Heterogeneous Catalysis and Catalytic Process
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Module - 04
Lecture - 11

Good morning, last time we were talking about determination of pores and pores size distribution. So, we were talking about two methods work depredation method and nitrogen adsorption desorption method or isotherm.

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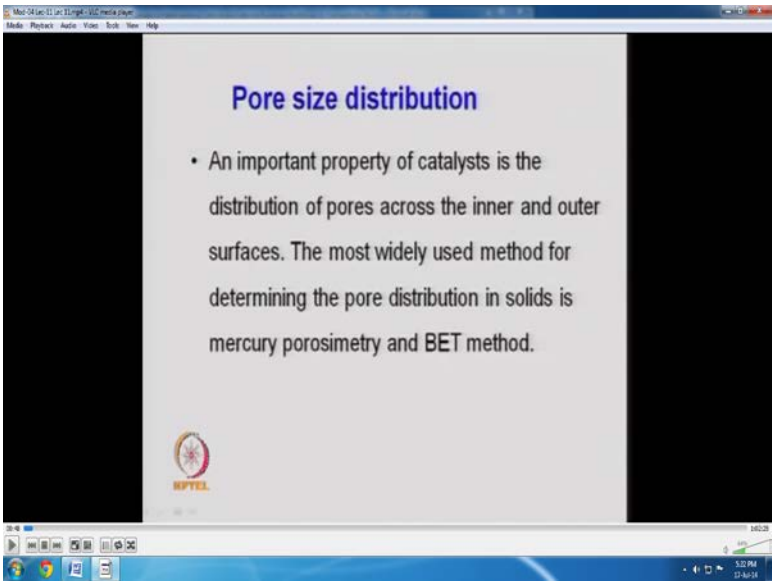

Pore size distribution

- An important property of catalysts is the distribution of pores across the inner and outer surfaces. The most widely used method for determining the pore distribution in solids is mercury porosimetry and BET method.

So, basically BET can be used whatever p upon b into p0 minus p the plot versus p by p0. You can find out the volume of monolayer coverage, you can determine the area of 1 molecule of nitrogen which is 16.21 is 21 square density of the nitrogen and from that also one can determine the adsorbed layer thickness, what you call t plot. So, the adsorbed layer thickness can be calculated by knowing the change in the volume or delta v during the mercury penetration or nitrogen adsorption or desorption isotherm.

So, principle remains the same what we discussed. So, these are the important property to determine the pore volume and pore size of a catalyst. So, basically I will just talk on nitrogen adsorption desorption method, in detail because, mercury penetration method we have already seen.

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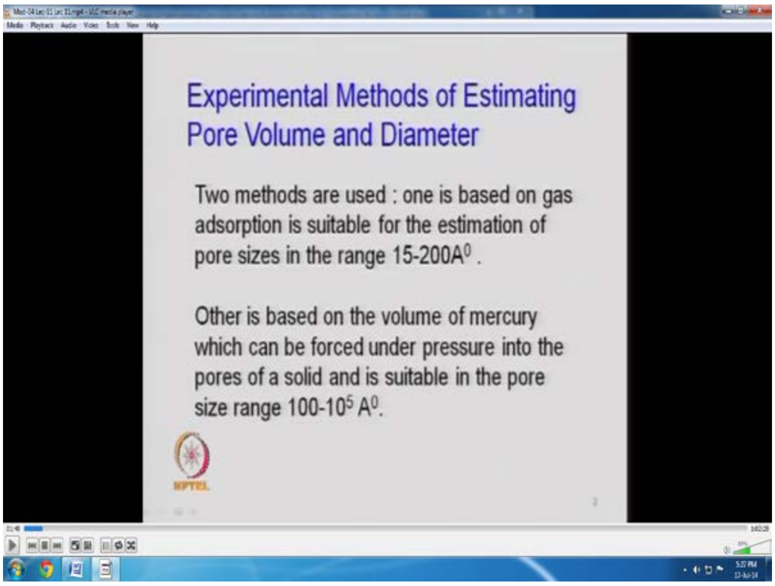

Experimental Methods of Estimating Pore Volume and Diameter

Two methods are used : one is based on gas adsorption is suitable for the estimation of pore sizes in the range 15-200A^0 .

Other is based on the volume of mercury which can be forced under pressure into the pores of a solid and is suitable in the pore size range 100-10^5 A^0.

So, how experimentally we determine the pore volume pore size distribution or thickness of the absorbed layer. So, these are the basic characteristics of the surface of the solid so, when new catalyst is to be prepared or is prepared based on certain preparation methods may be co-precipitation or just in method so, you look in types of the adsorption to look at the chemisorptions property.

So, you need to find out that actual pore size distribution because, the pores are selective for the distribution because the pores are selective for a given catalytic reaction. So, we will just talking last time this nitrogen adsorption desorption method basically which is based on the principle of capillary condensation. So, vapor pressure required to fill a pore. So, lower the smaller the capillary lower will be the vapor pressure so, those pores will get filled first and then larger .

So that, is what the condensation and when you release the pressure or desorbs then the volume from the larger pore will displace first or remove first. So, you can find out the delta v so that, is what we are going to look at here in terms of the methodology. So, your nitrogen adsorption desorption method, basically gives you the micro pore and miso pore, the second one which is helium mercury method or mercury penetration method basically b g s type direct zone or and applied also can be determine, can be used to determine the pore radius so, where you see two capillaries they are dipped and the trough, it is a chamber of volume something definite volume.

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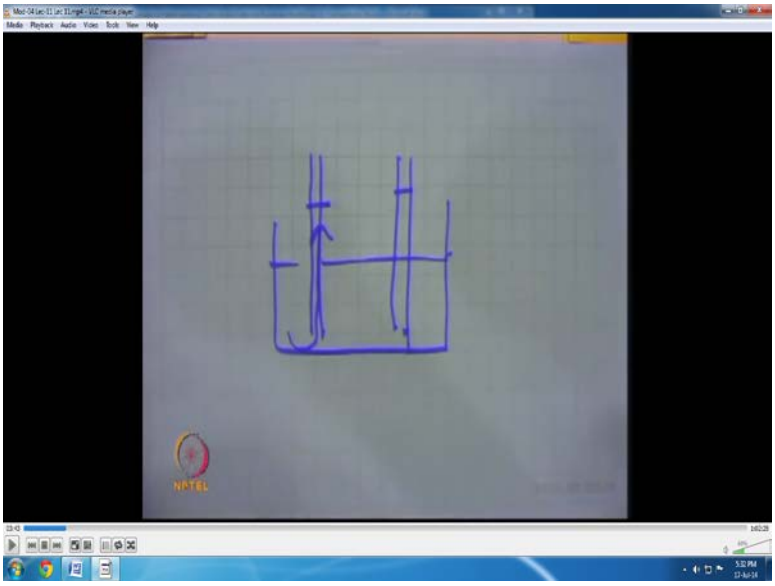

And something like this and there, you have the capillaries dipped in the nano-metric that is a mercury, here like this and this whole system is under pressure so, you increase the pressure. So, whatever the mercury volume displaces that will go up. So, if you have a known mass of the sample and you apply the pressure the mercury will start penetrating and whatever the volume of mercury that is get penetrated so, this will go up or if there is initially the level. So, mercury which penetrates inside the pore the level will fall down.

So, you can find out what is delta v and then you can find co-relate delta v with the pressure and that is what the mercury penetration method can also be used to find out the pore size distribution of the catalyst. So, this is what but, only as I said that based on the surface tension phenomenon so, it is use only for the larger pore 100 Armstrong to 1,00,000 Armstrong, not for the measure because the pores will get cracked.

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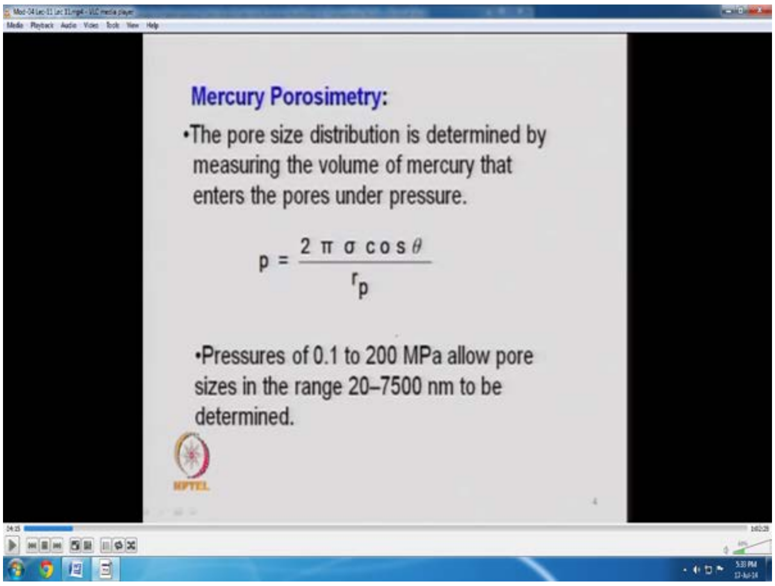

Mercury Porosimetry:

- The pore size distribution is determined by measuring the volume of mercury that enters the pores under pressure.

$$p = \frac{2 \pi \sigma \cos\theta}{r_p}$$

- Pressures of 0.1 to 200 MPa allow pore sizes in the range 20–7500 nm to be determined.

So, principle of mercury penetration method we have already seen the pressure force equal to the surface tension force and that can be used so, we have already discussed this.

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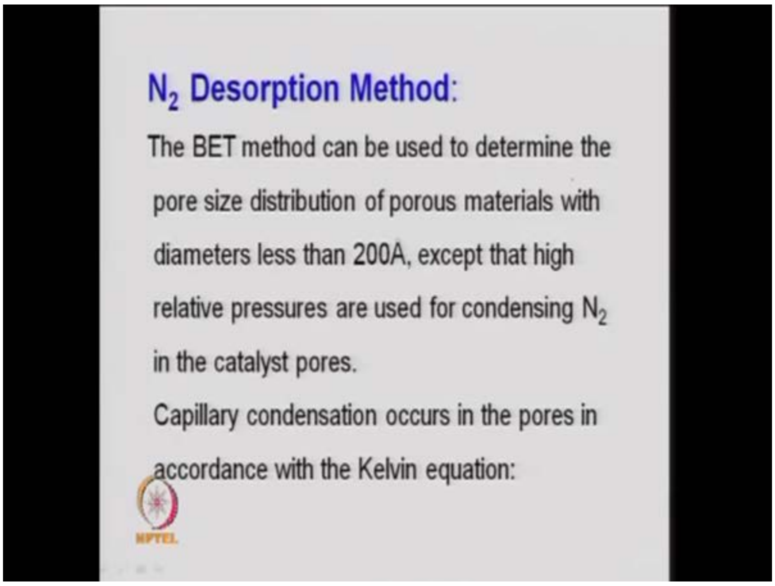

N_2 Desorption Method:

The BET method can be used to determine the pore size distribution of porous materials with diameters less than 200A, except that high relative pressures are used for condensing N_2 in the catalyst pores.

Capillary condensation occurs in the pores in accordance with the Kelvin equation:

Nitrogen adsorption, desorption method which I was talking earlier also so that is the BET method, which can be used to determine the pore size distribution but, whatever I said that by knowing the graph p upon v into p0 minus p versus p by p0 which is your BET isotherm and you can co-relate the pressure with the area of the molecule for a differential pressure and you can get the differential volume of the pore and then you can co-relate that adsorbed layer thickness and can find out the pore size distribution. So, same principle is extended here, is that the capillary condensation occurs in the pore and which is based on the Kelvin equation.So, let us look at the Kelvin equation also.

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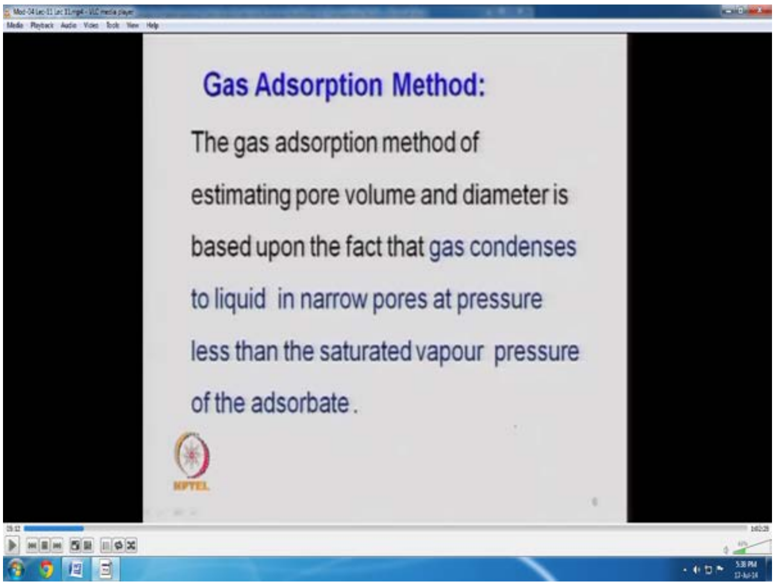

Gas Adsorption Method:

The gas adsorption method of estimating pore volume and diameter is based upon the fact that gas condenses to liquid in narrow pores at pressure less than the saturated vapour pressure of the adsorbate.

So,the method as I said the adsorption method of estimating the pore volume and diameter that is based on the fact, that the gas condenses to liquid in a narrow pore at pressure, less than the saturated vapor pressure of the adsorbed. So, this is your capillary condensation. So, you are applying the pressure and when vapor pressure is the partial pressure equals to vapor pressure so, either the vaporization will start, if you increase the pressure the condensation will start, if you release the pressure it will get vaporized.

So,the basic equation which you see in that relation because, it is related to the thermodynamics, how much work is being done to increase a drop because, droplets when the condensation is taking place the droplet size is increasing. So, it means between 2 radii R and R plus delta r there is some change in volume from v to v plus delta v. So, we are looking those differential volumes which are related to applied pressure or when you have a desorption steady over a larger drop vaporization will take place so, it will turn to a smaller one. So that, is again related to the pressure which is released and that is why we taking the desorption data there to look at the hysteresis also adsorption desorption hysteresis.

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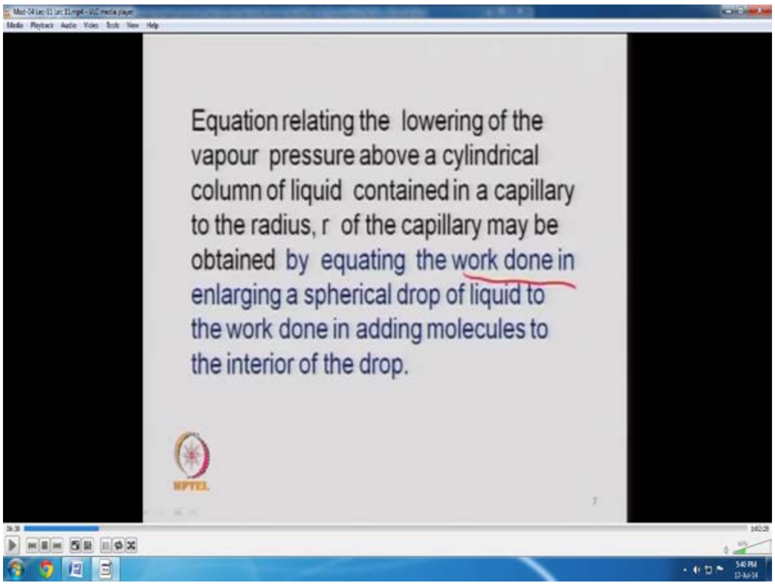

Equation relating the lowering of the vapour pressure above a cylindrical column of liquid contained in a capillary to the radius, r of the capillary may be obtained by equating the work done in enlarging a spherical drop of liquid to the work done in adding molecules to the interior of the drop.

So, basically if you look at the work done in enlarging a spherical drop of liquid and if you equated it to the work done by in adding the molecule to the interior of the drop. So, there is a change in number of molecule. When the volume is increasing you’re adding some number of moles of nitrogen on the layer, delta n so, these 2 can be co-related that is what the Kelvin equation principle. So, we are looking our thermodynamics which is related to the chemical potential and this work done.

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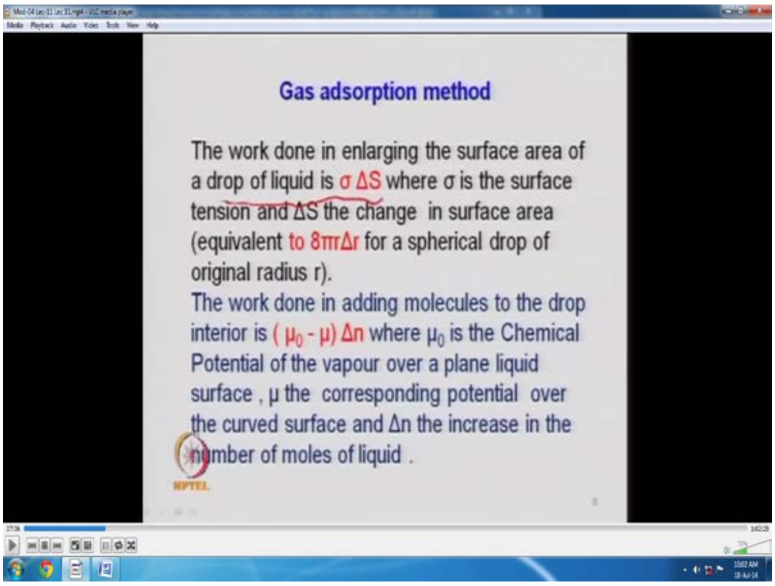

Gas adsorption method

The work done in enlarging the surface area of a drop of liquid is $\sigma \Delta S$ where σ is the surface tension and ΔS the change in surface area (equivalent to $8\pi r \Delta r$ for a spherical drop of original radius r).

The work done in adding molecules to the drop interior is $(\mu_0 - \mu) \Delta n$ where μ_0 is the Chemical Potential of the vapour over a plane liquid surface, μ the corresponding potential over the curved surface and Δn the increase in the number of moles of liquid.

So, if you look at this equation that the work done in enlarging the surface of a drop of liquid is sigma time’s delta S. Its surface tension is known which the force per unit length is. So, you can very easily find out this multiplied by change in area. So, sigma into delta S is the work done in enlarging the surface area of a drop of liquid, where sigma is the surface tension and delta S is the change in surface area of a spherical droplet.

So, how will you calculate change in surface area? The area of a spherical droplet is 4 pi r square and when changes from r to delta r it will become 4 pi r plus delta r whole square so, ultimately the change is 2 pi r delta r into 4. So that is 8 pi r delta r. So, this is the change in the surface area of the sphere, when the radii change from r to r plus delta r. So, this is the first thing what I have written here that by equating the work done of a spherical droplet to the liquid the first term.

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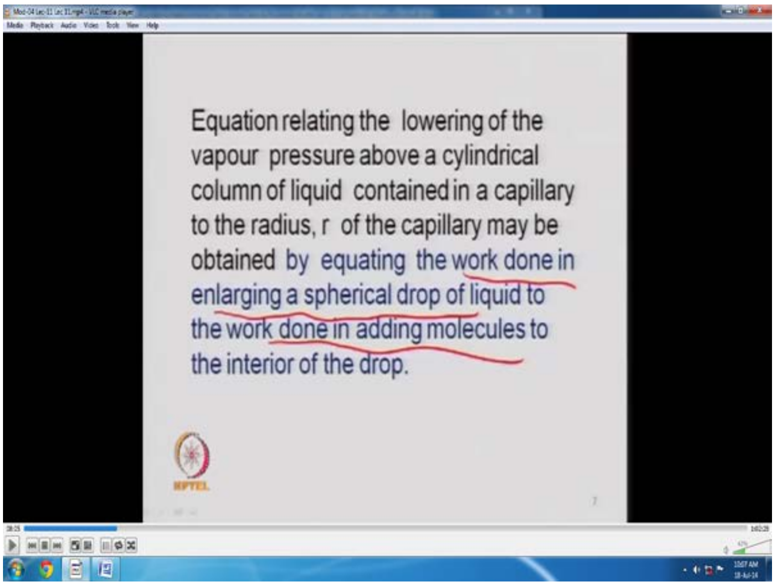

Equation relating the lowering of the vapour pressure above a cylindrical column of liquid contained in a capillary to the radius, r of the capillary may be obtained by equating the work done in enlarging a spherical drop of liquid to the work done in adding molecules to the interior of the drop.

Second term, is adding a number of molecules to drop interior because when the drop is increasing you’re increasing the mass of that droplet. So, the volume and the change in number of molecules what about delta n which is initially r radii changing r to r plus delta r so, accordingly volume is changing from v to v plus delta ,v something like that .In that we are changing calculating the change in the volume. If you know this can change in chemical potential v 0 minus mu. So, mu 0 is when it is a droplet on a bear surface and mu is on the curved surface.

So, you can if you know what is change in chemical potential and multiply with the change in number of moles that is equal to the. So, when your mu is equal to mu 0 no droplet size or no further condensation will start take place. So, no because that is the first thing to have a process. So, thermodynamics relation. So, mu 0 is the chemical potential of the vapor over a plain liquid surface, that is a wet surface and mu is the corresponding potential over a curved surface.

So, between these two you can find out the change in number that is delta n is the increase in the number of moles of liquid which has changed the volume of the droplet. So, related to that was a shape of the droplet, here we are assuming spherical but, it changed from spherical to elliptical, which is related to your principle of thermodynamics. Because; surface tries to maintain its minimum area so and so that is nothing but, related to thermodynamics that is change in the chemical potential.

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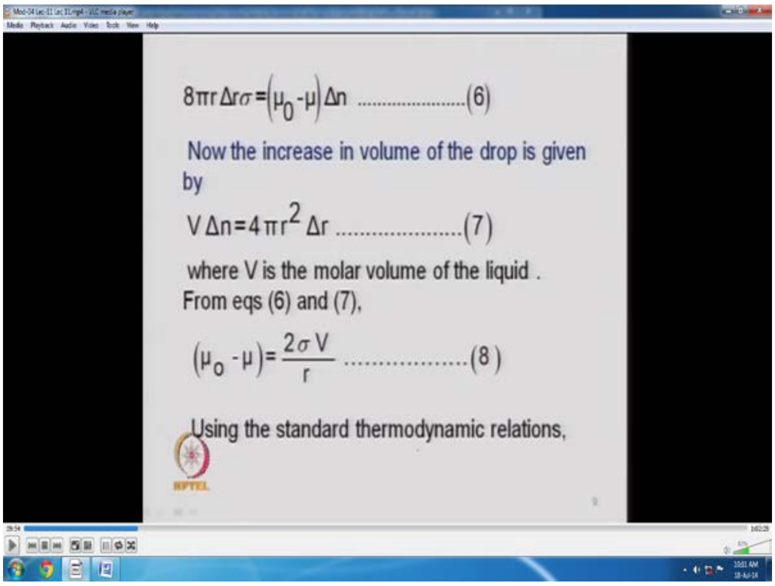

$$8\pi r \Delta r\sigma = (\mu_0 - \mu)\Delta n \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Now the increase in volume of the drop is given by

$$V\Delta n = 4\pi r^2 \Delta r \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where V is the molar volume of the liquid .
From eqs (6) and (7),

$$(\mu_0 - \mu) = \frac{2\sigma V}{r} \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Using the standard thermodynamic relations,

So,this equation is written here, 8 pi r delta r into sigma which is the work done to create a surface, or to create a drop or change in that size is equal to change in the chemical potential multiplied by the delta n because, when it is a plain surface and then when there is a some addition of the molecule the size or shape will change curved surface. So, change in the chemical potential of the two and that is the relationship for the determination of the pore size distribution of pore radius because, we are just looking at how these that surface had been created first thing From thermodynamics.

And now, you can very easily because the increase in volume of the drop that is nothing but, what about the change in number of moles time portable about the volume in that volume that is we are just calculating initial volume and final volume.So, initial volume is your whatever v and changing to v plus delta v in that there is a change in number of moles initially n i now n i plus delta i. So, if you just look at this is related to your 4 by three pi r cube. That the initial volume of that drop and when it change to final side that will become 4 by 3 pi r plus delta r whole cube, you just explain that term that will give you whatever the three term together .three, three cancels which are 4 by three and there it will be three i square delta r.

So that, term is delta square delta r here and this should be here delta n correct change in number of moles is that clear? So, volume of the drop which has increased between 2 successive adsorption in one way. So, if I just look at these 2 equations so, very easily you can this and this so, I can very easily write the value of mu 0 minus mu in terms of these 2 numbers just divide these 2 equations. So, you have 2 sigma v upon r but, sigma is the surface tension v is the volume of the liquid which is adsorbing on the surface, and that volume is basically related to your pore volume. So, this is how a drop is forming and when there is a desorption, its volume drop will the size will be decreasing same thing has been related with thermodynamics.

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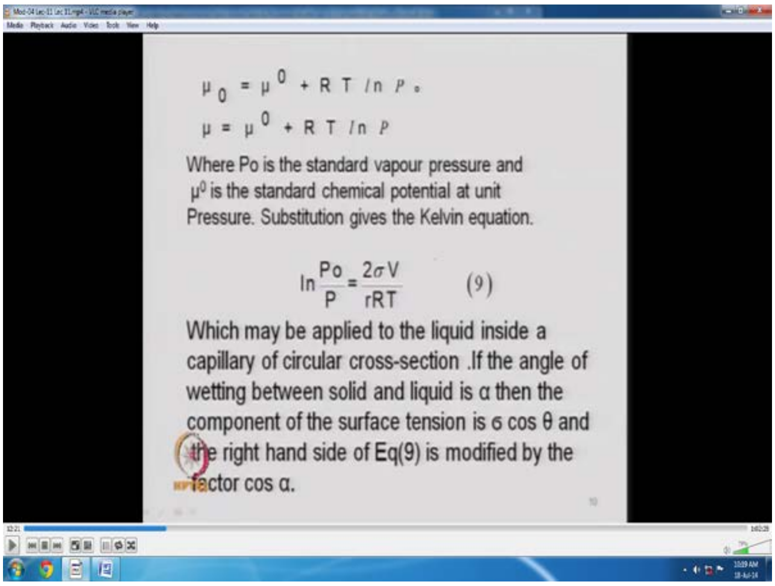

$$\mu_0 = \mu^0 + RT\,ln\,P_o$$

$$\mu = \mu^0 + RT\,ln\,P$$

Where Po is the standard vapour pressure and μ^0 is the standard chemical potential at unit Pressure. Substitution gives the Kelvin equation.

$$\ln\frac{P_o}{P} = \frac{2\sigma V}{rRT} \qquad (9)$$

Which may be applied to the liquid inside a capillary of circular cross-section .If the angle of wetting between solid and liquid is α then the component of the surface tension is σ cos θ and the right hand side of Eq(9) is modified by the factor cos α.

Because, now you know because this equation gives you mu 0 minus mu we have to find out these 2 values. So, let us look at the thermodynamics so, mu at any standard state if you know the chemical potential plus R T l n p 0 at that pressure saturation so, you have the mu 0 chemical potential at any when the drop forms or the more number of molecules are coming to the surface it mu is changing. So that, mu is again at the standard state plus R T l n o p depending on the pressure. Chemical po10tial relation mu is equal to mu 0 plus r t l n p so, there are 2 different pressures so, you can easily find out mu minus mu 0 from this equation which is simply R T l n of p by p0 if i take mu minus mu 0.

So, it means this equation is equivalent to this so that, is equal to RTl n p by p0 so, this is what your Kelvin equation. So, a derivation of the Kelvin equation which is related to your thermodynamics principle is here. So, l n of p0 by p is equal to 2 sigma v upon r R T where small r is the radius of the capillary. So, the only thing but, we have discussed earlier that this is talking the Kelvin radius because, the part of that is the absorbed layer here we are talking the liquid which is vaporizing or condensing.

So, once the monolayer has formed so, t is the layer where adsorption is taking place and after when the pressure increase to a certain pressure then the condensation phenomenon takes place capillary condensation.So, this equation is valid for condensation phenomenon. So, this equation may be applied to the liquid inside a capillary of circular cross-section because, we assume them meniscus as a circular if the angle of wetting between solid and liquid is alpha or theta so, here it is theta basically, that is for nitrogen I told it wets almost all the surfaces.

So, your theta is 0 contact angle alpha then component of the surface tension will becomes sigma cos of theta. That we have already discussed because, the is same surface 10sion force you’re relating with the just like in a mercury penetration method pressure force. And here it is the only thing that this is the condensation phenomenon, which is related to the chemical potential and change in the size of the droplet. So, this equation here you have a sigma cos of theta but, since as I said that nitrogen wets almost all the surface so, its contact angle is 0 cos theta becomes 1. So that, is what the here alpha or theta as of it can be writ10.

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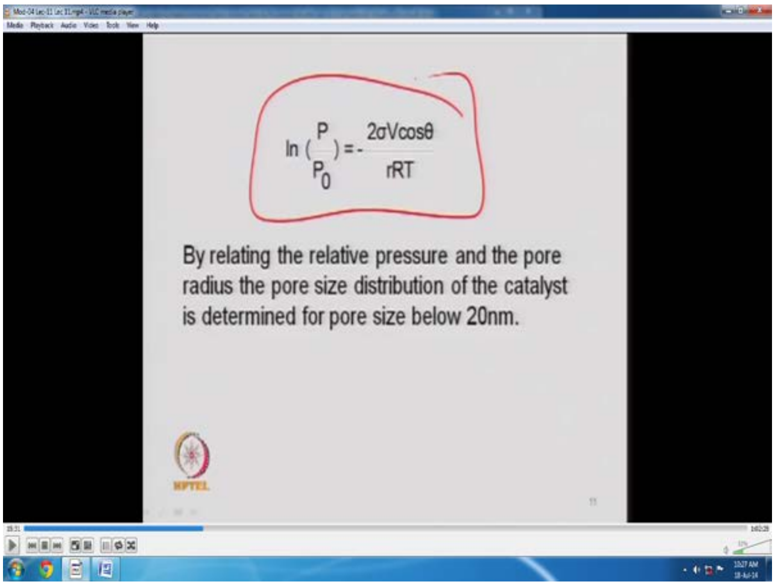

$$\ln\left(\frac{P}{P_0}\right) = -\frac{2\sigma V\cos\theta}{rRT}$$

By relating the relative pressure and the pore radius the pore size distribution of the catalyst is determined for pore size below 20nm.

So, ultimately the equation is in general is this for any gas on the surface of the solid where cos theta is generally 1 because, for most of the wetted surface. So, if you use this equation I told you that this is based on the capillary condensation phenomenon where So, it means that pressure should increase in the capillary small vapor and then condensation which will take place.

So that, is the principle here. So, it means this should be used only in the small pore not in the larger pore because; the larger pole the capillary condensation phenomenon will not be valid. So, that is a meniscus has to form a kind of meniscus, when you look at in a capillary type the concave upward or the concave downward so, here it is a wetted surface. So it will be concave onward.

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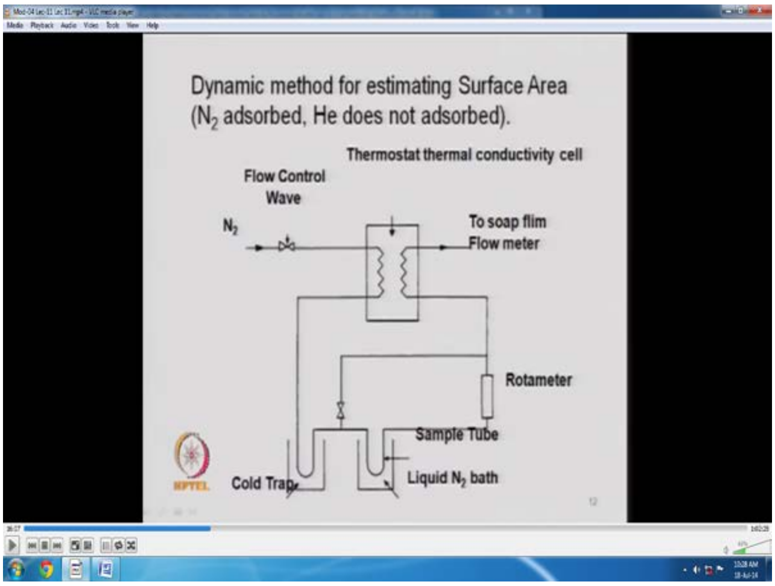

Dynamic method for estimating Surface Area (N_2 adsorbed, He does not adsorbed).

So, if you look at any principle of that adsorption desorption isotherm. So, we have a basically a detector so, this is a detector you are passing nitrogen through a sample which may be a reference sample here and that is a reference and that is your measuring detector. So, the gas passes through this so, generally we use a mixture of nitrogen plus helium and assuming that the helium does not adsorb on the surface.

So, it is an in most of the time it is an inert material so, does not absorb on the most of the solid surface under each condition. So, helium does not absorb on the surface nitrogen will absorb and they are that is why you have your liquid nitrogen bath. So this will have a temperature of minus 196 degrees centigrade. So, your gas which is here and you put your catalyst sample or which surface area of pore volume or pore size distribution is to be determined that is the sample is placed here inside the tube.

So, this is basically capillary here a small tube and in that tube you put a known mass of the catalyst sample and that this is just that you have to take generate some preliminary data to identify the limit of that pressure because, volume this surface area because, if the surface area is too high then there maybe error. So, generally we said that the total surface area should be in the range of 20 meters square per gram. So, if the sample has a surface area 1200 meters square per gram then you take a smaller mass of that sample.

So, the detector it is a limitation of the volume of the gas adsorbed. So, the range should not be more than 20 meter square or 10 meter square or like that. So, accordingly you to adjust the mass of the solid and that you can get from some preliminary data. So, you have to take a known mass of the sample which may be 1 gram which may be point 1 gram also or 0.05 gram also. So, depending upon the sample area so, you take that and put it in this and initially you need a kind of pre-treatment pre-treatment means evacuation of the pores of the solid.

So, you have to remove the gases which are inside the pores you have to remove the moisture from that pore so, you need to give a certain kind of pre-treatment that is known as pre-treatment of the sample so this can be done just by heating the sample in this chamber which is under flight vacuum. So, you can treat the sample and once that desired conditions have arrived then you start passing the gas adsorbed the gas. So, your sample is adsorbing nitrogen. So, when there is nothing is adsorbing then you will have a constant peak inside.

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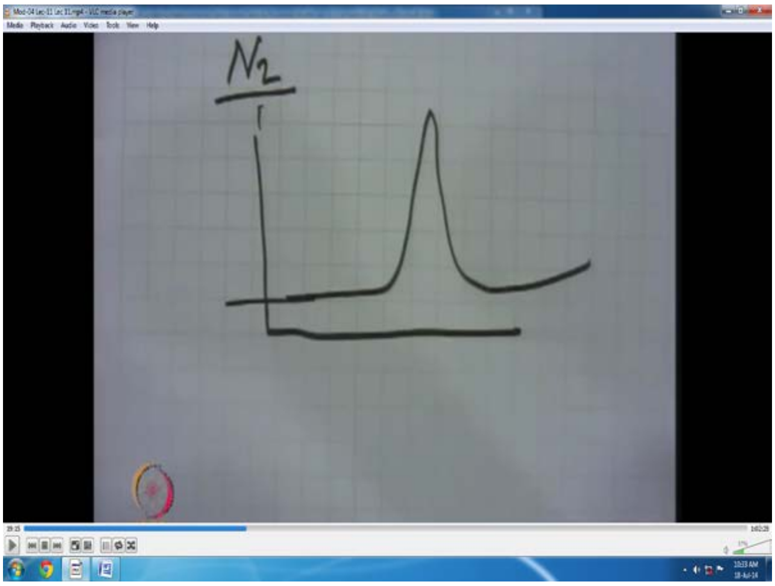

So, if you look at the detector is basically can be a thermal conductivity detector most of the time because, you are absorbed indicating nitrogen. So, basically if you look at here so, it is the volume you will get a peak like this something which is a reference so, basically suppose if I say that at any time when there is nothing is being absorbed all the nitrogen will come out without adsorbing in this chamber.

So, it means all the gas which comes and from here it passes through the reference cell. So, nothing is being adsorbed so, all the nitrogen will come here. But, as soon as your adsorption starts what will happen, the volume of gas will adsorb part of the nitrogen will adsorb. So, this area is decreasing basically, So, you will get a peak like this and this may decrease continuously and finally, it comes to the same initial value so, with this the adsorption is complete is now.

So, you can find out these areas or volume you can find out what is the volume of the gas which is at your ambient condition it absorbed and you convert that volume into the temperature of the liquid nitrogen which is minus 196 degree centigrade. So, experimentally these all are sophisticated systems, where you directly determine or can measure the surface area through using some software's or so, but the principle is something like that gas is being pass through that and it absorbs and the volume change is being measured.

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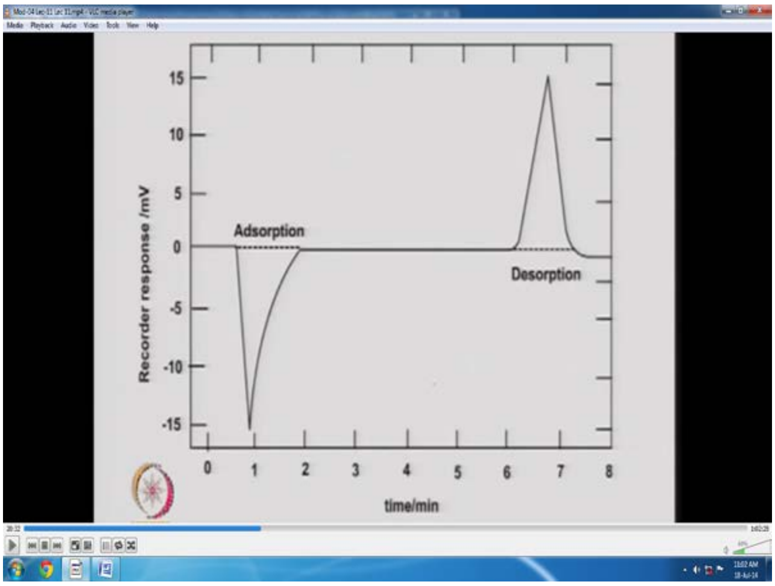

So, this is what if you have a reference of already so everything nothing is adsorbing you see a something like a 0 and then when something adsorb is always negative and when you look at the desorption it is a positive. If you change your reference electrons per plus or minus the sign may be reversed. So, basically we are just saying that this much volume is absorbed so, volume of nitrogen is decreased in that and when you have the desorption steady now everything will come out from the gas. So, this is the increase in whatever the area from that reference. So, this is your reference basically this guideline 0. So that, is the principle so, we can measure the response which may be in terms of mille volts signals 0 to 1 mille volt and versus time. Same principle will be used for chemisorptions also you can use any reactive gas hydrogen and you can find out.

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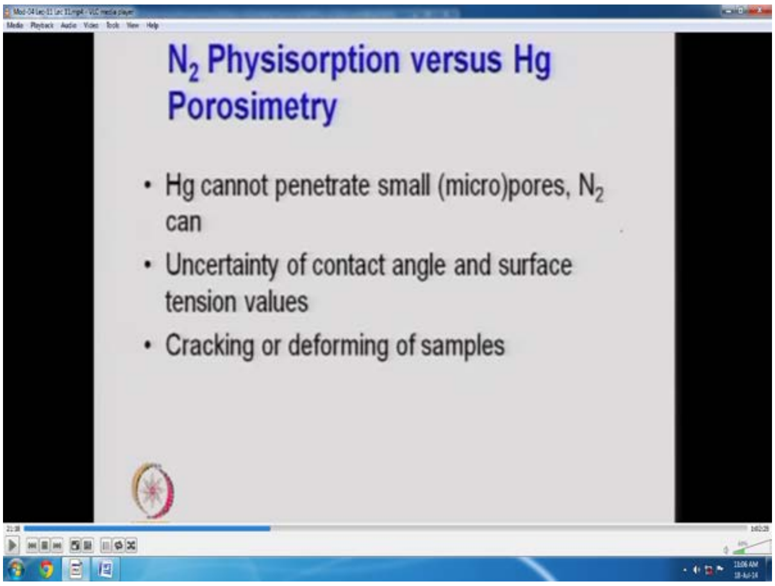

N_2 Physisorption versus Hg Porosimetry

- Hg cannot penetrate small (micro)pores, N_2 can
- Uncertainty of contact angle and surface tension values
- Cracking or deforming of samples

So, mercury porosimetry it can be a kind of b j s plot which I was discussing. The limitation is that it cannot penetrate a small pores or micro pores but, nitrogen can. So, that is why this second one nitrogen adsorption desorption method is for the smaller pore. Uncertainty of contact and surface tension values in for the case of mercury is another problem because, mercury does not wet many surfaces most of the solids of also does not wet.

The angle 4040 we take most of the time but, it can vary from 130 to 105 you have to use a different method to find out the contact angle like goniometry. So, you have to use that first, what is the contact angle for the mercury on that surface and then so, otherwise there will be a kind of uncertainty, if you measure that but, for larger we pores we are still using this but, there may be some limitations, if the angle is not correct. Surface tension also it depends on the surface mercury and surface of the solid.

So, it may also vary and when you apply this for a high pressure, there may be a cracking of the sample , the cracks may form or the sample may deform. So that, is another problem because, it reaches high pressure because under normal condition mercury does not go inside a pore of a capillary. So, you need to apply a pressure and if the pressure is significantly high then the pore may crack.

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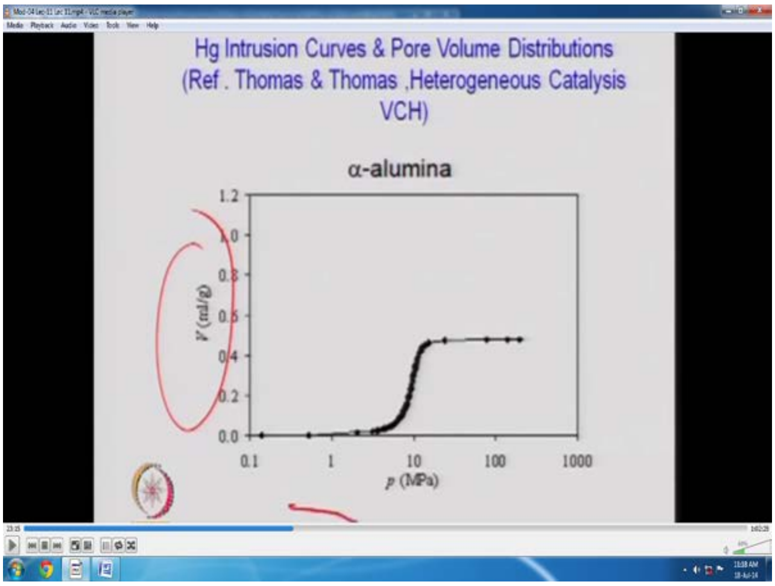

Hg Intrusion Curves & Pore Volume Distributions (Ref . Thomas & Thomas ,Heterogeneous Catalysis VCH)

α-alumina

In just a typical sample results, which I have taken from Thomas and Thomas book heterogeneous catalysis under VCH publishers. So, if you look at here the one generally in every experiment, but we do we measure the volume of the gas or volume of the liquid, if it is mercury penetration method adsorbed per gram of the sample, and this is a function of major pressures. So, in terms of the mega Pascal so, 1 mega Pascal littrangle phosphor you know.

So, we can very easily use this principle so, you can see the pore size distribution and this is the point. Some where the pores are saturated now to the pore volume; it is a kind of indication of total pore volume. So, this is it cumulative plot which I was talking earlier also, where you have measured the volume of mercury penetrated versus pressure so,the pressure can be shy of the order of say thousand ampere here or 10 thousand atmosphere very high pressure, than v to v apply.

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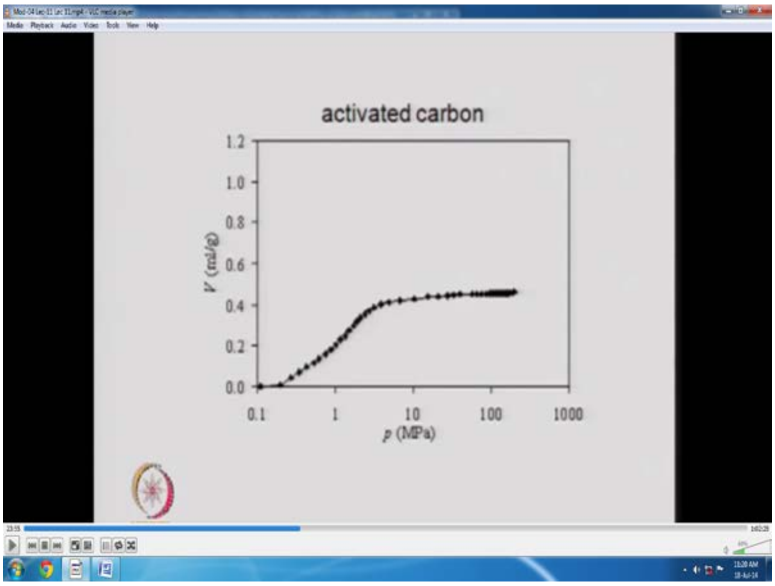

It similarly, this is the curve for activated carbon. So, you can see that depending upon the type of the sample and their pore size.You have the different kind of behavior here the smaller pressure, because it maybe a wider pore here. So, the pressure requirement is smaller to fill the all the pore here; something like this just that if you look at her 9 or 10 MP and the all pores are filled where there in this case it can be a kind of alpha alumina, I told you it is a micro-porous material basically.

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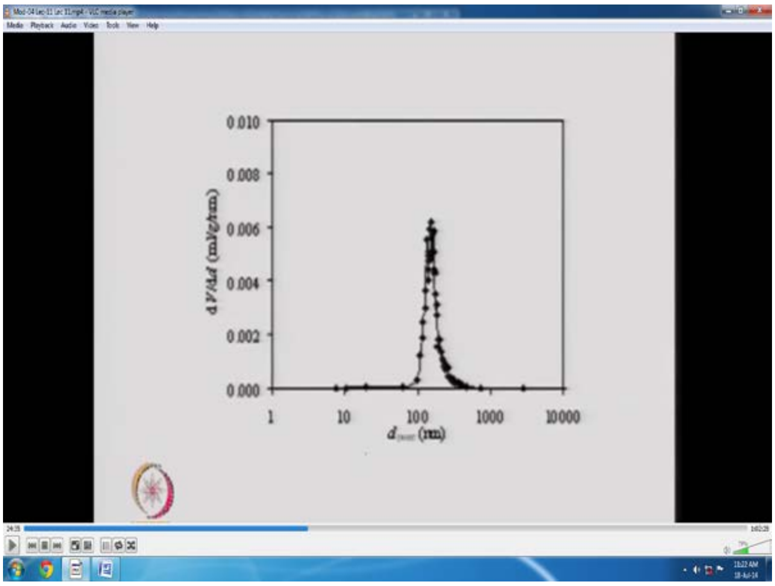

So, the causes are very high pressure, and then when once you have that so, the first thing is that you generate the data the volume as a function of a fashion or of p y p0 and then you plot that cumulative plot and this is nothing but, a plot of d v over d of log a You can have a log on that x axis versus the pore diameter.

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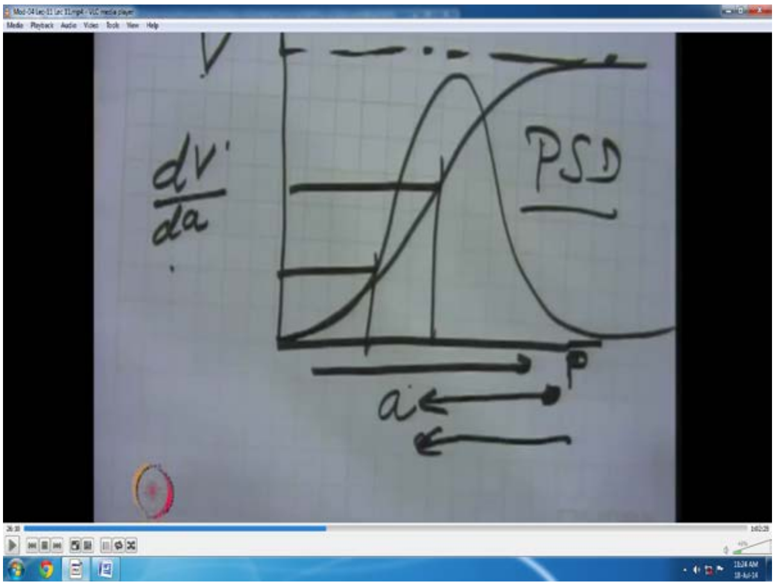

So, sometimes what I told last time also that, you kept d v over d a versus pore radius or pressure. So, when you’re pore radius is increasing like this. It means pressure will go like this or generally we apply pressure like this. So, most of the time you have higher pressure this side so, it means your pore size is increasing in this side. So, this will be p applied pressure and this is your pore size. So then, cumulative is like this and now you have to find out.

So, what does this mean? So, this is representing, if I just say this is the cumulative pore volume. So, this is representing the total pore volume of the solid, for a given mass and if you want to see between 2 pressure differential between 2 radii.So, you have to look at this 2 volume. So, a slope can be measured delta v upon delta a since a is a small number. So, you can take a log of that d v upon do log of a and you can plot another graph and that will give you a kind of pore size distribution like this. So, this is known as pore size distribution which is d v over d that is delta v upon delta a versus a measured from the tangent or you can just plot a log of that semi-log d v over d a versus this so, this is known as a pore size distribution.

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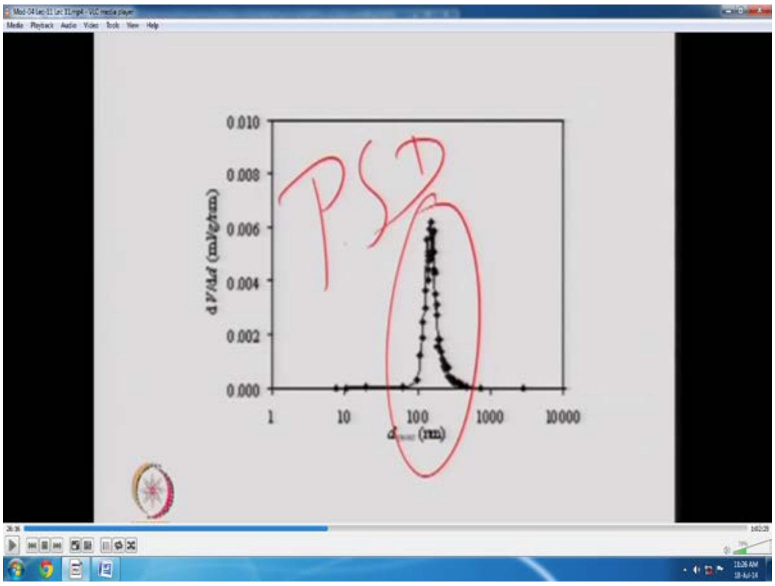

So,this does it indicates, that the most of the pores or all the pores in the solid are between 100 and 1000 nanometer. So, this is the indication of that, and these are the kind of pores which are which have the maximum number of pores are of this size so that, is the meaning of distribution what you say, when you do the sewing, then also you have this kind of distribution and you call that differential cumulative method of analysis for determination of particle size. So, this is the indication of the pores available in a solid.

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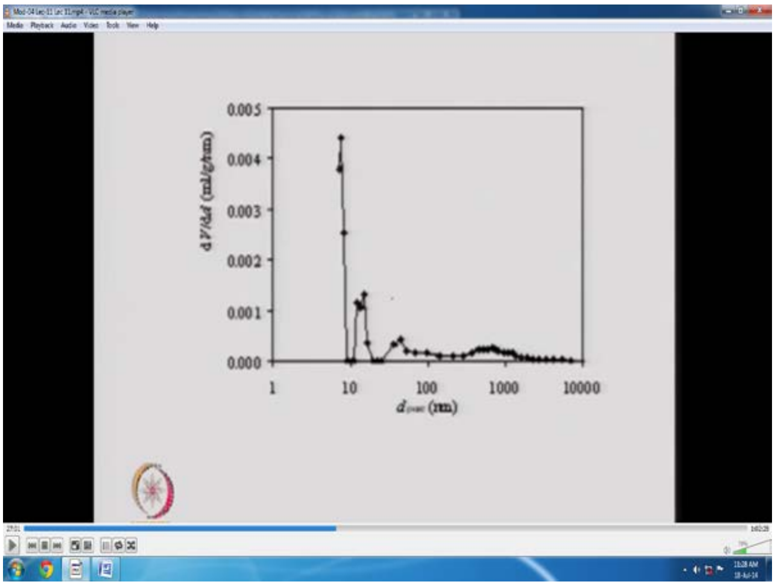

So, the pores size distribution may be like this also by model multi-model. So, there are just indicating the different kinds of pores available in 1 solid, micro-pore miso-pore and micro-pore all types of pores are available is there the distribution, of the pore size distribution. So,this that depending upon the type of solid, the pore size distribution may be different this may be a case of your alpha aluminum, and this maybe a case of something like carbon area which is very high, white pore size distribution.

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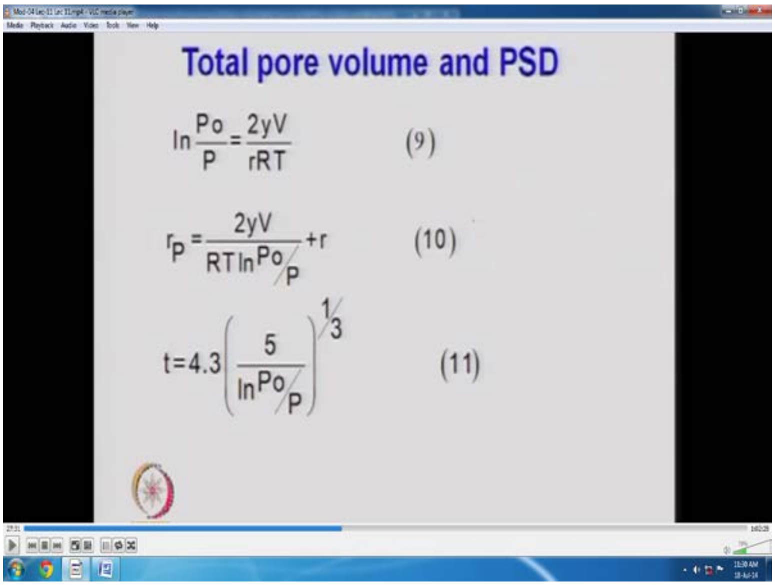

Total pore volume and PSD

$$\ln\frac{Po}{P} = \frac{2yV}{rRT} \qquad (9)$$

$$r_P = \frac{2yV}{RT\ln Po/P} + r \qquad (10)$$

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

So, basically the determination of total pore size distribution we have now already understood about that and the principle steps which because, in between to find out we can have the intermediate properties also just like t plot. I said thickness of the adsorbed layer thickness of the monolayer.So that, is also equally important to characterize surface. So, the principle equation, we have already seen. So, whatever you need to find out the thickness of the monolayer or multilayer which is formed the pores radius. So, r that is r p is related to your thickness of the plot plus, this is your whatever the equation Kelvin equation and plus the thickness of the adsorbed plot. So that, is your total pore radius. So, hysteresis of this is like this and you have the wheeler model also, by which 1 can determine the thickness of this t so, this is a wheeler model. So, I will come back to that again.

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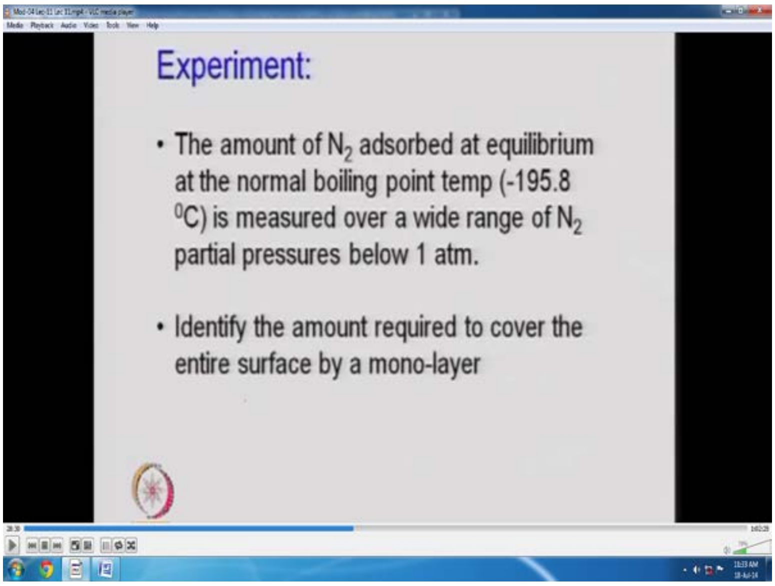

Experiment:

- The amount of N_2 adsorbed at equilibrium at the normal boiling point temp (-195.8 ^{0}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

So, in experiment what we are doing the amount of nitrogen adsorbed at equilibrium at the normal boiling point, which is from nitrogen roughly minus 196 degree centigrade that is measured over a wide range of nitrogen partial pressure and that is below atmosphere. So, saturation pressure of nitrogen 750 millimeter of mercury and then you identify the amount required to cover the entire surface by a mono-layer t m. So that, is what we are talking for nitrogen what is the value t mono-layer thickness that can be determination of the area of 1 molecule and then total volume of the gas absorbed and at a standard condition 1 gram mole of the nitrogen, has how much volume. So, by using this gas log you can calculate and knowing the density of liquid nitrogen.

One can determine the thickness of the absorbed layer and assuming that they have some hexagonal closed pack array because molecules are absorbing on the surface and you have to get that in a mono-layer form these are the number of molecules area of 1 molecule is known so, mass of that molecule can be determined. So, per molecule how many mole per mass per unit mass. How many molecules have adsorbed, you can find out and then you determine from the thickness of 1 layer. So, you can find out.

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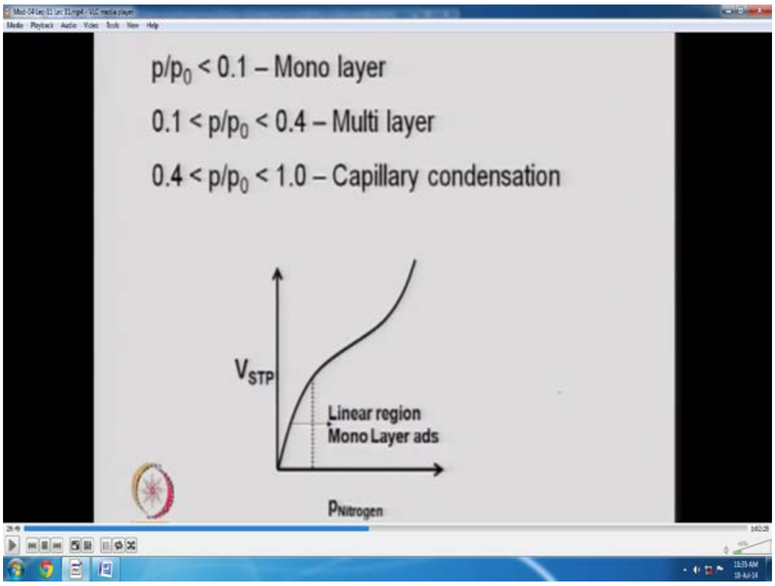

$p/p_0 < 0.1$ – Mono layer

$0.1 < p/p_0 < 0.4$ – Multi layer

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

So, we have already seen this, that p by p0 less than point 1. We say that a mono-layer is formed which is just the indication of this here and point 1 to point 4, it is a multi-layered adsorption which is here like this is a multi-layered adsorption and when it goes more than this then the capillary phenomenon takes place. So that, typical BET isothermal curve. If, you look at that when you apply the pressure so, generally we do not go more than p by p0 0.3 all or so, even less because we know we can understand that up to that the mono-layer has formed.

And that those data are sufficient to give you the total surface area of the solid but, when you want to do the pore size distribution and then you need to go to a higher pressure. So, you may have 0.7 form points.You need more than0.7 because that time you need to go to a larger number of data point, in the same range also you have a 0.3, 0.5, 0.7, even in the mono-layer that is in this z1 to get more and more accrue ratio of the data.

But it is advisable that when you look at a complete pore size distribution, you go with the wider range of the pressure because, that is related to the capillary condensation phenomena note that jobson we this is only if you go p by p0 less than 0.1, you will get a just a monolayer and that is sufficient for determination of total surface area or average radius of the pore.

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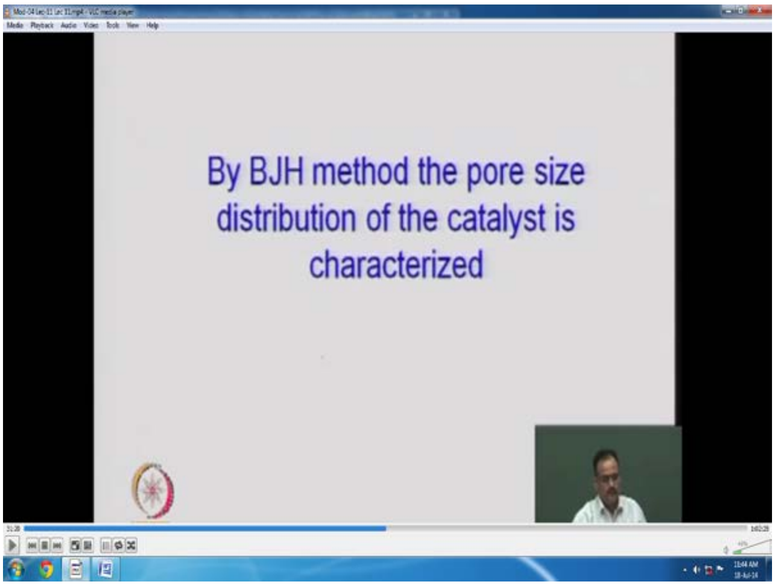

By BJH method the pore size distribution of the catalyst is characterized

So that, is what write here by BJH method, the pore size distribution of the catalyst is characterized, that is BJH is direct joiner and holanda. These three scientists they have developed this method and basically it is a t plot method, when you look at the adsorbed layer thickness, and then you can calculate.

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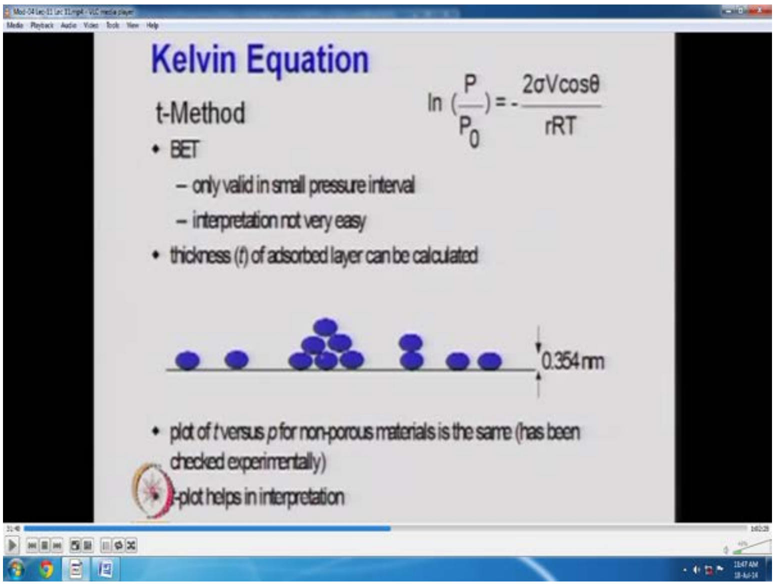

Kelvin Equation

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

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,we will just look at those steps so, related to kelvin equation so, in this we have already seen this earlier also so, I am talking about this 0.354 nanometeror 0.354 angeostrom is the mono layer, when the mono layer forms that is the thickness of the nitrogen, adsorbed layer nitrogen for a monolayer. So, I was talking last time the total layer thickness t, t is your total thickness and that is equal to if you know that the number of layers how many formed and what is thickness of 1 mono layer t m. So that, is the number of layers you can go with the BET isotherm because, it is a multilayer so, you have to calculate the total number of molecules or mass of the nitrogen adsorbed or volume of the nitrogen adsorbed and then you calculate the surface area or volume for a monolayer and related with the thikness so that, is what we are looking now.

That we have already said this that BET is only valid for small pressure intervals you need to give the pressure differentials for say smaller pressure differential the results will be better and interpretation may have some problem. So that, is where the BET because otherwise this t the BET can also give you the thickness of the job level that he volume of the that what I said earlier the volume of the gas adsorbed and you correlate so but, that is not a very correct method.

So, that is why nitrogen adsorption desorption method is better. So, we are looking that so plot of this thickness, thickness t of the adsorbed layer can be calculated that is what we have seen earlier where viewer’s model is 1 so v that is based on a Kelvin equation itself and that is what we are talking is that in general you have the layers which are forming like this and we are interested in this kind of monolayer thickness. So, if you know that t for all BET equation as I said just the volume of the gas adsorbed in that volume how many mass is adsorbed and if this 1 monolayer formed this is the thickness. So, how many what is the multilayer thickness that is t as a function of pressure because, that is a function of pressure.

So, if you plot t versus p for any non porous material that is same and that has been checked experimentally because the only monolayer will form no capillary condensation. So, generally to have our base we select a non porous material and then calculate this 0.354 what I have said there no multilayer will form but, once you have a porous material then the material condensation will take place and condensation will give you the multilayer thickness.

So, this helps you to interpret that how many layers have formed and when the actual reaction is taking place what number of layers may form or when you look at the surface area or determine the metal surface area or dispersion that is also related to the thickness of the adsorbed layer.

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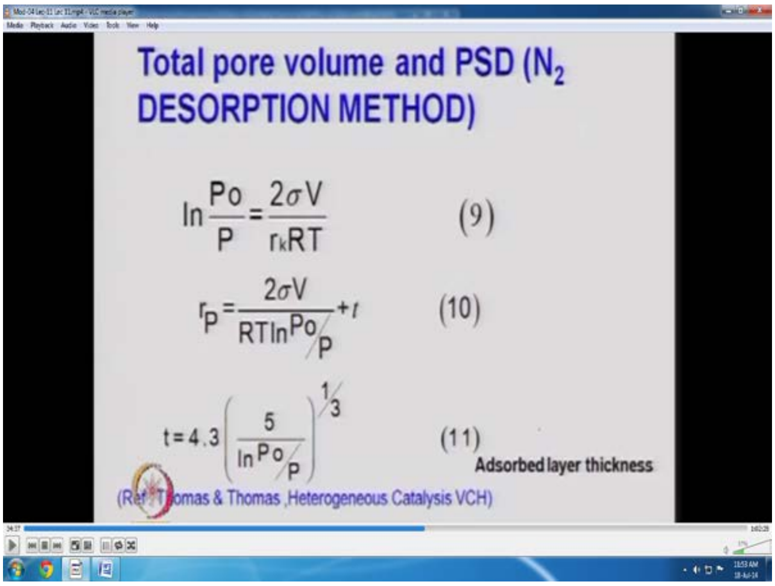

Total pore volume and PSD (N_2 DESORPTION METHOD)

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

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

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

Adsorbed layer thickness

(Ref Thomas & Thomas ,Heterogeneous Catalysis VCH)

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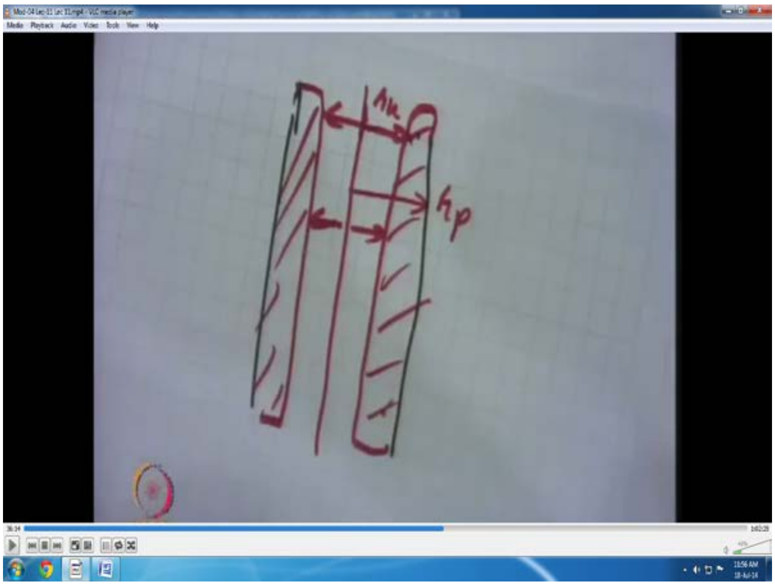

So, this equation I am saying again and again because, these equations are related the first thing is that Kelvin equation which is related to the vapor pressure to fill a pore of a capillary. So r k I have written here, it is a now Kelvin radius so, because this is not the total layer or total related to the pore volume rather it is only the thickness which is above that. So, if I talk this layers these are adsorbed layer so, after that the equation will come.

So that, we have already seen and just equate look I am just talking suppose this is the capillary now as I said that part of the layers are adsorbed. So, they will not be available for condensation so, this layer thickness is adsorbed layer and now this is the surface where the condensation and vaporization will take place on this. So, what we are getting from Kelvin equation, because that is talking the vapor pressure of these layers so, this is your r k basically from this side to this side centre to this whereas, the total pore radius is your r p correct.

So,this delta v is the nothing but, the volume of gas which is adsorbed for making adsorbed layer and here the whatever the vaporization takes place that will give you the idea that the volume of the pore which or which have been vacated because, of the capillary desorption phenomena because, it is related to the vapor pressure and vapor pressure is related to Kelvin equation.

Now for this adsorption so that, is the first part here that the Kelvin equation which we have written here in this so that, is your Kelvin radius r k so, actually pore radius will be this what you get from here plus the thickness of that adsorbed layer. So, this your r k which is calculated from this and this and thickness of the adsorbed layer as I said BET method or you use this viler model so, this is again given to the power 1 by n so, roughly n is 3. So, this can be used to determine the thickness of the adsorbed layer and that is a function of pressure. So, you can find out t as a function of pressure as I said in the BGH method also, let us see that.

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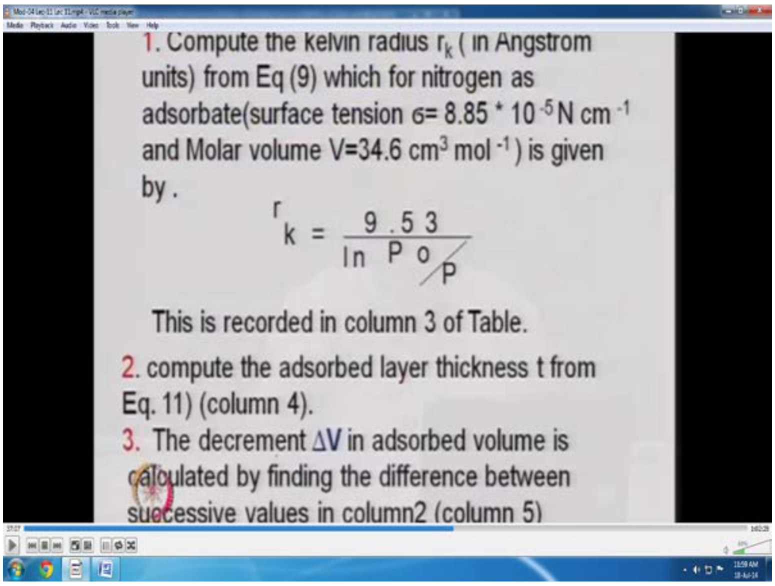

1. Compute the kelvin radius r_k (in Angstrom units) from Eq (9) which for nitrogen as adsorbate(surface tension $\sigma = 8.85 * 10^{-5}$ N cm^{-1} and Molar volume V=34.6 cm^3 mol^{-1}) is given by .

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

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, there are several steps and these steps I have taken from the thomas and thomas so, this is given in chapter 4 so, basically what we have now we have the data something in this form.

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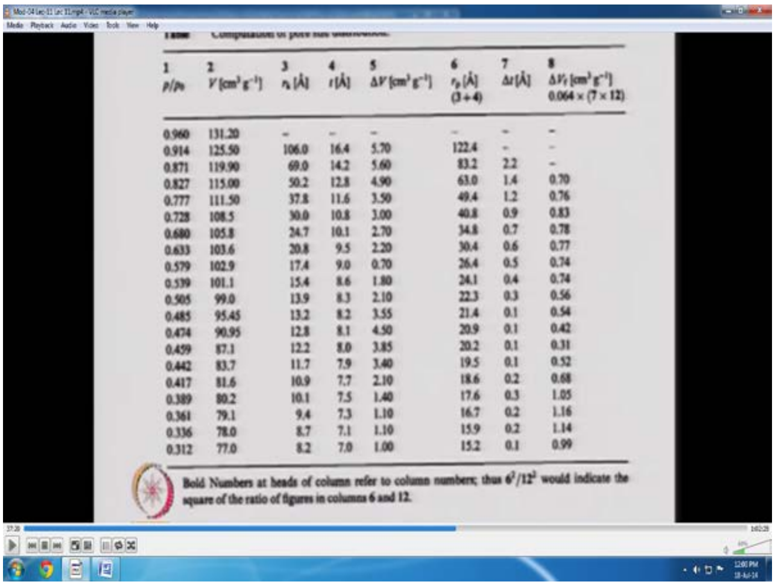

1 p/p_0	**2** V [$cm^3 g^{-1}$]	**3** r_k [Å]	**4** t [Å]	**5** ΔV [$cm^3 g^{-1}$]	**6** r_p [Å] (3+4)	**7** Δt [Å]	**8** ΔV_t [$cm^3 g^{-1}$] 0.064 × (7 × 12)
0.960	131.20	-	-	-	-	-	-
0.914	125.50	106.0	16.4	5.70	122.4	-	-
0.871	119.90	69.0	14.2	5.60	83.2	2.2	-
0.827	115.00	50.2	12.8	4.90	63.0	1.4	0.70
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.

Experimentally you are having this if you just carry out lab experiment without using any software then you are basically determining the volume of the gas adsorbed under normal condition as a function of pressure differential pressure 1 condition and this is set up. So, we have this data and now what we need to find out we need to find out Kelvin radius, we need to find out adsorbed layer thickness, we need to find out the change in volume between 2 successive pressure differential volume desorbs and then we need to find out pore radius, that is the pore size distribution and then we can find out the thickness or deta of that thickness between 2 chain that how the adsorbed layer thickness decrease when the pressure is appliedor increase when the pressure is applied because; when you are applying the pressure the thickness is changing,

And then you have the change in volume in the between 2 successive pressure differentials. So, likewise what I mean to say where you can find out the Kelvin that is the volume differentials between 2 radii r and r plus delta r surface area change in pore volume. So, plenty of information can be obtained from that p by p0 versus volume.

So, these are the steps which I have I shown here. So the first point is that from p by p0 versus v you have plotted that cumulative graph in 1 way and simplest as I told you are calculating d v over d of log at that is your pore size distribution graphically, If look at the software algorithm it goes like this. So, just compute the kelvin radius r k which is an angstrom unit and that is from the equation which we have already talked here.

So, your r k is calculated surface tension is known to you for nitrogen 8.85 into 10 to the power minus 5 newton per centimeter molar volume, that is in the unit of centimeter cube per gram mole you know 1 gram mole of the gas which has 22.4 liter so, for nitrogen you can very easily calculate the volume per gram mole so, roughly comes 34.6 so,35 centimeter cube per gram mole.

So, r k is in simple 5d way is calculated like this. So, Kelvin radius is simply 9.53 divided p0 by p where p0 is the saturation pressure and p is the pressure applied pressure. So, at different pressures you will have different value of Kelvin radius that is the first term and this is shown in the table what I have shown here once this is known.

Second point is compute the adsorbed layer thickness t from equation 11 here so, this is the thickness of the adsorbed layer. So, the algorithm is now provided and you can direct your software there and your system like micro merits you get directly these values but, 1 has to understand these thing that how these value came or if you want to develop your own core you can use these algorithm.

So, this is the thickness of the adsorbed layer so, once this is known you calculate the decrement in the adsorbed volume because, when there is a vaporization the volume is decreasing which I have talked earlier related v and v plus delta v and related to the radius 4 by 3 pi r cube of a sphere. So, change 4 by 3 pi r plus r whole cube. So, you can very easily calculate from this by finding the difference between the successive values in column 2 and that has been shown in column 5. So, basically what I am showing here in this is the decrement in the adsorbed volume so, let me show you that table first this 1.

So, this is the change in the volume if you look at this value and this value so, between 2 successive pressures so, this curve is used to calculate that when you have changed the pressure from p to p's plus delta p what is the difference in volume. So, at this pressure the volume adsorbed was this and when the pressure this is representing a if I go from here to here it is a cumulative volume basically so, this 125 and 131 so, difference of this minus this is reported here this same thing for the this minus this will be reported here. So,this indicates simply the successive difference in volume of the gas which is vaporized between 2 successive pressure. If I have adsorption then this will increase in this way if I have desorption then it will decrease in this way.

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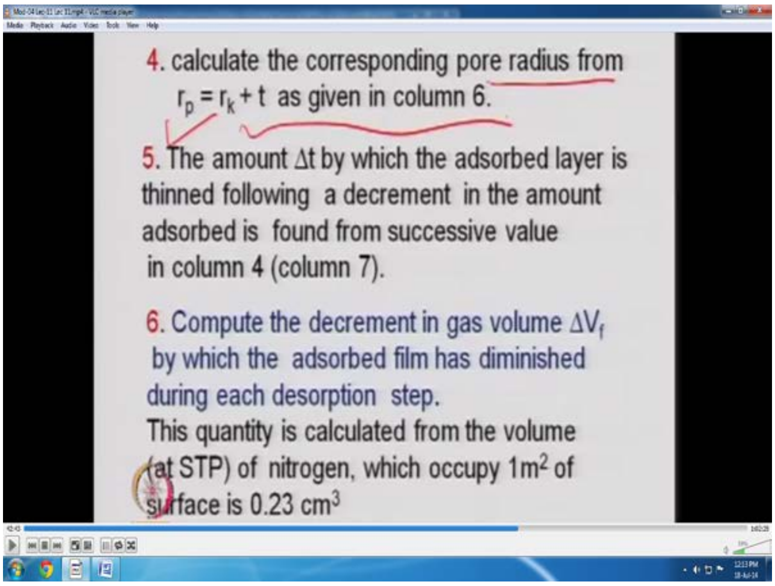

4. calculate the corresponding pore radius from $r_p = r_k + t$ as given in column 6.

5. The amount Δt by which the adsorbed layer is thinned following a decrement in the amount adsorbed is found from successive value in column 4 (column 7).

6. Compute the decrement in gas volume ΔV_f by which the adsorbed film has diminished during each desorption step.
This quantity is calculated from the volume (at STP) of nitrogen, which occupy 1m^2 of surface is 0.23 cm^3

So,this is reported in column 5 as I discussed and then you calculate the corresponding pore radius from r p is equal to r k plus t because, now adsorbed layer thickness is known r k you have already calculated so, pore radius can be determined. So, r p is equal to to r k plus t and that has been shown again in the column so, I will go back then later. Once this is known so, I told you that I want a delta t at between 2 successive pressures if differential volume has been vaporized or reduced changed and between so, when these 2 volume change how much thickness of the layer is decreasing or increasing when it is adsorption increasing desorption decreasing. So that, is the delta t which the adsorbed layer is thinned when it is a desorption now following a decrement in the amount adsorbed is found from successive values in column 4.

So that, is what here this is your column 4 so, if i just take a differential between these 2 14. 2 and this so that has been shown here 7. So that, is when the pressure was this the thickness at this pressure 0.960 so, I am talking 0.914 the thickness was 16.4 angstrom and when you change it to pressure 0.871 desorption so, reduce the pressure to this the thickness change to 14.2 so, what is the thickness which is changed between these 2 is 40 16.4 minus 14.2 and that value has been reported here and so on,you can get the idea that what pressure that is maximum vaporization or maximum release of the number of molecules or what is the distribution because, these thickness of the adsorbed layer is related to the capillary size.

So, you can get the idea about the capillary or you can have the idea about hysteresis also that is adsorption desorption hysteresis, which is related to this delta t of the adsorbed layer thickness or the pressure difference here. So, this is done and now compute the change in volume or decrease in the gas volume delta v f by which the adsorbed film has diminished during each desorption step. So, now we are talking that what is the volume change from 2 pressure differentials and that is related to in terms of the adsorbed layer thickness also.

So, a different approach basically because, we are saying that the quantity is calculated from the volume of nitrogen which is measured at a standard condition of temperature and pressure to occupy 1meter square of the area of the surface that is 0.23 centimeter cube if you calculate from your p v is equal to n r t then 1 meter square because,162 angstrom square is the area of 1 molecule of nitrogen and 35 centimeter cube per gram mole also I have talked.

So, 1 can very easily calculate that if you have the 1 meter square of the surface and nitrogen has a surface area of 16.2 angstrom square. So, how much volume of that gas will come to that at a density of 0.808 so that, comes roughly 0.23centimeter cube.

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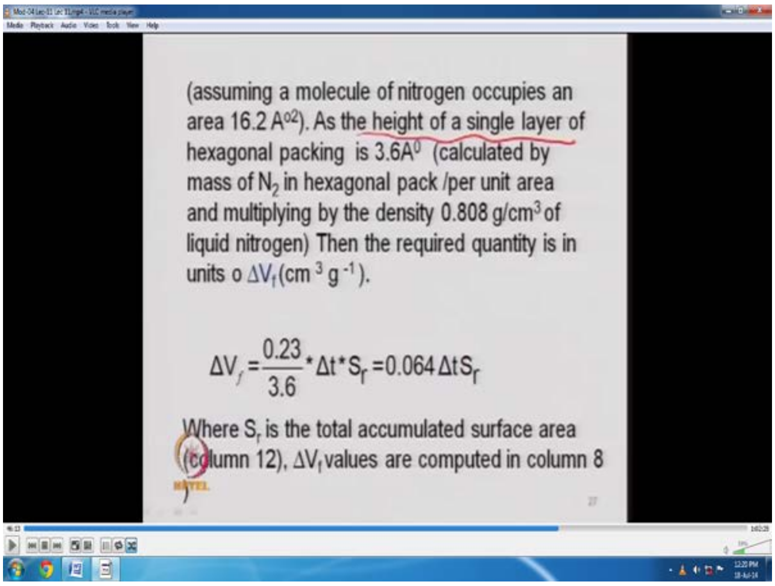

(assuming a molecule of nitrogen occupies an area 16.2 A^{o2}). As the height of a single layer of hexagonal packing is 3.6A^0 (calculated by mass of N_2 in hexagonal pack /per unit area and multiplying by the density 0.808 g/cm^3 of liquid nitrogen) Then the required quantity is in units o ΔV_f(cm ^{3} g $^{-1}$).

$$\Delta V_f = \frac{0.23}{3.6} * \Delta t * S_r = 0.064 \Delta t S_r$$

Where S_r is the total accumulated surface area (column 12), ΔV_f values are computed in column 8

If, you calculate that and now we are interested in calculating the height of single hexagonal layer height of a single hexagonal we are assuming that the nitrogen molecule that adsorbs on the surface are arranged in a array so, 1 over other stacked so, if you know this that what is the mass of nitrogen in hexagonal pack and you know the area mass of the nitrogen in the hexagonal pack per unit area which can be determined because, you know this is 16.2 angstrom square that volume is known molecular weigt of nitrogen is known. So, this thickness basically it is the thickness or height of a single layer I am calculating t so, which is I have already shown earlier also 3.54 the same thing here.

So, we have written it 3.6 angstrom. So, basically hexagonal pack per unit area mass of nitrogen and density is known 0.808 so, multiply these 2 if you get so, you can have the value of the nitrogen thickness. So that, is basically this number which I was talking and can be calculate, If you have a non porous material also but, basic idea is that what is the mass of the nitrogen molecule which adsorb, what is the thickness of that layer is to be calculated height of 1 monolayer. So, and that is nothing but, calculating that 116.2 angstrom square is the area covered by 1 molecule of nitrogen.

So, in that what is the mass of that molecule is m by m 0 rho. So that, is what earlier I calculated r is equal to m by m0 rho to the power 2 by 3 radius of that molecule nitrogen radius so that, is related to this. So, if you know that which we are saying that this is roughly 3.6 angstrom. So, you can calculate the required quantity in the units of delta V f. So,what is delta V f,you just try to understand again decrementin the gas volume by which the adsorption has diminished.

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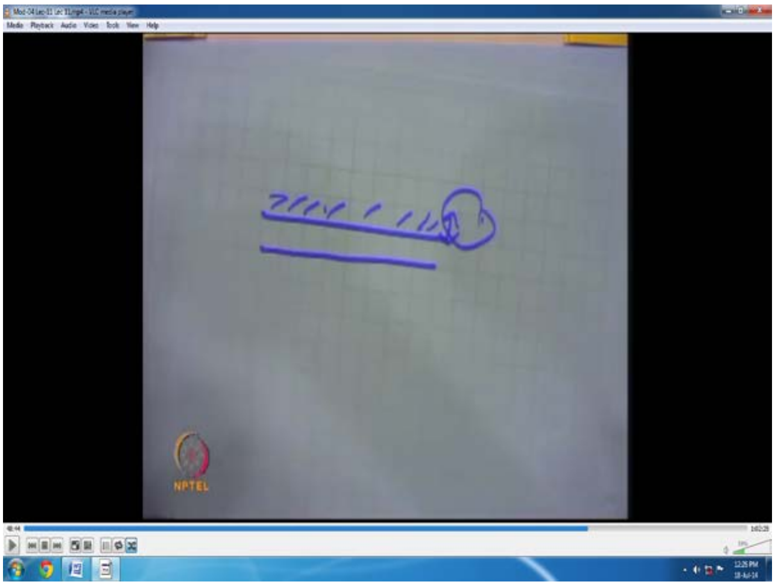

So, it means what we are talking there is a thickness and when the so, when there is a so I am saying this is the adsorbed layer thickness so, in this thickness has changed by this delta t what is the volume has g1,what volume of the gas has been or liquid has been vaporized because, it is a condense layer when you have released the pressure so, part of the volume has vaporized in that what thickness delta t, we already calculated because that is something which is related to basically 4 by 3 pi r plus delta r whole cube minus 4 by 3 pi r cube which I was talking earlier. It is related to volume also because the volume of the gas molecule is decreasing size is decreasing so that, layer thickness which we are correlating because you know this now. So that, is the change in thickness so, this delta t has been removed.

So, in that delta t and this is when the per layer thickness basically 1 thickness so, point 2 3 is this which we have written here that the volume of nitrogen per meter square has this much volume per unit area and so per unit area has this.

This is the thickness of 1 layer and this is the change in thickness delta t. So, it means and this is the surface area and 1 area s r is the total accumulated surface area which is given here. So, surface area multiplied by thickness that is something related to a kind of volume and this is what I am saying the per thickness, when the per unit this 3.6 angstrom is the height of the single layer which is basically. So, in 1 way you can calculate that change in thickness delta t when the or number of molecules in that delta t divide by if I take thickness of this. So it is talking in terms of number of layers basically roughly and in 1 layer what is the area i am calculating.

So, I have calculated the number of areas here, number of layers which has some area and 0.23 I told is the mass per meter square. So in that meter square what is the area so, this delta t upon t is talking number of layer s r is talking area.So in the per layer so, this s r into delta t is talking the total area of those layers and in meter square, what we have talked earlier and this 0.23 is per meter square. So, multiplied by that so, this is simply representing the change in the volume of the gas which has decreased from the surface.

So, s r I will just look at this thing delta v f which is related to the change in number of molecules,because you know delta t here thickness of this you have already calculated this. So, this change in thickness and when you see that the per molecule I have talked that 3.6 angstrom the when the they are arranged hexagonal pack then thickness or height of that layer adsorbed layer and this is the thickness.

So, if I just take 2.2 change in thickness divide by 3.6 it is talking something change in number of layers or thickness of that layer and now I am interested in this thickness of the layer, what is the area decrement delta a so,I know that 0.23per meter square. So, I have just calculated the area decrement and multiplied it with the total which is here s r. So that, is shown here basically this 1 meter square per gram for that given change in volume for the surface.

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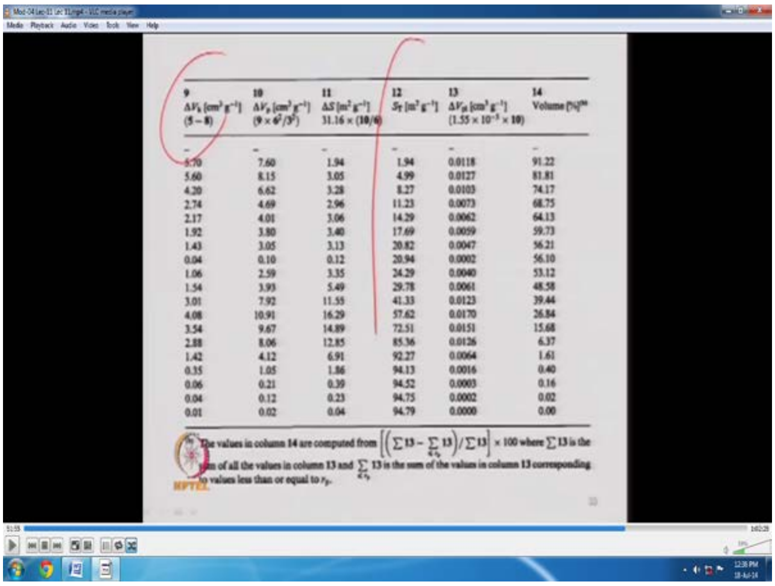

9 ΔV_k [cm^3 g^{-1}] (5 − 8)	10 ΔV_p [cm^3 g^{-1}] $(9 \times \bar{r}^2/\bar{r}_k^2)$	11 ΔS [m^2 g^{-1}] $31.16 \times (10/\bar{r})$	12 S_T [m^2 g^{-1}]	13 ΔV_{ft} [cm^3 g^{-1}] $(1.55 \times 10^{-3} \times 10)$	14 Volume [%]$^{(a)}$
-	-	-	-	-	-
5.70	7.60	1.94	1.94	0.0118	91.22
5.60	8.15	3.05	4.99	0.0127	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, multiply that so that, will give you the total surface area which is your and in that given volume which is 0.23 per So, the total volume of that decrement can be calculated. So,what I mean to say here, although this is not a very useful information but, this can give you the volume of the gas which is desorbed in a given differential pore size. So, if the pores are wider the drop will be faster in that range and when the pores are narrower the volume drop delta v s will be smaller in number.

So, you can get the idea that which kind of pores are dominating in your system or in your catalyst so that, is the important property which you or information which you can get from this information but, only for a differential size. So, this can be used when delta f is known you can find out the kelvin volume also because, see now we have calculated the desorb layer volume this is not the capillary condensation phenomena and so that, is why we calculate it from our surface area method of measurement s r is the surface area of the adsorbed layer 16.2 angstrom is the 1 molecule and then we are calculated the total. So, if this is known which is the volume of the adsorbed gas adsorbed not the condensate.

So, total volume is already known core volume minus this adsorb is your Kelvin volume which can also be correlated with pi r square l that is something like equal this is nothing but, equal to that 1 if I just calculate pi r square l and the same thing again at pi r plus delta r square l. So, you are 2 pi r delta r that is the surface area that 2 pi r delta r into l is the volume of the capillary condensate this is your r k.

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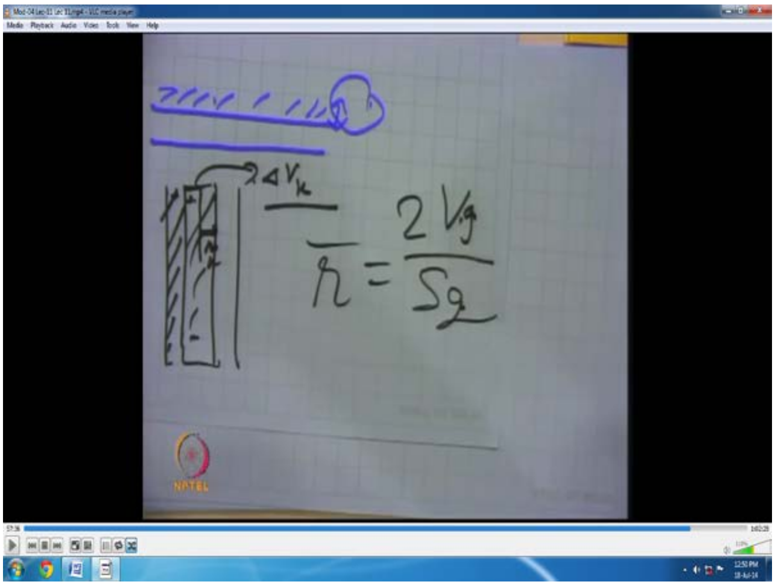

If you know the Kelvin radius and you know the length of the capillary. So, pi r square l is the volume of this and from there the desorption is taking place. So, when desorption is taking place your r k is changing that is what we have seen. So,desorption taking placemeans r k is decreasing. So, more some volume has g1 so, from this what is the volume left is your delta V k between 2 kelvin radius r k and r k plus delta k but, this time which i have talked delta v f is there for the adsorbed layer so,this delta Vf is the volume of the gas which has dissolved from the adsorbed surface.

So, basically we are not talking that part because, that we are calculated from our BET isotherm or for a pressure p by p0 because, we know the t for that adsorb layer or mono layer what 0.354 nano meter, we said and then we know that this 16.2 angstrom is this area. So, between 2 successive layers we are calculating what is the change in number of adsorbed molecule because; that is a monolayer and when multi layer forms then there is a change after that condensation.

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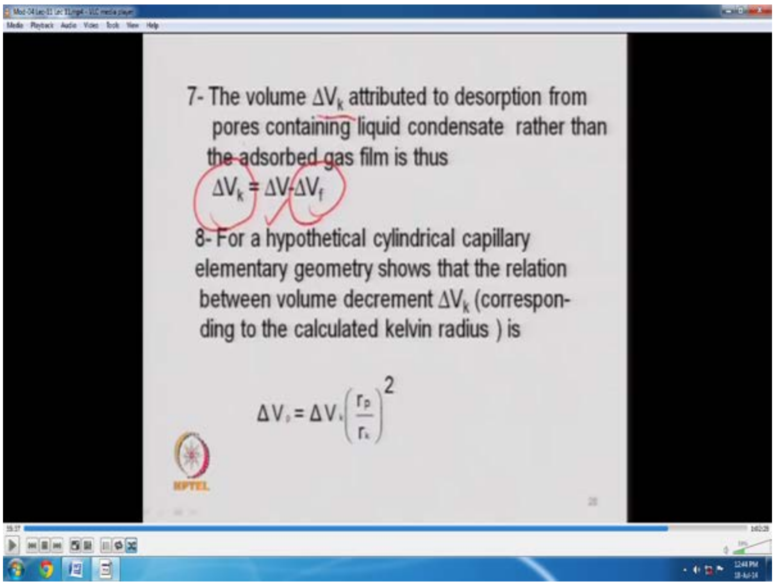

7- The volume ΔV_k attributed to desorption from pores containing liquid condensate rather than the adsorbed gas film is thus

$$\Delta V_k = \Delta V - \Delta V_f$$

8- For a hypothetical cylindrical capillary elementary geometry shows that the relation between volume decrement ΔV_k (corresponding to the calculated kelvin radius) is

$$\Delta V_p = \Delta V_k \left(\frac{r_p}{r_k}\right)^2$$

So, you can find out the volume Vk delta Vk which is attributed to the desorption from the pores containing liquid condensate rather than the adsorbed gas film. So just make this difference the adsorbed layer has a gas film and after that the condensation. So that, this is your basically your adsorbed gas and that is why we have used those surface area we have used the thickness change of that.That is above r k delta t within that mono layer and then we calculated delta t.

So that, you know this relationship as I said here phi r square. So for hypothetical cylindrical capillary If you know elementary geometry shows that the relationship between volume decrement delta v k corresponding to the Kelvin radius is related to this.So, delta Vp divide by delta Vk is equal to r p divide by r k whole square. So pi r square l is the volume of the Kelvin pore and pi rp square l is the volume of the total pore. So, you can find out the change in volumes of the pore that is total pore divide by the Kelvin radius pore volume and that is related to the radius of the pore and radius of the Kelvin radius.

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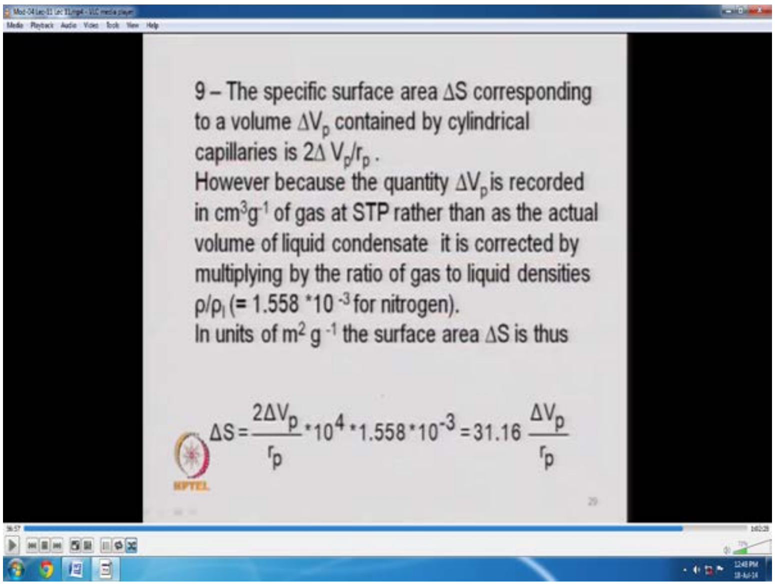

9 – The specific surface area ΔS corresponding to a volume ΔV_p contained by cylindrical capillaries is $2\Delta V_p/r_p$.
However because the quantity ΔV_p is recorded in $cm^3 g^{-1}$ of gas at STP rather than as the actual volume of liquid condensate it is corrected by multiplying by the ratio of gas to liquid densities ρ/ρ_l (= $1.558 * 10^{-3}$ for nitrogen).
In units of $m^2 g^{-1}$ the surface area ΔS is thus

$$\Delta S = \frac{2\Delta V_p}{r_p} * 10^4 * 1.558 * 10^{-3} = 31.16 \frac{\Delta V_p}{r_p}$$

So, this also we have already discussed that the specific surface area deltaS corresponding to a delta Vp volume contained by a cylindrical capillary is 2 delta V by r. So that, also we have discussed last time 2 times Vg by s is your r bar. So, last time if you remember r bar average pore radius is 2 times Vg divide by s g where Vg is the pore volume s g is the surface area BET area. So, here s g is calculated which is 2 times Vg divide by r radius of the pore. So, if I just talk for 2 differentials delta v is the volume.

So, delta S is the surface in so, we can very easily correlate it in terms of the change in the pore volume delta Vp and r p are correlated with respect to the specific surface area so, pi r square l is the volume of 1 pore and 2 pi r l is the surface area of that pore so, you can so, S is 2 pi r l for 1 pore pi r r square l is the v for 1 pore volume. So, you divide these 2 you will find r which is 2 times v by s. So, s is 2 times v by r so that, is known to you but, since there is a quantity delta Vp which is reported in centimeter cube per gram of the gas at STP rather than actual volume of liquid condensate, it is corrected by multiplying the ratio gas to liquid density rho by rho l.

So, you can convert very easily at 1 condition of temperature and pressure to the liquid condensate temperature because; the condensation is at minus 196 degree centigrade whereas,the gas volume which you are calculating is at standard condition of temperature and pressure. So, by using pv is equal to n r t or p1 v1 over t 1 is equal to p2 v2 over t2. So that, will be simply a ratio of the density of the gas divide by the density of the liquid.

So, liquid nitrogen density as I said roughly 0.8 gram per centimeter cube, gas density you can calculate p upon r t so, the order of magnitude comes roughly 1.6 into 10 to minus 3 for the case of nitrogen. So, you can very easily correct it the volume so, delta S is which is equal to 2 time delta Vp by rp in general and this is calculated at standard condition this. So, 1.5 into 10 power minus 3 chain this 1 0 4 has been introduced.

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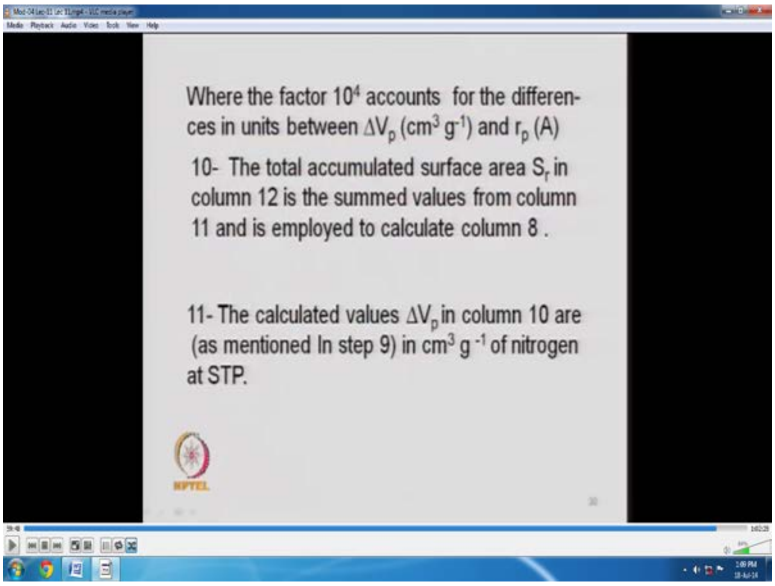
Where the factor 10^4 accounts for the differences in units between ΔV_p ($cm^3 g^{-1}$) and r_p (A)

10- The total accumulated surface area S_r in column 12 is the summed values from column 11 and is employed to calculate column 8 .

11- The calculated values ΔV_p in column 10 are (as mentioned In step 9) in $cm^3 g^{-1}$ of nitrogen at STP.

So,because there is a difference this is in centimeter cube per gram and this is in angstrom unit. So, just to take care of this so, V is in centimeter cube per gram, most of the time pore volume we report in centimeter cube per gram and radius is reported in angstrom. So just to take care of that so, factor 10 of 4 will come in picture. So that, is the factor and this is so, roughly it is 31.16 or 31.2 delta Vp up on r. So this is the surface area between 2 differential pressures.

The number of surface area is related to the number of molecules of the nitrogen adsorbed on the surface. So, when there is a desorption the number of molecules are released. So, how many molecules have released relieve the released from the surface. So that, is related to the decrease in the surface area in that way. So, the total accumulated surface area Sr in column 12 is sum of the value of column 11 and is employed in column to calculate 8.

So, basically just add these delta S. So that, is should be equal to the total surface area BET surface area because; these are nothing but, decrement in surface area of the catalyst. So, total accumulated surface area Sr in column 12 is the summed value of column 11 and is employed to calculate column 8. So that, we have already seen so, this is known so, calculated delta Vp in column 10 centimeter cube per gram of nitrogen. So, you convert it into any other convenient pressure.

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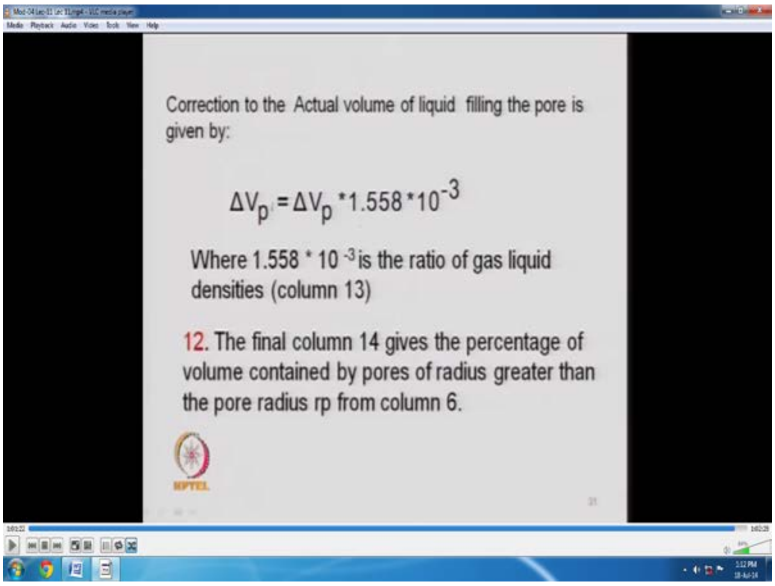

Correction to the Actual volume of liquid filling the pore is given by:

$$\Delta V_p' = \Delta V_p * 1.558 * 10^{-3}$$

Where $1.558 * 10^{-3}$ is the ratio of gas liquid densities (column 13)

12. The final column 14 gives the percentage of volume contained by pores of radius greater than the pore radius rp from column 6.

So, you can have the correction factor again for the density actual volume of liquid filling the pore. So that, is again multiplied by the density of the gas to the density of liquid, now this is just a conversion factor. So, final column gives the percentage of volume contained by the pore of radius greater than the pore radius r p from column 6. So that, is accumulative change or between 2 radius r and r plus delta p, what is the change in the volume percent of the pore. So that, may be equal to nothing but, change in volume divide by total volume and multiply in the terms of percentage so, I stop here.