Heterogeneous Catalysis and Catalytic Processes
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Module No. #03
Lecture - 08

So, last time we were talking about texture properties of the catalyst and I was discussing the determination of surface area, pore volume, pore size distribution of the catalyst. So, these properties are very important when you need to characterize the catalyst after preparation. So, I was just talking about the different methods. So, one is the mercury porosymetry method, which is just based on the surface tension effect and the second one is the nitrogen capillary condensation, which is based on Kelvin equation that is the pore pressure and the pore radius both are very important.

So, if you use these 2 techniques one can determine the micro pore present in the catalyst because, this is here nitrogen can go inside the pores of all the catalyst. Mercury can go only in the larger pores under normal conditions this will not go but, if it is sometime pressure in the pore so, that is related to the surface tension effect and you can determine the larger pore size here and the complete pore size distribution can be determine. So, the basic fundamental thing what is used to determine the pore volume of a catalyst? So, we are interested here in terms of the total pore volume first, then density of the pellet. So, density when I am saying pellet density which is for the pores material. So, we represent it by rho subscripted as p rho p and second will be the solid density that is the particles from which the pellet has been made. So, that is known as particle density or solid density.

So, we represent it by rho s. So, once these 2 are known then the porosity represented sometimes by epsilon or E. So, which is defined as pore volume divide by total volume. When I say total volume for a pellet, it is the volume of the pore plus solid volume. So, basically, fundamentally, if you know the pore volume. So, pore volume is one which is generally reported in terms of centimeter cube per a gram. So, we represent it by v g is the pore volume. So I will write p dot v subscripted as this. So, that is represented by v g unit hours generally, centimeter cube per gram rho p I have already defined. So, rho p I told you are the pellet density. So, one by rho p is basically representation of the volume of the pellet. So, it means by porosity epsilon can be go co-related with rho p v g. This is for per gram of the solid. So, volume of the pore per gram of the solid divide by this density. So, they sorry multiplied by density because one by rho p is your representation of total volume correct. So, this is another definition and I can also write the same porosity based on these 2 densities also that is 1 by rho p and 1 by rho s.

So, 1 by rho p which is I have written here is a representation of the total volume of the solid skeletal that is what I am say skeletal plus the volume of the pore and if you subtract it just from 1 by rho s which is now volume of the solid. So, I have another equation for this is 1 by rho p minus 1 by rho s. So, this 1 by rho p is the volume of the pellet which includes your volume of the solid and its then volume of the pore 1 by rho s represents only the volume of the solid so the difference will be nothing but, the pore volume and you are defining it per gram of solid so this is again the porosity. So, this is pellet porosity sometimes we write it epsilon p also. Not in the bed.

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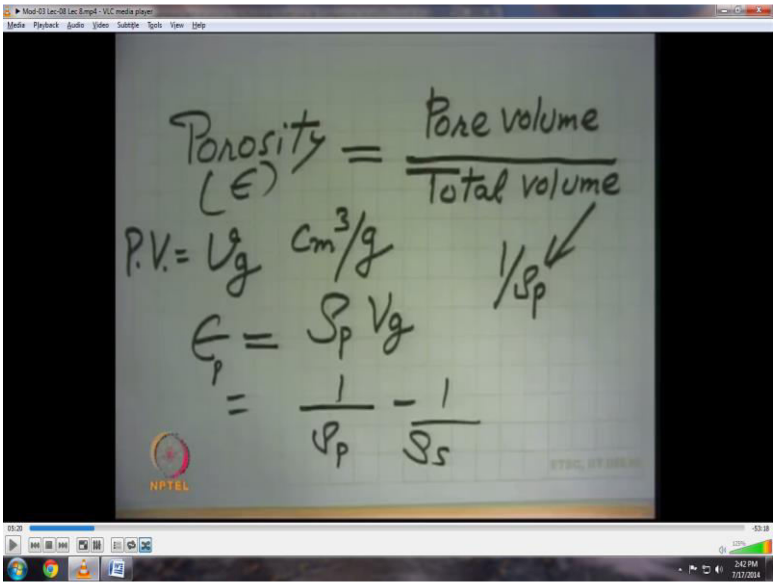

$$\text{Porosity } (\epsilon) = \frac{\text{Pore volume}}{\text{Total volume}}$$

$$P.V. = V_g \ \ cm^3/g \qquad 1/\rho_p$$

$$\epsilon_p = \rho_p V_g$$

$$= \frac{1}{\rho_p} - \frac{1}{\rho_s}$$

But, bed porosity will be different and now singularly, you can have the micro pore volume. So, based on micro pore volume you call it micro porosity, macro pore volume, macro porosity and meso pore volume based. So, meso porosity and summation of all that can be the total porosity so, these are some textural property which is required in order to characterize the pellet. So, basically the porosity as I said the wider large porosity that is because, why large porosity is high means 0.8 it can be upto a level of 0.8 and very low porosity. It is a kind of non pores also so, that will be very very high, it has good strength. If it is a non pore but, as you increase so, it means you are making a pellet more and more skeletal like this.

So, these are the cavities inside a solid material. So, you have just like if you look at a calcium carbonate powder. So, it is a pores material but, if you look at the solid something like a glass so, it may be a non pores type metal. So, all these soft materials they will have kind of porosity. So, now determination of the pore volume so, this is one of the most important or very common method. In one way to define the pore volume and pore size and porosity and if I use the nitrogen adsorption, desorption method along with this I can determine the pore size distribution also.

So, the helium mercury method, why these 2 terms have been used, the reason is that helium is a light gas. So, under normal condition, it can go in to the small pore it can diffuse easily into the pores of the solid. But, mercury cannot penetrate into the pore because mercury is a heavy metal it is a normally it is liquid but, it is a heavy metal it cannot penetrate the pore of most of the solid under normal condition. So, how can you do that you apply some pressure. So, if you apply pressure the mercury will start penetrating. So, we can co relate the pressure required with the radius of the capillary because it is a nothing but, the principle which is here is your surface tension principle. So, which are written here and if I just show you the slide here.

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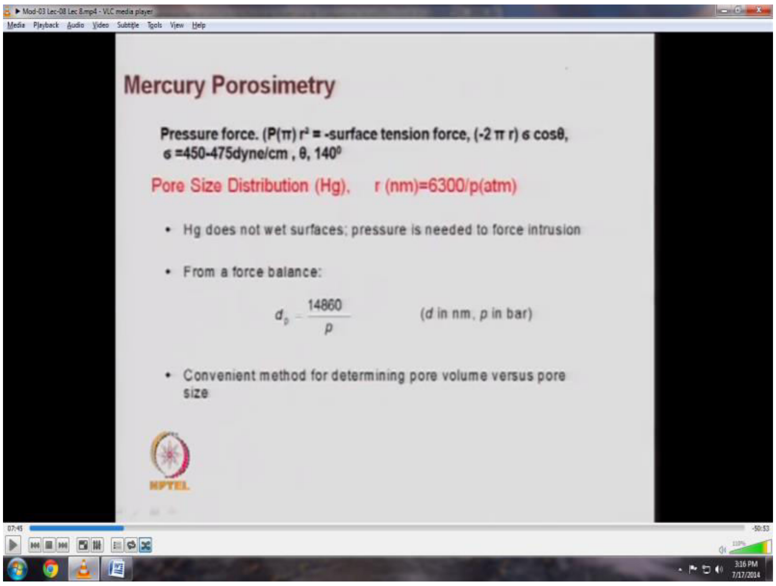

Mercury Porosimetry

Pressure force. $(P(\pi)\ r^2 = $ -surface tension force, $(-2\pi r)\ \sigma \cos\theta$,
$\sigma = 450\text{-}475$ dyne/cm, θ, 140^0

Pore Size Distribution (Hg), r (nm)=6300/p(atm)

- Hg does not wet surfaces; pressure is needed to force intrusion
- From a force balance:

$$d_p = \frac{14860}{p} \qquad (d \text{ in nm}, p \text{ in bar})$$

- Convenient method for determining pore volume versus pore size

So, this porosymetry principle mercury porosymetry principle is based on surface tension forces. So, if you look at the structure so, basically this is a pores a cylindrical pore. So, mercury under normal condition does not wet the surface so, most of the surface because it is a hydrophobic in nature. So, most of the surface will have a structure like this. When you have a mercury if you just in contract if you have any hydrophilic material, they will have the meniscus like this they wet the surface just like, if you put a water drop on a glass surface, it will wet, it will spread but, when you have something which has high surface tension. So, it show you meniscus like this because of the surface tension effect.

So, mercury will not wet the glass surface. But, water can wet the surface and this is nothing but, the wet ability and wetting characteristics which is related to surface tension. So, here this is what you say contact angle theta so, the when you apply a pressure because the mercury is trying to come out of the pore because of the surface tension force. So, this force is in this direction which is your surface tension force and that will be proportional to the length and radius if so, this term which is written here minus 2 pi r sigma cos of theta is your surface tension force. So, sigma is the surface tension of mercury.

So, mercury and that contact angle theta that will depend on the solid and the liquid property. So, for mercury on most of the solid surface it is roughly 140 degree that is the value of theta and surface transformation of mercury is roughly 450 drain per centimeter. Now, what is the applying pressure to penetrate the mercury into the pore and surface tension is trying to pull it out. So, it means depending upon the pressure which you have applied a definite volume of the pore will get failed.

So, v if I just write that volume of the mercury which has penetrated inside at a given pressure that is co related with the radius of that pore. So, the simple mathematical balance or pressure balances if you write p into pi r square which is written already there. So, this is the r is the radius of this capillary. So, pore radius here, so p into pi r square is your pressure force and that is equal to which is written there minus 2 pi r sigma cos of theta surface tension force which is opposite so use this substitute the value.

So, roughly we get r in nanometer unit which is roughly 6300 divide by p which is in atmospheric unit there can be the slight variation in value. So, in the second one depending up on the value of surface tension depending up on theta value sometime is your 130 sometime 135, 140 so, there may be a slight variation but, roughly the pore radius in nanometer is 6300 divide by p where p is the applied pressure. So, you have given the pressures p p plus delta p and in that differential pressure you are calculating what is the differential volume of mercury which has been penetrated. So, that can give you the idea about the pore size distribution also which we will talk later but, now we are using it just to calculate the pore volume.

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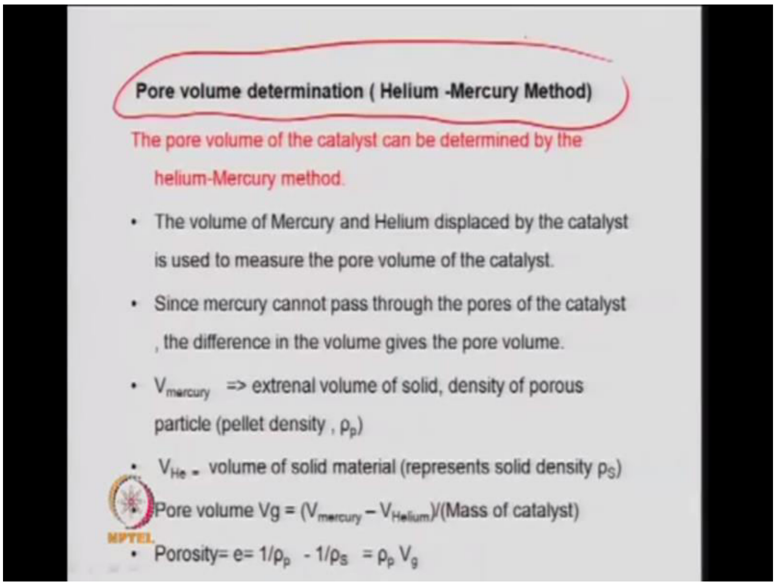

Pore volume determination (Helium -Mercury Method)

The pore volume of the catalyst can be determined by the helium-Mercury method.

- The volume of Mercury and Helium displaced by the catalyst is used to measure the pore volume of the catalyst.
- Since mercury cannot pass through the pores of the catalyst , the difference in the volume gives the pore volume.
- $V_{mercury}$ => extrenal volume of solid, density of porous particle (pellet density , ρ_p)
- V_{He} - volume of solid material (represents solid density ρ_S)
- Pore volume $Vg = (V_{mercury} - V_{Helium})/(\text{Mass of catalyst})$
- Porosity= $e= 1/\rho_p - 1/\rho_S = \rho_p V_g$

So, it means this principle is used here to determine the pore volume the reason is that now when you have any solid material. So, under normal condition so, when you apply pressure this thing will happen but, under normal condition the when this is actually very specific chamber where you pass the helium first and measure the volume of the helium displaced by the sample.

So, helium will penetrate into technology pore and only the volume of the solid will be displaced so it means the volume of helium displaced by the sample will be a measurement of the volume of the solid material because, part of the helium has gone into the pore and now you activate the chamber remove the helium and then pass the mercury in the same volume of the chamber same volume of the catalyst same mass of that solid catalyst. Now, helium wills not helium has gone inside part of the pore but, mercury cannot penetrate into the pore like what I have shown here because you need a pressure to penetrate the mercury.

So, the volume of the mercury displace by the sample is representing the total volume of the solid plus the pore because it has not gone into the pore. So, it will displace the volume of the mercury which is outside that is in the skeletal part of the solid as well as the pore part so this is a representation of the external volume of the solid as well as the there that is the volume of the pore.

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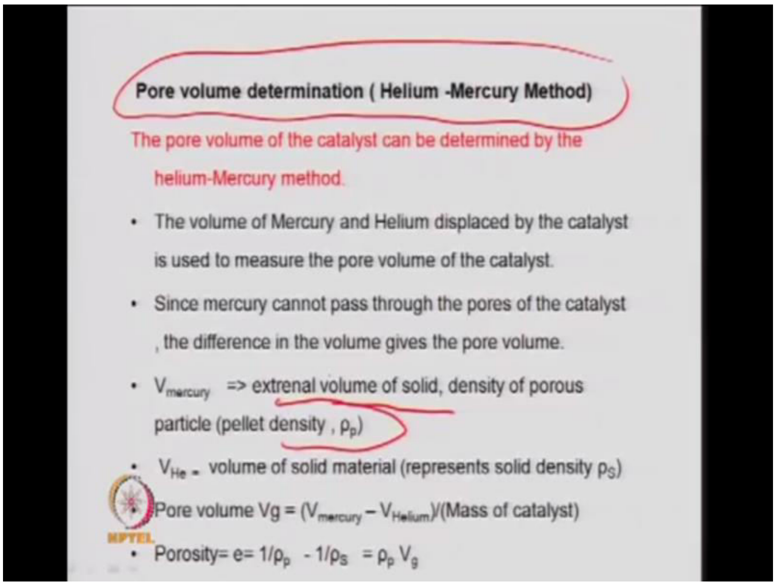

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So, this gives you the idea about the density of the pores material. So, this is representing the total volume of the solid which is a pores material that is volume of the pore such that the solid in the case of helium. So, this is already written here now mercury cannot pass through the pores. So, you can find out the volume of the helium displaced which is lower number. Now, volume of mercury displace will be larger number. So, volume of mercury displace minus volume of helium displace that is what pore volume because, in the first case when you have pass the helium has gone into the pore. So, it will displace less volume only solid material density and when the mercury has been passed. It cannot go into the pore it will displace the solid as well as the pore volume that is represented because it cannot go into the pore.

So, the mercury volume displace is higher compared to the helium volume displace. So, volume of mercury displace minus volume of helium displace is your pore volume of the solid divide by the mass of the catalyst placed. So, that is actually pore volume per gram of the solid. So, this is the first thing and that is why I written here that volume of mercury displace by the sample is representing the pellet density. Pellet density means it has pores structure and volume of helium displace is representing the solid density because the part of the helium gone into this pore of the catalyst and remaining is a skeletal part.

So, you can very easily find out the pore volume that is volume of mercury displace minus volume of helium displace divide by the mass of the solid. So, that is your pore volume and second term which is porosity because I have now already defined it here, 1 by rho p minus 1 by rho s because the porosity is pore volume divide by total volume so, most of the time when you have this kind of equation. So, porosity epsilon which you are writing is pore volume so, m p is the mass v g is the volume divide by m p v g that is the pore volume plus the volume of the solid so rho p v g divide by rho s v g so, it will be 1 by rho s here, this is also in the definition.

So, basically what I am writing that this is the volume of that total volume of the pore. This is the volume of the pore divide by the total volume of the solid. So, it should be the mass because mass almost same so m p by rho s so mass divide by the density so down this is the volume of the solid material. Mass is same correct so, m p by rho s so you can simplify it and you will have expression what I have written earlier so in the form of this so, you can very easily write it in terms of rho s v g divide by 1 plus rho s v g correct.

So, this is what the determination of pore volume by using the helium mercury method. So, you can determine the volume of the pore you can determine the density of the solid material you can determine the dos density of the pores material. The second thing is the pore size distribution. So, pore size distribution now approach is same where that is surface tension effect but, that because the mercury requires certain amount of pressure to allow or to diffuse into the pore of the catalyst.

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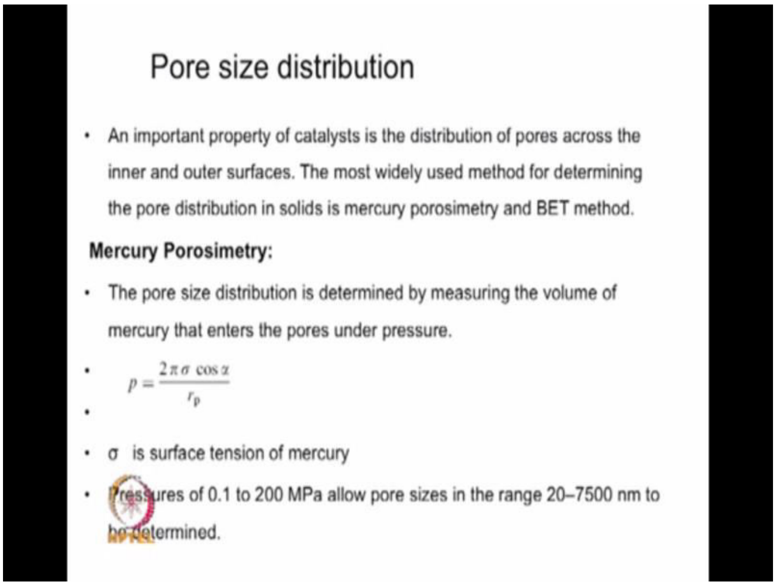

Pore size distribution

- 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.

Mercury Porosimetry:

- The pore size distribution is determined by measuring the volume of mercury that enters the pores under pressure.
- $p = \frac{2\pi\sigma \cos\alpha}{r_p}$
-
- σ is surface tension of mercury
- Pressures of 0.1 to 200 MPa allow pore sizes in the range 20–7500 nm to be determined.

So, only up to a certain range of passage you can do this thing when you apply higher pressure or higher stress the pore will get crumbled. So, if the material is highly pores then this mercury porosymetry method may not work good because, it will crumble the pore. So, it means not all the pores or not all size of pores can be determine by using the mercury penetration method. So, only macro pore distribution can be determine by mercury penetration method or to some level of meso pore.

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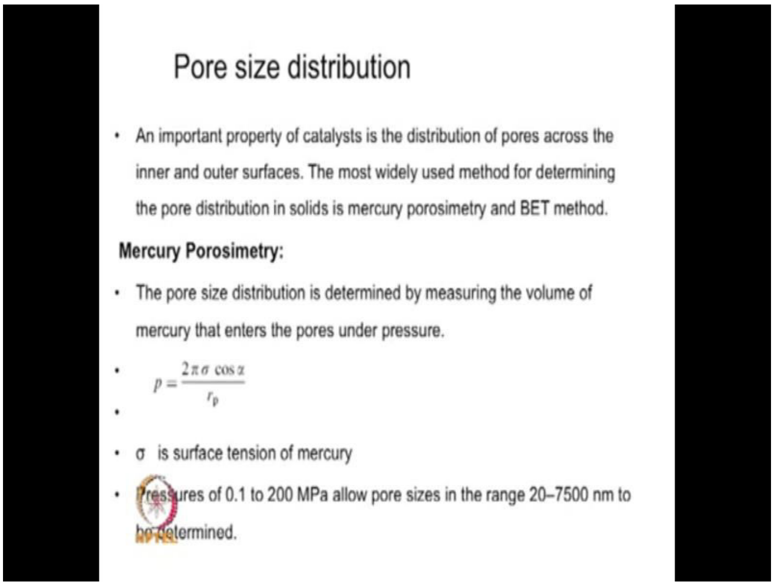

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The reason is that the higher pore smaller pores will require a much higher pressure because it is inversely proportional to pressure. So, if you have a micro pore the pressure requirement may be very very high 10000 p s i at that time the pore may get crumbled. So, nitrogen adsorption desorption peacefully use to determine those pores. So, that is based on Kelvin equation which is related to vapor pressure require to fill the pore and then it desorbs from the pore. So, that that we will discuss later but, this mercury porosymetry or pore size distribution determination which is an important property of the catalyst. So, it is nothing but, the distribution of pore across the inner and outer surface that is we are interested in micro pores, macro pores and meso pores. So, the most widely used method for determine the pore size distribution in solid is mercury porosity meter method.

So, surface area which determine by the b e t method but, the pore size distribution when I mean to pore size distribution. I am interested something like the volume suppose if I have write here or delta volume. So, I will write it first this sometimes we write it d v upon d a also that is a is the radius or d r if I write. So, d v over d a which is nothing but, we are trying to find out delta v upon delta r or delta of a. Here we put the just radius or small a or r.

So, this means the distribution of the pore when I say it may go like this the pores may be of wide size that is volume versus radius. If I am calculating the same thing can be plotted in terms of pressure also because, this d v you are calculating from differential pressure. So, I am interested in determining this kind distribution. So, this can be a just like a narrow pore size distribution and it is when you have only a definite size of the pores are available in our catalyst. But, if you have micro pore, meso pore so, this value can be say 1000 angstrom here. These can just a 2 angstrom or 10 angstrom here.

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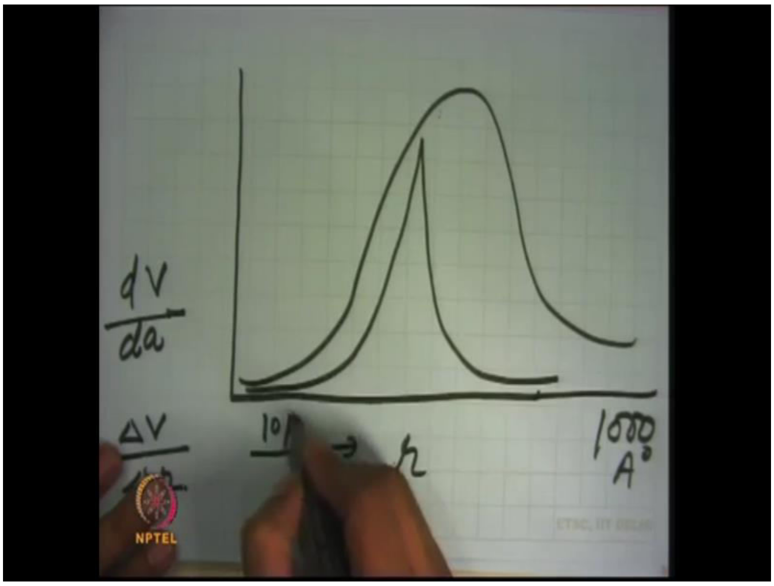

So, you can have a wide distribution in a catalyst and that you get when you sinter a catalyst when you edge a catalyst when you decide the crystallize size. You can have a wider pore size distribution also but, most of this we like to have a narrower pore size distribution. We want to make it more selective or specific in its exca. So, the mercury porosymetry the stressful I have just termed the pore size distribution can be determine by measuring the volume of mercury that enters the pore under a given pressure.

So, this is based on surface tension effect so, this is your pressure here, it is 2 pi sigma cos alpha or theta whatever and divide by r p which is radius of the pore same thing 6300 divide by the pressure where that gives you the radius in nanometer unit. So, depending upon the value of sigma in a specific unit you will have the different this radius units and pressure unit can be p s i. It can be Newton per meter square also, sigma is the surface tension it has different values. So, as I said 480 drain per centimeter or 450 drains per centimeter. So, it can have a different units you can write that and pressures the range which we give it can be 0.1 to 200 mega Pascal.

This allows the pore size which may be in the range you can very easily calculate here. You know the value of pressure suppose you give this pressure or you give sorry you apply give this pressure 0.1 mega Pascal, 1 mega Pascal is 10 atmosphere or sorry 100 atmospheres. So, you can very easily find out that and a different conditions you can have that. So, this 200 mega Pascal the because this is very high pressure that time the radius will be very small. So, you can very easily calculate that.

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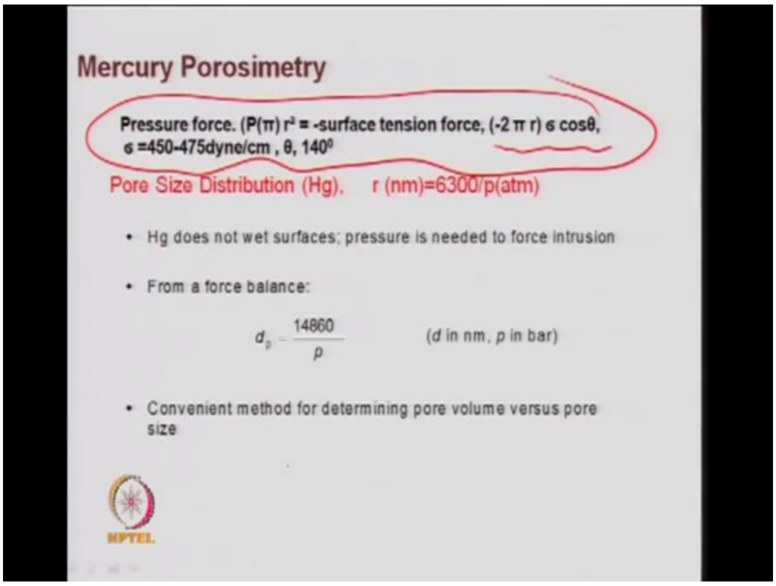

Mercury Porosimetry

Pressure force. $(P(\pi) r^2 = -$surface tension force, $(-2 \pi r) \sigma \cos\theta$,
σ =450-475dyne/cm , θ, 140^0

Pore Size Distribution (Hg). r (nm)=6300/p(atm)

- Hg does not wet surfaces; pressure is needed to force intrusion
- From a force balance:

$$d_p = \frac{14860}{p} \qquad (d \text{ in nm}, p \text{ in bar})$$

- Convenient method for determining pore volume versus pore size

So, this I have already discussed that is the related to the surface tension effect. So, pressure required to penetrate the mercury into the pore is equal to surface tension force. So, you can calculate the pore size distribution and either of these equations can be used and you can find out the pore size distribution. So, this is one method you determine so, basically what we have to do, we have to make a differential or cumulative analysis type. So, when we use this marsupialization method.

So, at different conditions of pressure we calculate the volume penetrated by the mercury that is what delta v I have written. Now, it is delta v between 2 pressure differentials p and p plus delta p. You can calculate, what is the volume of mercury which has been penetrated into the pore? And that volume is related to the radius of that? So, you can very easily calculate the pore volume because pi r square into l that is kind of length if I have that is a pore volume.

So, if I have n number of pores and r is the radius of that pore and l is length. So, I can very easily find out the pore volume of that and that is what the calculation? Which you have done there in you is helium mercury method. So, total pore volume of the solid id determined I am calculating the fraction of the pores which has occupied the volume between v and v plus delta v at a given pressure of p to p plus delta p. So, when you are increasing the pressure the pores are getting freed. So, in a differential pressure what volume fraction of the pore volume has been filled and t volume fraction is related to the radius because of the surface tension equation which you have already calculated.

So, I can co relate that volume with the radius so, I am writing the cumulative curve in the form of so, if I have a cumulative plots so that will relate your pore size distribution so, volume of the pores getting filled versus pressure if you look at here and which is related to your or radius I can say pore radius a or so this cumulative pore size distribution will go like this. So, this is indicating that the pores are totally filled here.

So, basically this will be your v g here, the volume of the total volume of the pore but, I will say because it is a mercury penetration method. So, this will include only the macro pore volume or pores of certain radius upto which the pressure has been applied whatever it can your 5000 or it can be even 500 something whatever in the units 5000 p s i. So, this can be of that order.

So, you can very easily calculate this and then you can determine the total value. So, I can have the idea that starting from a pressure which is atmosphere here one atmosphere 14.7 p s i here and then you have calculated a differential volume. So, I can very easily find out between these 2 pressures what are the radii here a and a plus so, this basically this side when I am going this radius is smaller. So, be because here this is the smallest pore so, radius is increasing in this side pore radius. So, this is the smallest pore which is getting filled and this is the largest pore here.

So, basically this is a and this is a plus delta a. So, I can have a relationship for delta v upon delta a that is change in radius or change in volume per radius d v upon d log a sometime we put because the number is very very small so, we just try to look at in a integral form. So, on larger scale, we can very easily plot this in the form of delta v up on delta of radius and then plot it versus p or radius. So, that will become a cumulative pore size distribution so, this is a cumulative pore size distribution and from this you can find out the pore size distribution that is d v over d of log a whatever I was saying something like this. So, this can be a graph of delta v up on delta a or delta of log of a. So, this one is your pore size distribution where as this in a cumulative plot of that.

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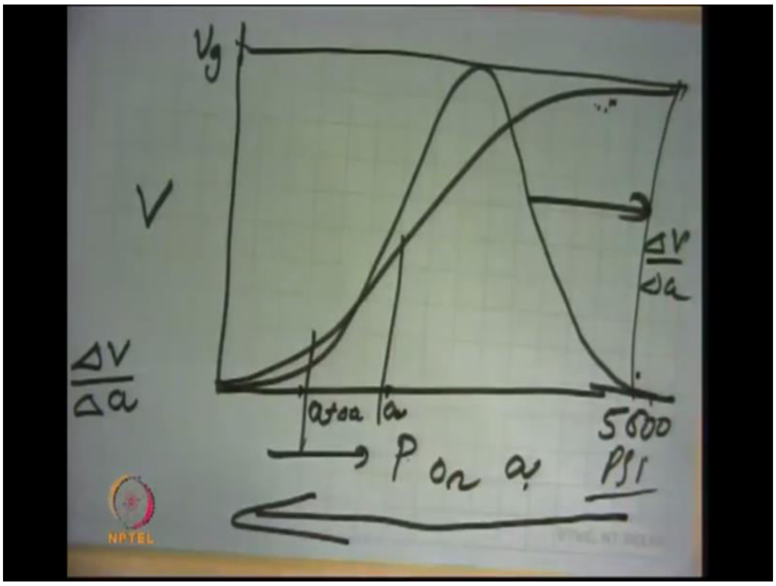

In this case, this nitrogen adsorption desorption method the principle is different because this is based on the vapor pressure or Kelvin equation. So, this is your Kelvin equation which relates the vapor pressure required to fill a pore as I function of radius.

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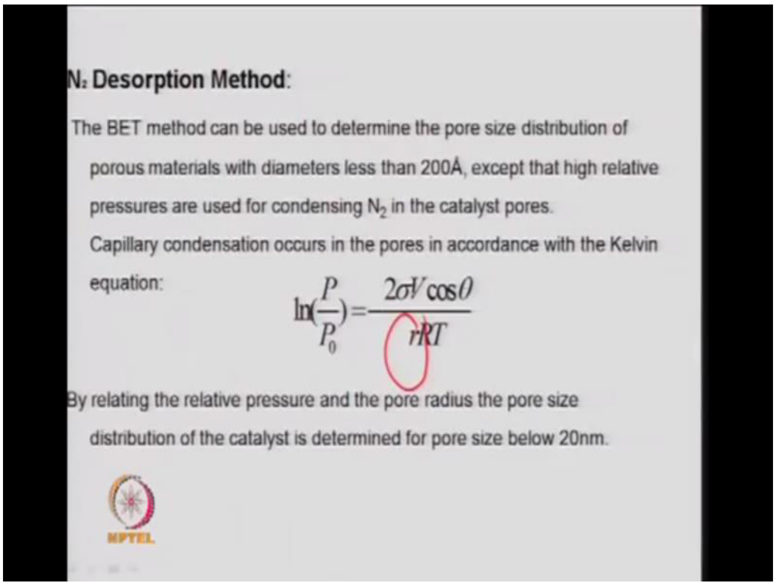

N₂ Desorption Method:

The BET method can be used to determine the pore size distribution of porous materials with diameters less than 200Å, 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:

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

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

So, at a given condition what volume of the gas is penetrating or at entering into the surface. So, the pores are getting filled accordingly because the pores may be of different shape and size. So, this nitrogen adsorption, desorption method can give you the idea about the pore geometry also because, the pores it may be larger, it may be smaller it may have an ink bottle shape also. So, there will be a kind of adsorb layer thickness and then the desorption starts.

So, first the gas adsorbs and when it the all pores are filled and when you release the pressure so the pores will get start disrobing. So, largest pore will empty it first and a smaller pore will emptied at a later state when you are releasing the pressure because the that Kelvin equation which relates the vapor pressure required to fill a pore and then there will be kind of adsorb layer thickness generally, if you look at this Kelvin effect. So, you this pore so this there is a kind of adsorption here so, there will be a thickness of that adsorbed layer.

So, actually the vaporization takes place from this radius whereas, the actual pore radius is this. So, if I tog, this is the diameter. So, this is my a actual pore radius from here to here but, when you have done this nitrogen adsorption or nitrogen adsorption, desorption method then you are getting because this is and adsorbed layer this will not adsorbed at that time the Kelvin effect is only from this point whereas, the pores are filled not adsorbed. So, this if I tog this that is indicate to your adsorb layer thickness which I say delta thickness of the adsorbed layer.

So, my Kelvin equation is talking about this radius which may be your r but, actual thickness, actual pore size or pore radius is which a r plus delta. So, when you use this equation you have to use a different integral co-relation to calculate the thickness of the adsorbed layer and that can be determined by using the t plots. There are different methods will talk on that but, one can find out this adsorbed layer thickness which is based on the imperial co-relation but, the funda is related to your Kelvin equation.

So, some saturation what is the saturation pressure what is the pressure and then one can very easily calculate for nitrogen because the every all the nitrogen has the property not like the mercury which is trying to oppose. It is it can wet the surface of the almost of the pores so adsorb that is that is when the adsorption is possible. So, that is why there is an adsorb layer thickness and then this is the radius of the capillary the capillary condensation phenomenon is for this radius.

So, your Kelvin equation this r is togging this not this. So, whatever r you get from Kelvin equation you add delta to that and that will be your actual pores actual pore it is so, this is what we need to calculate when we use this nitrogen adsorption, desorption method and since, the property of the pore will depend or this r and delta will depend on the type of pore ink bottle effect what I said adsorption hysteresis. Now, what I am saying that what is the adsorption basically? It is a surface phenomenon as I said and you get the different temperature or at constant temperature. When I say isotherm so, at one temperature you are looking the effect of pressure. So, that is known as adsorption isotherm.

So here, generally in this case adsorption, we are looking something that the molecules which come to the surface they will get adsorbed first and now increasing the pressure. So, when the further increasing the pressure so this is the adsorbed layer and then the condenses take place. So, smaller pores will get filled first and gradually it will go into the larger pore. So, when it reaches to the saturation the all the pores are filled with nitrogen and now you start desorption to release the pressure.

So, when the pressure is released then the vapor pressure will get lower and lower and the pores will get empty. So, we are calculating the volume of the nitrogen disrobed as a function of the pressure and in each differential intervals that is the release of pressure from highest pressure to some pressure delta p p minus delta p and so on so on p minus 2 delta p and you are just measuring this volume of the gas which is disrobed and that volume is related to the radius of this capillary and to that radius you calculate this delta and add you will have the total pore size distribution or for different this can give you the micro pore because, capillary phenomenon is only applicable in a small pores not in the wider pores.

So, that is why the mercury penetration method works only for the larger pores and nitrogen adsorption desorption method works for the smaller pores. So, by relating the relative pressure and the pore radius the pore size distribution of the catalyst can be determined but, only for the macro, micro pores less than 20 nanometer. So, this is written here that this b e t method can be used to determine the pore size distribution. So, there only the surface area b e t is used for the surface area determination.

But, when you are using this for pore size distribution your u z plots are the barrette zone and isotherm. So, you can determine the pore size distribution which is basically on the nitrogen adsorption, desorption phenomena. So, this is just what I said that less than 20 nanometer or 200 angstrom except that high relative pressures. So, that is required because we are condensing the nitrogen on the capillaries. So, capillary condensation this is known as Kelvin equation.

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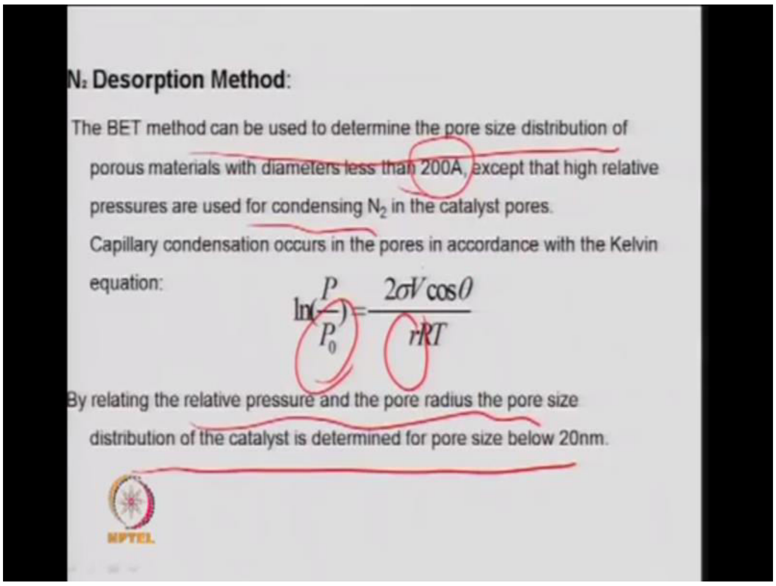

N_2 Desorption Method:

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:

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

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

So, in of p by p 0 where p 0 is the saturation pressure, sigma is the surface tension for nitrogen, V is the volume of gas adsorbed theta is the contact angle. So, generally we take it 0 because nitrogen generally wets off all this surface liquid nitrogen I am talking and r is the gas constant and t is the temperature in Kelvin.

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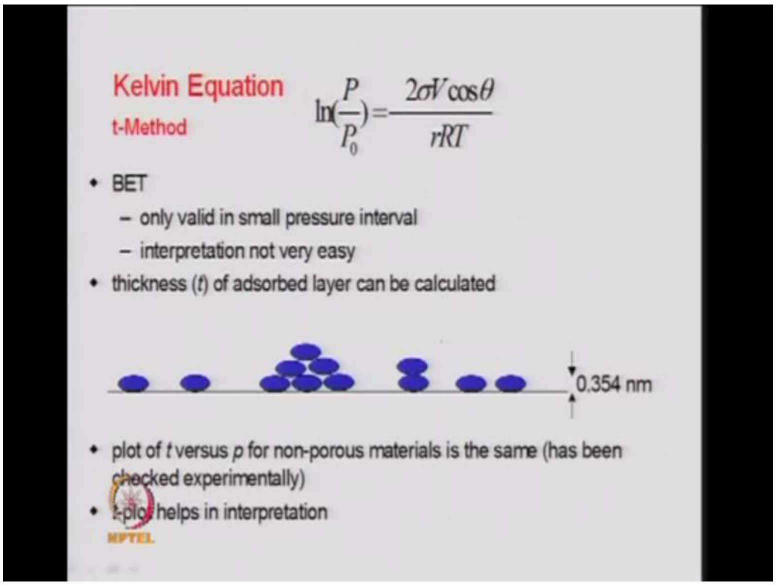

Kelvin Equation

t-Method

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

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

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

So, this is what the b e t method what I was talking that is generally used. So, b e t is only valid for a small pressure interval so, we have to give a differential pressure which is of a smaller order. So, that the pores because we are talking a micro pores here between say 10 to 20 nanometers what we are talking those kind of pores we are talking here or sometime, we go up to the 50 or 70 angstrom nanometer.

So but, the results may not be very good because the Kelvin equation is valid only for the capillary. It is a capillary condensation phenomenon. So, small pressure intervals and interpretation is not very easy because delta is also here and the pressure differential which you are calculating and corresponding to that the volume of the gas which is disrobed that is important at different condition you are measuring the volume of the gas adsorbed.

So, again we can have a cumulative plot that what we discuss for the case of mercury penetration method. So, thickness of the adsorbed layer which I am writing here delta sometime we call it t also so adsorbed layer thickness t plots so, that can be determine so this is what we are talking a monolayer thickness of the adsorbed layer. So, t is roughly this is related to this only but, integral correlations are available for the calculation of this delta thickness adsorbed layer which is nothing but, calculated from the same equation that time we calculate this r and taken to other side but, there are integral collision for calculating this technique of adsorbed layers. So, this we will talk later because this is the t plot which is generally used to get this information and finally, the pore size distribution.

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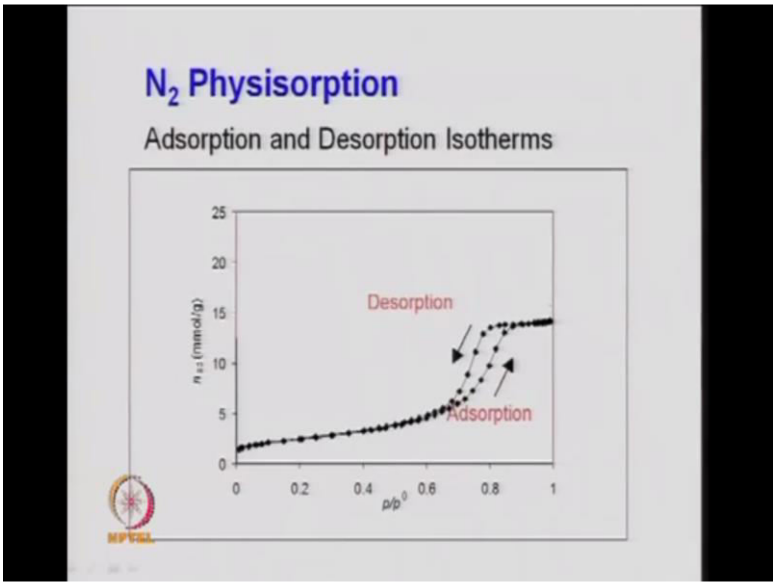

N_2 Physisorption

Adsorption and Desorption Isotherms

So, there are there any kind of hysteresis here that is what adsorption, desorption hysteresis and that hysteresis gives the idea about the micro porosity and the shape of the pore size ink bottle, if I put on talking so, this gap which I have talking. So, when the pore size distribution is wide then this gap will be more and more or when they are sum suppose you have alumina type pellet you may not get this kind of affect.

But, when you have a kind of structure which is complex the micro pores and the pores are irregular in shape zigzag type or ink bottle effect. So, this phenomenon we call is the ink bottle effect because it is a nothing but, as I said the condensation and vaporization when you are applying the pressure that nitrogen gas is being adsorbed on the surface and when you release the pressure it disrobes. So but, principle which is we defines here a and a plus delta a that is the volume of the gas which is disrobed at given pressure differential.

So, this adsorption desorption kind of hysteresis because the pores you are not vacate completely at that time. When you apply release the pressure or that is why a higher pressure may require to higher pressure release may be required to vacate all the pores and that is known as hysteresis. So, generally when you have a single a single kind of distribution or simple pore single one size pore distribution then this kind of hysteresis may not arrive but, when the pore complex geometry very very complex then this hysteresis will be more and more. So, we basically the moles which are disrobed or adsorbed as a function of p by p 0 t is here will saturation.

So, adsorption a curve goes like this because it is related to the pressure and then you release then your moles, will disrobe like this. So, here you can see at this, when you look at the desorption pressure the number of moles which have been release from the surface they appear to be high because of the ink bottle effect or hysteresis. So, adsorption isotherm as I said that is basically but, we are talking at constant temperature. We try to study the effect of pressure.

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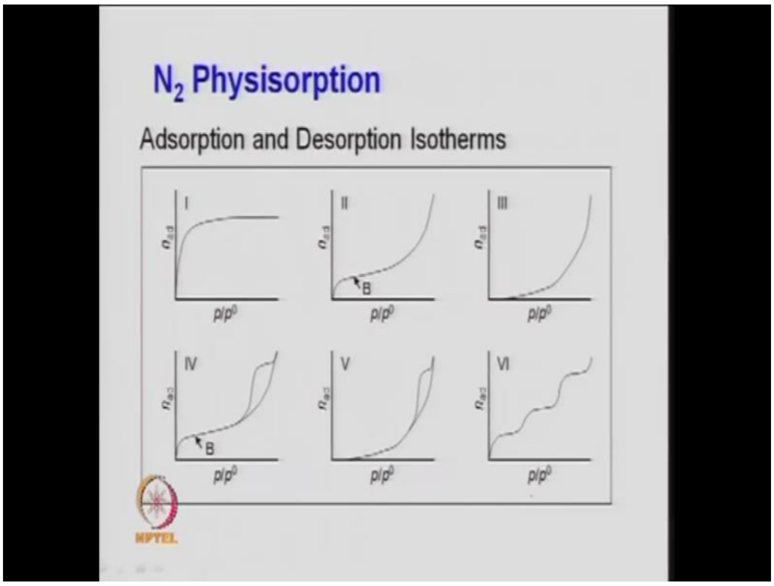

N_2 Physisorption

Adsorption and Desorption Isotherms

So, plot of amount of gas adsorbed as a function of pressure versus pressure at constant temperature is known as adsorption isotherm. The other side if you plot adsorption of moles adsorbed as a function of temperature at constant pressure that is isobar. So, generally in most of the heterogonous catalyst are solid when the gas is adsorbing. It is more a pressure phenomenon because it is something which is related to the sticking probability and that is related to the pressure less on temperature so, we generally talk in terms of the isotherms at one temperature you calculate the molecules which adsorb on the surface at different pressure.

So, you can see here that the v b m may be different the depending up on the type of solid property or depending up on the weaver of the gas because it depending on the type of the gas, it depends on the type of the solid surface and its textural property. So, the pressure versus this p by p z over is written here is basically p 0 is the saturation pressure so and p is the applied pressure. So, p by p 0 is just representing this that what I say here, if you look at here this is the first type one adsorbed on isotherm which just indicates that once the saturation appears or when the pressure is saturated no molecule can further adsorb on the surface all most constant. So, this cannot be physical adsorption because I said that physical adsorption is basically the condensation of the molecule.

So, when you have the molecules and you apply the pressure then more molecule will come and sit the water if you apply pressure more and more water will get condensed on the surface so this with this kind of phenomenon is very specific. So, it means once the saturation is arrive then molecules are not adsorbing further so, it is something like a chemisorption when you say that active sides are available and the gas is adsorbed on that surface or adsorbing on that surface. So, that time this may be effective or this may be considered.

So, that is known as just like a type one adsorption which is known as languor adsorption basically, we say that the adsorption is related to pressure and the concentration of the vacant side. So, when is the within sides are not available the adsorption will not possible. So, that is what the indication here whereas, this if you look at here so this type second adsorption it shows that some saturation which you have seen here now has appeared here something like this. So, this could be a mono layer here in this but, continuously further adsorption is possible. So, this is a phenomenon of multi layer physical adsorption.

So, 1 layer is formed and there can be the subsequent adsorption. So, these are not getting any kind of hysteresis in these. So, type 1 type second so physical adsorption or chemisorptions here. But, mono layer coverage this is multi layer coverage and here again it is a kind of multi layer coverage but, this kind of where ever you can see here it. Generally, possible only in the very layer substances or when the material has very low porosity micro pores materials then you can see this kind of wavier that you are applying the pressure and then at higher pressure very high pressure on the pores can get filled.

But, these are rare and here you can see the adsorption hysteresis that is the adsorption desorption with because of the complex pore geometry. So, pore geometry may be micro pores macro pores and then the ink bottle effect what I said the pores are narrower and wider at some other ends they are very torches in path. So, these kind of behaviors are very rare this one is again a very rare behavior but, it represents a similar to this so there can what I mean to say depending up on the type of solid and the gas the adsorption phenomenon may be different or depends on the type of solid and their physical chemical property.

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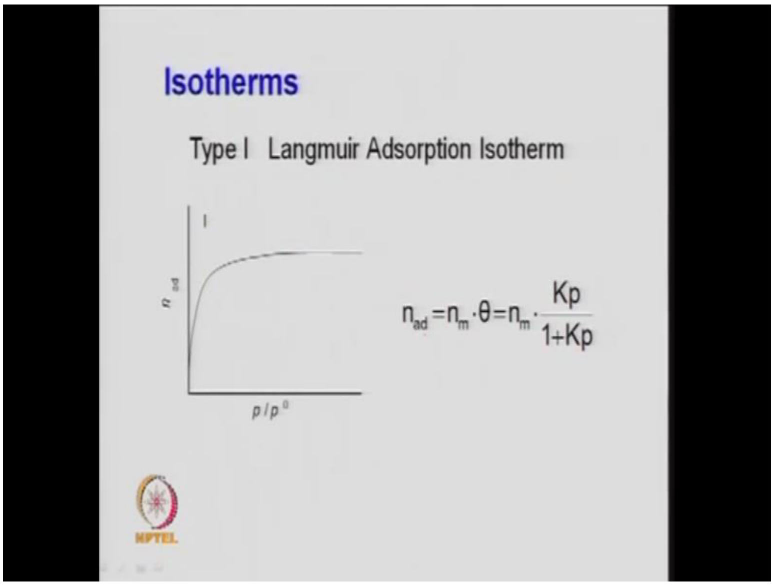

Isotherms

Type I Langmuir Adsorption Isotherm

$$n_{ad} = n_m \cdot \theta = n_m \cdot \frac{Kp}{1+Kp}$$

So, this is what the type of adsorption which I was talking a Langmuir adsorption. So, that is related to your mono layer coverage so once the mono layer is formed no further adsorption and this phenomenon can be used to determine the monolayer coverage so, basically the total surface area of the solid material which contains the active sides. So, when you have a chemical reactive gas it will adsorb only on those surfaces where the active sides are available. So, this can be used to determine the surface area of the active metal. But, if you have the physical adsorption then here there volume may not be correct because this will report a larger value.

So, the just equation which is written and later on we will use it to determine the kinetics also the basically we are saying that rate of adsorption is related to some kind of a sticking probability. So, this is proportional to whatever the fraction of the sides which are vacant like this theta and the pressure of the gas. So, 1 minus theta when I am saying so, theta is the fraction of the sides which are already covered. So, 1 minus theta is the fraction of the side which are available.

So, you can write sometimes in terms of c v times the pressure also. Where c v is the concentration of the vacant side and desorption, the desorption takes place only form the sides which are already covered nothing else. So, desorption is proportional to the fraction of the sides which is covered. So, you can put some constants here sometimes we call here is sticking probability so k 1 times 1 minus theta times the pressure and this is related to only the concentration of the vacant side. So, k 2 times I can write here k 2 time theta and when the system because whenever you are talking the equilibrium then rate of adsorption will be equal to rate of desorption.

So, it means at equilibrium, your rate of adsorption is equal to rate of desorption. So, you will have simply k 1 times 1 minus theta times the pressure of the gas is equal to k 2 times theta and this k 1 by k 2 is your adsorption equilibrium constant capital k. So, you can very easily write this theta which is written here k p over 1 plus k p. So, if you just do this so your theta from this theta over 1 minus theta is equal to k 1 by k 2 times p as however writing it capital k times p and you will solve this for theta. So, theta becomes k p divide by 1 plus k p where capital k is your k 1 by k 2 adsorption equilibrium constant.

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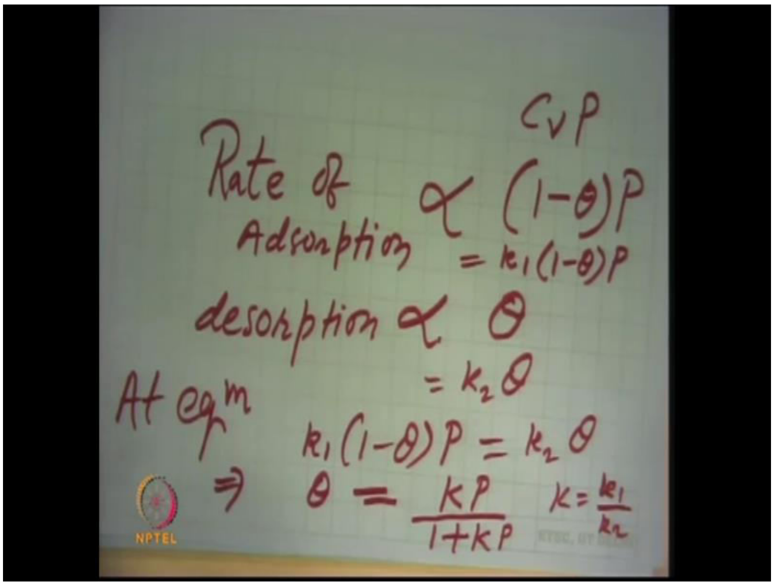

$C_v P$

Rate of Adsorption $\propto (1-\theta)P$

$= k_1(1-\theta)P$

desorption $\propto \theta$

$= k_2\theta$

At eq^m

$k_1(1-\theta)P = k_2\theta$

$\Rightarrow \theta = \frac{KP}{1+KP}$ $K = \frac{k_1}{k_2}$

So, this is the chemisorption type thing chemical reaction chemically adsorbed in the gas and that is why we use this equation for determination of kinetics of adsorption and later on we will call it Langmuir model or Langmuir isotherm or Langmuir based filled expression for heterogenic catalytic reaction. So, the funda is that at equilibrium the rate of adsorption is equal to the rate of desorption the adsorption rate is proportional to the partial pressure of the gas. So, there may be the series of the gases and so, it will depend on all those partial pressures which are effective coming and that. So, k 1 is kind of that temperature effective and depending on the sticking coefficient or probability of the gas to adsorb on the surface.

So, this equation is very important and we will use it throughout course. So, an adsorption which is written in terms of a fraction of the surface covered sometimes theta I have told earlier also the theta can be written in terms of v by v m where v m is the volume of monolayer coverage. So, this is nothing but, v m volume of monolayer. So, monolayer coverage so, this basically this is the volume of the gas which is adsorbed at any pressure it will increase but, when it reach to v so, there will not be any adsorption.

So, this is basically the number of molecules which are adsorbed here at v m the surface is covered and that condition. So, the num this is maximum number of molecules of the gas adsorbed on a monolayer forms. So, will talk on that later also but, there are certain assumptions of Langmuir adsorption because it represents a kind of chemisorption it is not valid for physical adsorption. So, it says that the surface is homogenous whereas, the surface cannot be homogenous we are talking heterogeneous catalysis reaction the surface is heterogonous.

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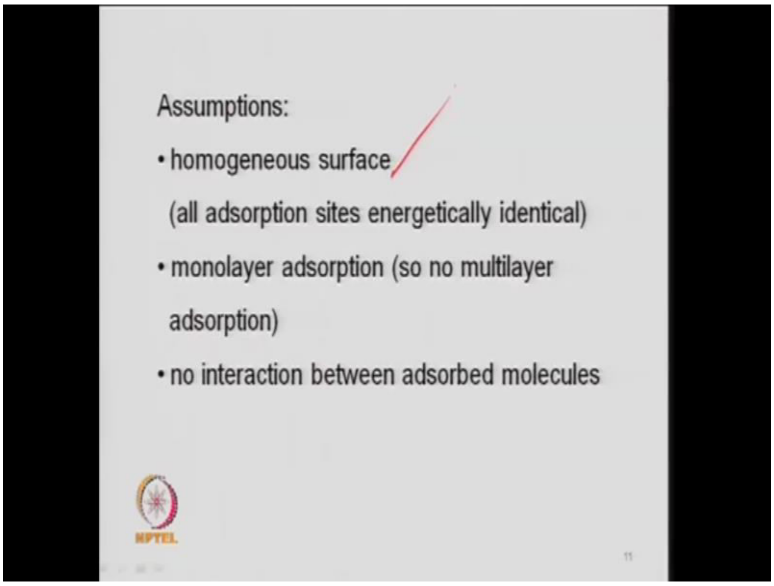

Assumptions:

- homogeneous surface
  (all adsorption sites energetically identical)
- monolayer adsorption (so no multilayer adsorption)
- no interaction between adsorbed molecules

They are at the centers and at some of the locations there are no active centers active sides. So, which says that the Langmuir isotherm says that the surface is homogenous so, it means the adsorption sides are energetically uniform? It means the adsorption will take place at all locations at the same rate which is not right correct. The monolayer adsorption we are talking that once the monolayer forms there will not be any further adsorption that is the dilution this is also not correct in all cases.

So, there are certain modification required which use the later and there is no interaction between the adsorbed molecules actually, it says that heat of adsorption is independent of surface coverage because when the molecules are adsorbing the phenomenon is exothermic. So, heat will release now, when you are looking the adsorption on the bare surface so, solid surface the gas is coming and the where given the or that surface is covered the gas molecule may come and again seat over that so, multilayer coverage when we are talking.

So, the heat of adsorption will be different but, it says that whether it is a bear surface or a fresh surface or covered surface than heat of adsorption in all cases will remain same which is not right. So, generally the heat of adsorption decreases the surface coverage. So, the other isotherm has or isotherms have taken care of that.

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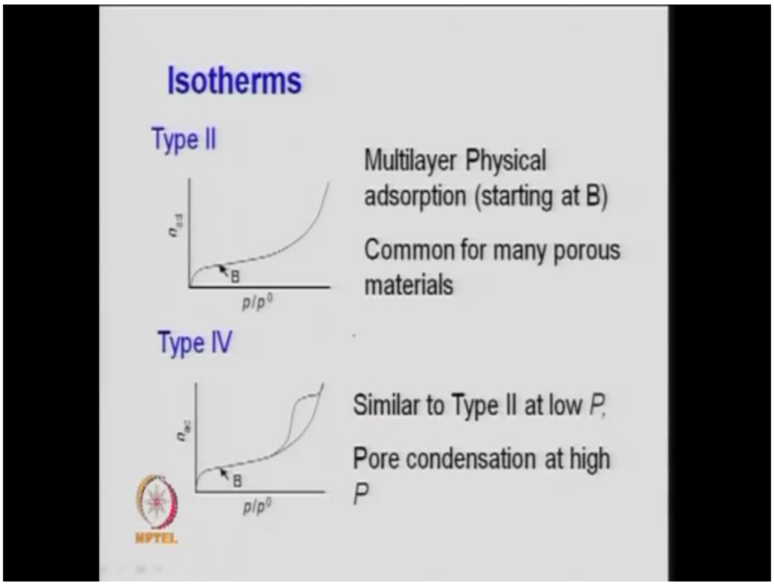

Isotherms

Type II

Multilayer Physical adsorption (starting at B)

Common for many porous materials

Type IV

Similar to Type II at low *P*,

Pore condensation at high *P*

So, type second type four which have a stocking so type second is a b e theta pass come so it talks on multilayer physical adsorption. So, it is starts from this point and this is common for many pores material. So, when you have physical adsorption like b e t isotherm as we are talking. So, the isotherm takes care of this so, Langmuir isotherm say that when this forms p has arrived point no further adsorption will take place that. In the case of b e t isotherm the adsorption may be possible and the heat of adsorption may vary with surface coverage. So, this point which is say here the surface is energetically uniform has been taken care by a second isotherm which is known as b e t isotherm, this type 4 again as I said here the hysteresis is there.

So, it means the condensation is taking place at higher pressure what I said especially in the smaller pores capillary condensation phenomena otherwise the other things are same they if you look at this is just like this curve this type. But, here the desorption has started or condensation has started. So, this is similar to type at low pressure but, the pore condensation starts at high pressure the pores get filled rather adsorbing. Whereas, type third it talks on strong cohecent force between adsorbed molecule.

So, when the molecules are adsorbed on the surface there is a kind of cohesive. So, it is similar to the b e t type second but, only thing that the molecules the there are certain kind of forces certain kind of force between the similar kind of molecules because they molecules are already adsorbed on the surface and when they are adsorbed there will be a kind of force. So, the adsorption energy or the probability stacking what you say that will change when the converge is already there.

So, that has been taken care in this isotherm and this is what says that there is a strong cohecent force between the adsorbed molecules something like say water which adsorb on the hydrophilic activated carbon. So, you will have this kind of isotherm similar to the b t e isotherm. Whereas, type if its 3 rd 4 is similar to 3 rd at low pressure. So, this is similar if you look at here but, again the pore condensation phenomenon at high pressures. So, this is what you see here, the condensation phenomena it is a kind of stress so, otherwise this isotherm and this isotherm same. So, generally this kind of isotherm 3 rd 4, 5 they are rare and only available when the material is micro pores with irregularity in the pores. So, micro pores and irregular pores, the hysteresis is always there when you look at the adsorption desorption phenomena.

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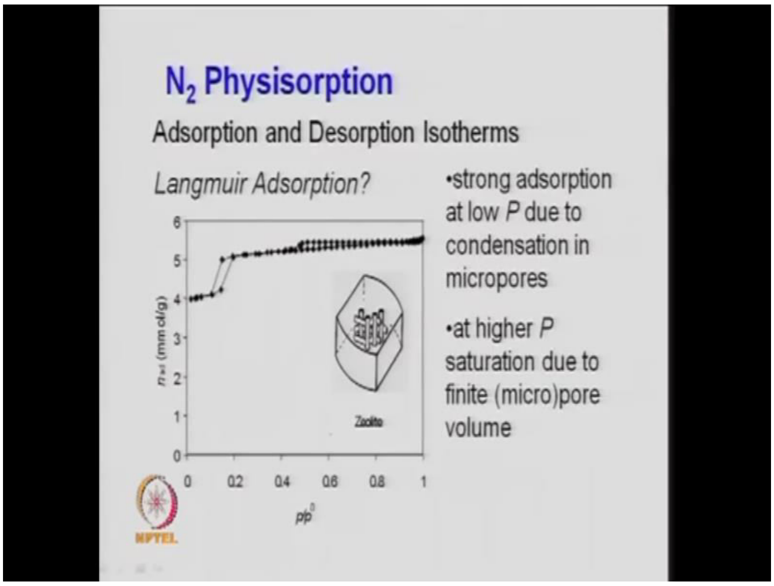

N_2 Physisorption

Adsorption and Desorption Isotherms

Langmuir Adsorption?

- strong adsorption at low *P* due to condensation in micropores
- at higher *P* saturation due to finite (micro)pore volume

So, Langmuir isotherm when you are doing. So, this is just like a zeolite catalyst there if you look at here which is nothing but, the silica alumina material and having a channel type structure like a strong channel structure. So, here by strong adsorption at low pressure, you can see here that due to the condensation of the in the micro pore because zeolites are mainly the smaller more size say meso pores materials. So, because in this type of material that capillary condensation phenomenon is common and this condensation phenomenon shows this kind of hysteresis.

And at higher pressure, if you look at the saturation due to finite pore volume because that time when the higher pressure though almost the pores are saturated but, there are again the micro pores. So, here the condensation within the zone and but, at very high pressure. So, these type of isotherm are valid or available or can be seen only in a very small pore size it is a 10 angstrom pores. So, micro pores material not even the meso pores material so, will talk on that later also.

So, determination of surface area that is very important as I said the b t e isotherm is generally used for determination of surface area of the solid material. So, then we look at the gas type of gas so generally as I said nitrogen argon carbon dioxide krypton any gas can be used oxygen can also be used as an adsorbent gas for determination of surface area. It will be related to their boiling point because the condensation it is a kind of condensation phenomena you have to put the bath of that temperature cryogenic conditions are to be created in order to allow the gas molecule to adsorb on the surface.

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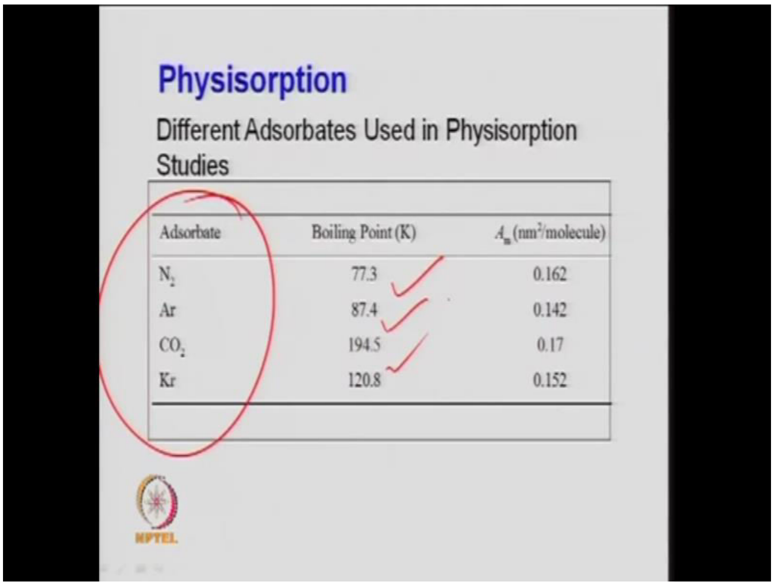

Physisorption

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 is just the liquid nitrogen say at 77 Kelvin, organ 87 Kelvin, carbon dioxide requires minus sorry 194 Kelvin. So, high temperature and krypton is 120 Kelvin roughly and area per molecule is also equally important nanometer square per molecule. The idea is that when you determine the surface area of a catalyst a molecules gets adsorbed on this surface like this. So, I am talking a pores structure and on that there is an adsorption of the molecule physical adsorption of the gas molecule. So, you get a curve when you look at the adsorption phenomena your curve will be something like this whatever. So, what we are looking at this when the monolayer forms we are calculating this v m volume of the monolayer coverage and to cover the so to form this monolayer how many molecules of that gas? So, this is the molecule of the gas which may not be completely spherical a projected area we need to consider.

So, this and when the monolayer has formed we are assuming that this layer has been covered by these molecules. So, we are calculating this surface area actually we need to calculate this surface area but, this surface area is related to the number of molecules because we are saying that a monolayer has formed. So, we can use the principle of the molecular area of the gas for the determination of surface area.

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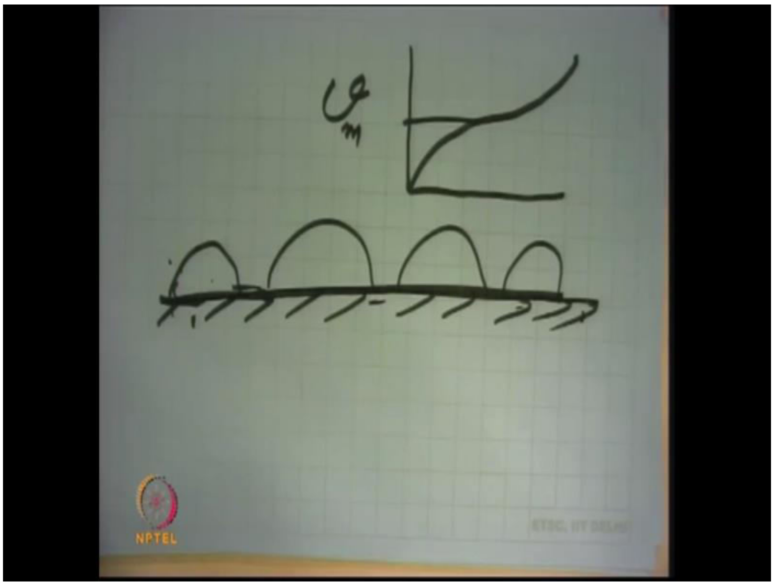

So, I stop here and will continue it next time.