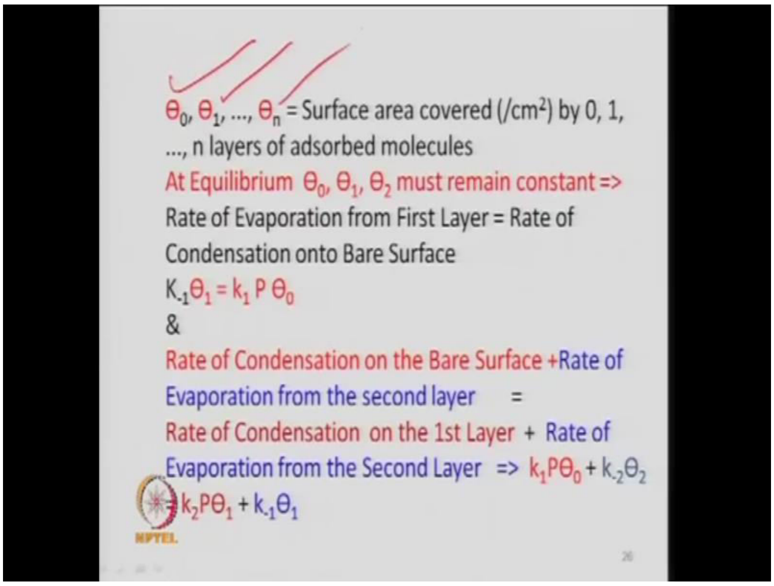

$\Theta_0, \Theta_1, ..., \Theta_n$ = Surface area covered (/cm^2) by 0, 1, ..., n layers of adsorbed molecules

At Equilibrium $\Theta_0, \Theta_1, \Theta_2$ must remain constant =>

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

$K_{-1}\Theta_1 = k_1 P \Theta_0$

&

Rate of Condensation on the Bare Surface + Rate of Evaporation from the second layer =

Rate of Condensation on the 1st Layer + Rate of Evaporation from the Second Layer => $k_1P\Theta_0 + k_{-2}\Theta_2$ = $k_2P\Theta_1 + k_{-1}\Theta_1$

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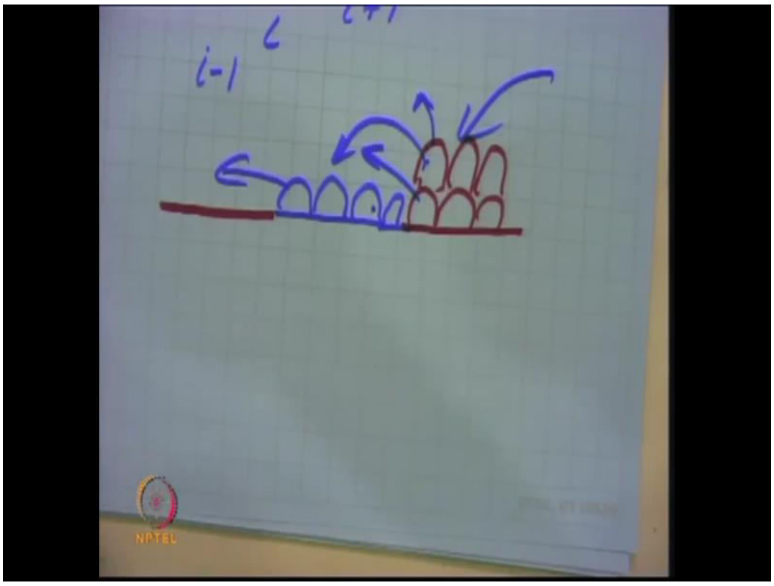

So, this is a bare surface n then, you have a surface which is adsorbed. So, here you have the molecules adsorbed and then, you have another surface where, there are two layers like this and so on. Now, we are talking a kind of dynamic equilibrium between these two layers. So, what will happen? Because, these layers are at equilibrium. So, from here, the operation will take place from here also the operation will take place and from this layer. The operation is taking place and something will come to this layer also condensation here, the evaporation is taking place but, whatever the molecules evaporate, they may condense here. So, what I am saying that, there for any i layer, you have to look at i plus 1 and i minus 1 for layers after the second, third and four so on. What we are talking but, for first layer and a bare surface there is no other layer. So, the in the first layer, the adsorption rate of adsorption rate of desorption is related to between the back end sides and the first layer.

So, which is written here, for the first layer, you have one equilibrium ah relationship but, for subsequent layers you need to look at the i and i plus 1 for i layer, you have to go i minus 1 and i plus 1, because from i plus 1, there will be vaporization and it will condense into the i'th layer from i'th layer, there is a vaporization, it will come to the lower layer and so on. So, this is what here, if you look at rate of evaporation from first layer is equal to rate of condensation onto the bare surface. This is for the first layer adsorption equilibrium.

So, rate of evaporation from first layer, that is because evaporation when, I say it is a desorption adsorption when, I say it is condensation o the first layer, because the already the molecules are there and when there is an equilibrium will desorb something and something will come from second layer onto that, because there is an equilibrium no further adsorption is possible but, the equilibrium does not mean that. It is stopped, the process of adsorption desorption is simultaneous but, the net change in system is 0. So, whatever the molecule adsorbs the same equal number of molecules gets desorbed also, there is always a kind of dynamic equilibrium between the 2.

So, this relationship is very important in that way, that is the rate of evaporation from first layer. So, rate of evaporation may desorption and desorption is proportional to the surface, which is already covered. It has nothing to do with the pressure, that we have discussed during the Langmuir adsorption isotherm rate of desorption is proportional to the fraction of the surface, which is already covered and desorption is taking place from first layer, which has the covered fraction of theta 1. So, rate of desorption is simply K minus 1 time theta 1, which is evaporation from first layer and that is equal to rate of condensation onto the bare surface.

So, this is your bare surface here and bare surface, it means, the absorption which is the function of pressure of the gas times the fraction of the sites, which are vacant and theta 0 is the concentration of the vacant side of the surface. So, theta 0 is not the fraction, which is covered. It is bare surface I am talking which does not have any site absorbed site. So, this K 1 time's P time's, theta 0 is nothing but, the adsorption on a bare surface is that clear of the first term. So, then I am talking first layer and the bare layer and then, for subsequent. Now, we have to talk in terms of first, second and third or if I talk for second layer, I will talk first and third like that. So, for every i'th layer, you have to look at i plus 1, you have to look at i minus 1 but, in the first layer and the bare surface there is only 2.

So, now look at this is very important here, when rate of condensation on the bare surface plus rate of evaporation from second layer. So, this is what, we are talking for the rest of the layer. So, I am just defining in terms of the condensation on the bare surface plus rate of evaporation from the second layer will be equal to because, there is a kind of dynamic equilibrium, that will be equal to rate of condensation on the first layer. So, condensation on the first layer, condensation means adsorption. So, absorption on a first layer, where from it will come from the second layer. So, adsorption on the first layer will be equal on plus rate of evaporation from second layer. So, rate of evaporation means, it is desorption from the second layer, which will be related to this thing simple. The fraction of the sites, which are already covered and this is condensation on a first layer simply related to the K 1 times sorry, this 1, which is equal to here. So, this is what I am saying here, rate of condensation on a first layer which is simply K 2 times, P times theta 1 and plus K 1 times, K minus 1 times, P K minus 1 times, theta 1, which is desorption from the second, this layer rate of evaporation from the second layer, where the surface which is covered is nothing but, related to the desorption. See, what I am saying that, I will just continue it next time but, basically what I am saying here is that, the rate of evaporation from the first layer all the times, there is a kind of dynamic equilibrium between the i'th and i plus 1 and i minus 1 layer.

So, when there is a top layer from there will take place and it will come to the lower layer and something should it means, vaporization from there or desorption from there will be proportional to the surface which is covered here and this will adsorb on this. So, this will be proportional to a fraction of the site, which are available here for adsorption and the pressure same thing for if you have three layers suppose, there is one more layer then, from there the vaporization will take place but, on this, the condensation will take place on this. That is, because it is vaporizing but, fourth layer will also vaporize, which will adsorb on this layer. So, from here, there is the vaporization. So, there is always a kind of dynamic equilibrium between the rate of adsorption and rate of desorption for each subsequent layers.

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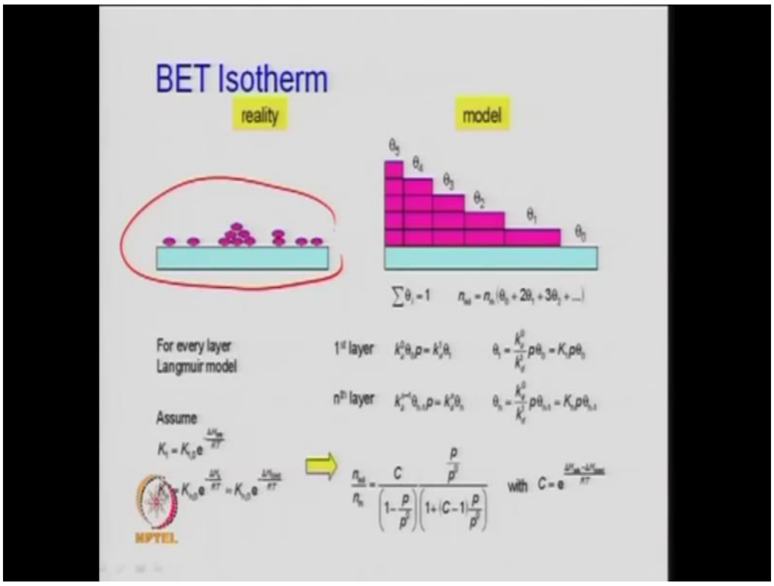

BET Isotherm

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

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

Assume

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

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

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

So, I will just come back to this term again, the before that just look at this what I have shown in terms of the another picture, because reality is this actually, this is happening but, we have made it uniform, because this is theta 0, theta 1, theta 2, theta 3 and theta 4 like that. So, we have developed a model but, reality is something like this, that should be in mind and all the time when, I am talking a dynamic equilibrium say for this layer. So, I am looking this and this also sigma of theta is 1, because it is the fraction of the all the layers and this I have already discussed. i theta i, this is your i theta i here and this is N adsorption divide by N M, this is equal to theta 0 plus 2 theta 1, what is your meaning of i theta i.

So, first layer is for every layer or for between 2 layers if you are writing you have to apply. We are applying our Langmuir adsorption isotherm, we say that at equilibrium, the rate of adsorption is equal to rate of desorption but, that is for one layer but, now we are talking a multilayer adsorption. So, we are considering the dynamic equilibrium between two layers, some layers there is vaporization which will, because it is vaporizing, it will sit on some other layer in a lower layer and same thing for the adsorption also. So, adsorption because in that layer also,there is a kind of adsorption which is coming from the other layer. So, we will continue it next time in depth.

Thank you.