Course: Adsorption Science and Technology: Fundamentals and Applications

Instructor: Prof Sourav Mondal

Department: Chemical Engineering

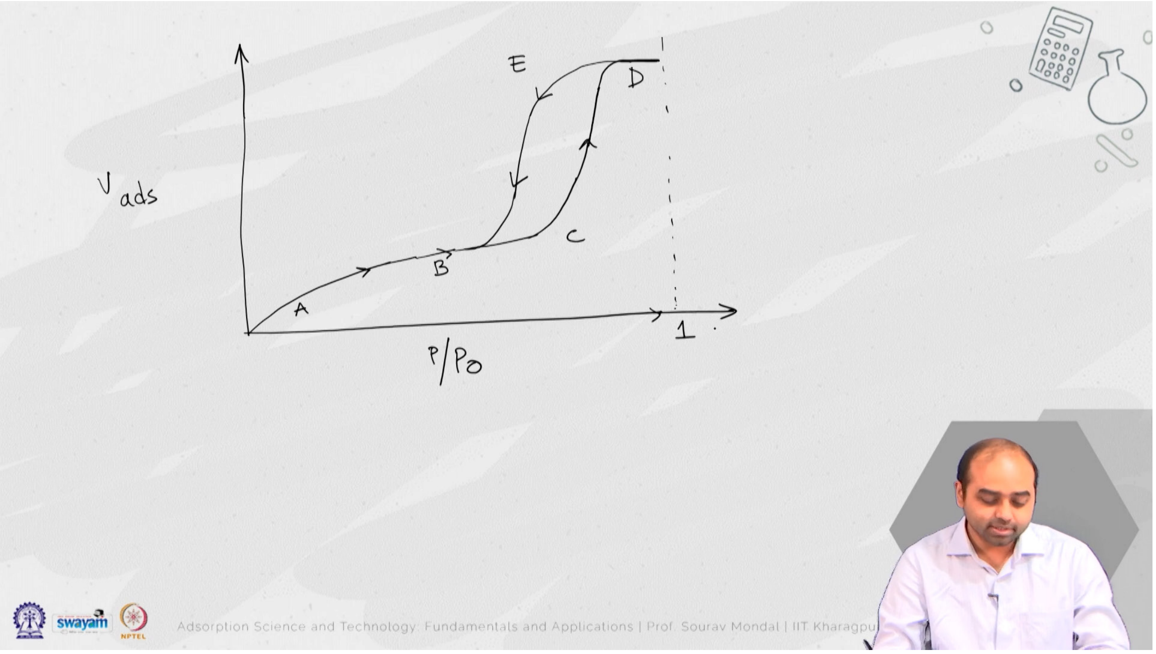
Institute: Indian Institute of Technology Kharagpur

Week 03

Lecture 14 | Pore Size Analysis

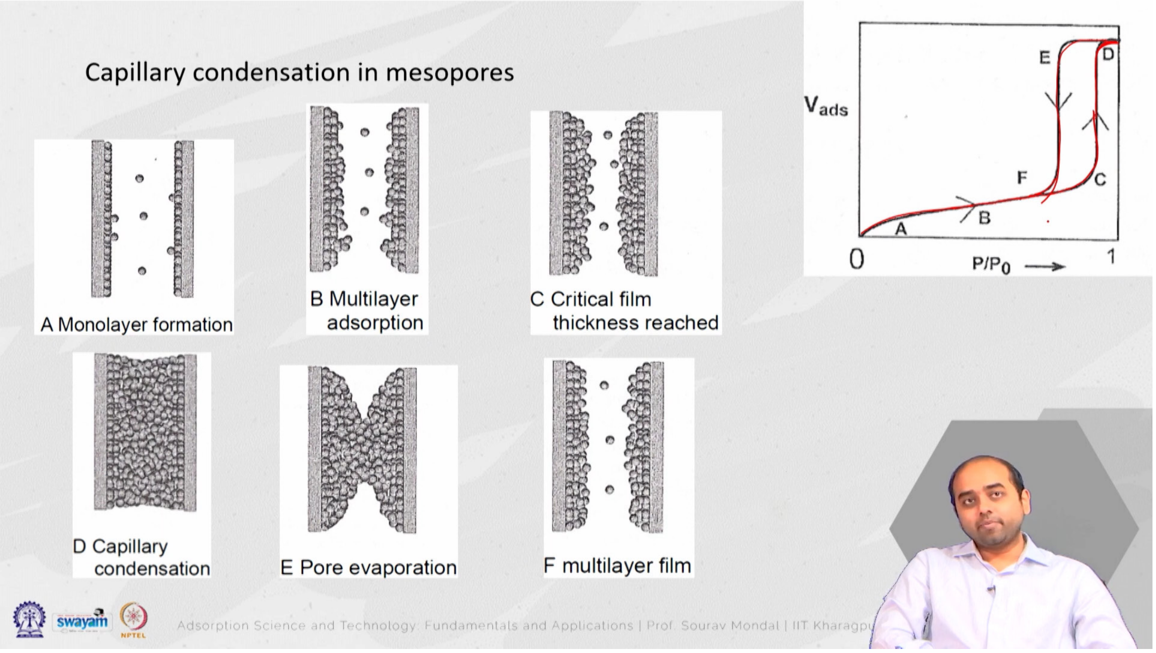
Hello everyone, welcome to this lecture on pore size analysis. Pore size is a very important you know factor or a important consideration in determining the efficiency or the capacity of the adsorbent. So, pore size distribution as well as pore size measurements particularly its volume and its you know pore diameter is very fundamental to the BET equipment and that is what that is why we have decided to have a dedicated you know lecture on this topic itself. Now, one of the important characteristics or the physics that happens during this adsorption is the capillary condensation. Now, capillary condensation happens when the inside particularly inside you know mesopores when the adsorption forms too much of multilayer. And the surface energy is significantly sorry the free energy change is significantly lower in this case resulting in the formation of the local you know condensation of this gas molecules or the adsorbate molecules.

So, typically a liquid like you know flim or a phase inside the pore is produced at a pressure p which is much less than its saturation pressure at that test condition. So, due to the formation of this capillary condensation. there is a hysteresis loop in the adsorption desorption cycle and that is what is particularly exploited in the case of the pore size analysis calculation. So, we will see the details into it. So, typically classical you know this adsorption desorption cycle looks something like this. So, there is this six different phases. So, let me try to draw them. So, initially there is monolayer formation at low pressures. So, this is the part of formation from A and then slowly multilayer starts to evolve.



And then there is significant you know multilayer depositions layer resulting in the formation of the critical film thickness. And then when you know there is too much of multilayer and the films you know completely occupy the pore volume or the pore diameter you start to see the capillary condensation. Now this is what the first adsorption cycle is up to that is the limit of the you know capture of the or the adsorption and beyond once the capillary condensation starts there is no further adsorption that is possible. So, next is the desorption cycle if you start from that point there will be a initial phase where the pores would try to evaporate right as the capillary condensation is not reversed in the disengagement of the multilayers the there is actually pore evaporation. And after a significant pore evaporation then the the multilayers are reverted back and then the classical path of B to A to monolayer during the desorption is what you know is observed.

So, let us get some illustrative idea about what are these actually looks like. So, this is what we mean by the formation of the monolayers and this is particularly what is happening during the phase of initial phase at low pressures. Then we start to see the multilayer adsorption profiles as this is something very pertinent in the case of physisorption. Once the multilayer adsorption is way too much then we start to see the critical film thickness which has reached right and beyond that the entire pores is actually pore volume is actually occupied by the adsorbate molecules and at that stage you start to see the onset of the capillary condensation as the, you know this adsorbate free energy on further increasing the pressure leads to the condensation of these molecules. Now once so this is the end of the adsorption phase once the capillary condensation starts further adsorption is not possible, as you can realize physically what is the scenario in that situation.



Capillary condensation in mesopores

A Monolayer formation

B Multilayer adsorption

C Critical film thickness reached

D Capillary condensation

E Pore evaporation

F multilayer film

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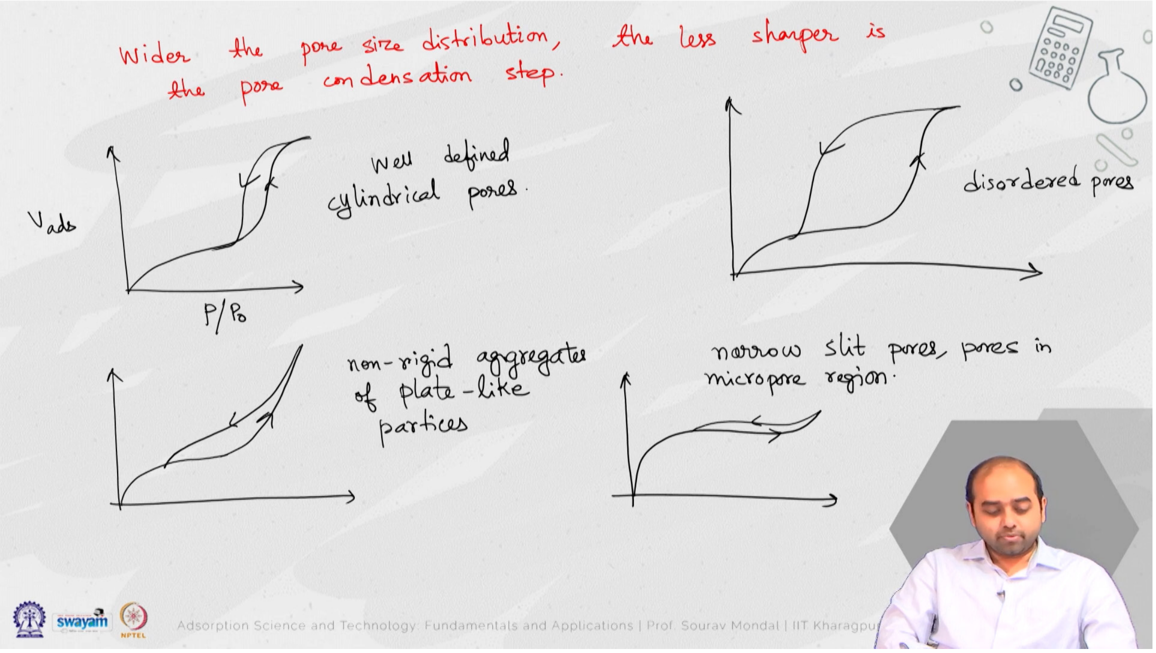
Now, when the pressure is reduced to initiate the desorption, first the pore evaporation happens it is not like you know the condensation is reversed, by by just the disengagement of the molecules instead the evaporation starts to happen. So, this is particularly different from the you know whatever you see from C to D, from D to E it is actually a different phase and this continues till you know this multi layers are reverted back. So, that is the state when from E you go all the way up to this F. So, when the multi layer films is again reinstated you start to see further you know multi layer depletion resulting in the formation of the you know this mono layers finally. Now, these hysteresis loops are you know classically observed at high pressures when there is capillary condensation.

If there is hysteresis which happens at low pressure then you know the pore size analysis is not possible. So, how the pore size analysis is done is actually when the capillary condensation starts you use the famous Kelvin equation from the surface energy balance which helps us to consider that if for a particularly for a fully wetted surface what would be the radius of curvature and from there the you know pore area or the pore diameter can be worked out we will talk about we will talk about that in details. But first let us try to understand the hysteresis associated with this pore condensation step. So, the wider one important comment or remark that I want to make that wider the pore size distribution is the less sharper is the condensation step. So, now based on the hysteresis phenomena there could be different types of you know understanding or situations and I will quickly try to explain some of them.

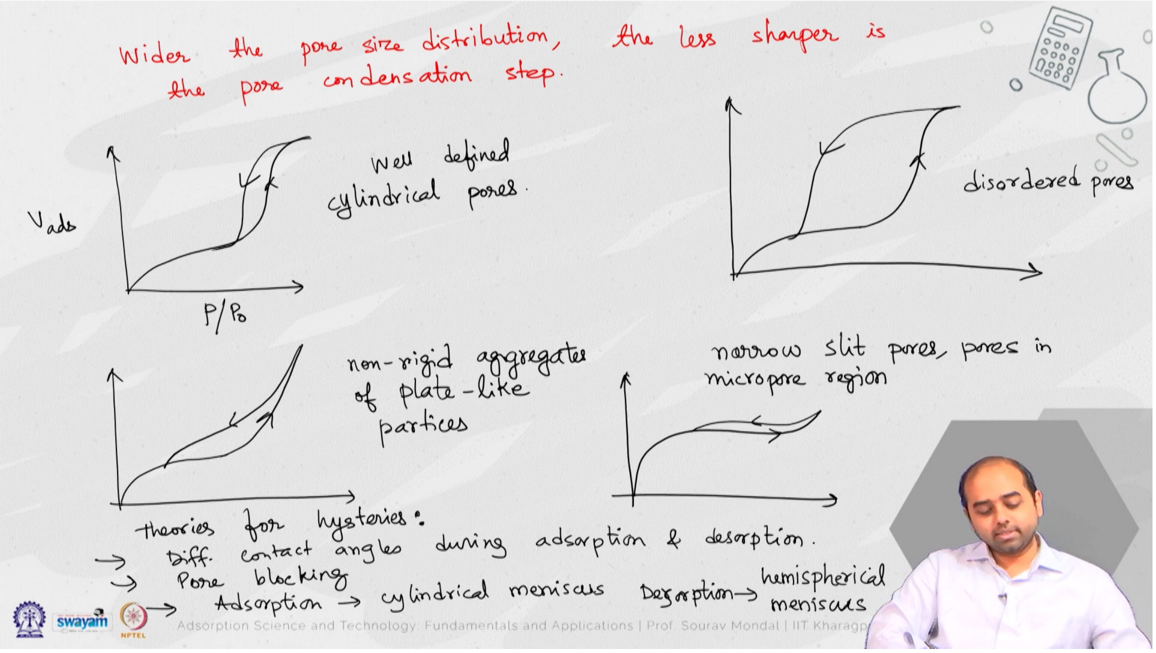
So, in this case where the picture of the hysteresis looks something like this is very. So this is the situation for very well defined cylindrical pores or cylindrical pore channels. If the situation is this hysteresis is way too much something like this then you see disordered pores pore blocking percolation phenomena etcetera is also very prominent in these kind of scenarios. There are other possibilities like this. So if this is the scenario then we say that non rigid aggregates of plate like particles slit shaped pores is something that this represents and if this is the hysteresis phenomena. Maybe I should draw this properly.



Wider the pore size distribution, the less sharper is the pore condensation step.

If this is the situation it is again narrow slit pores, but with the possibility of you know pores in micro pore region. So, if there is hysteresis in the low pressure regime then pore size analysis is not possible because that represents you know the formation of or or formation of capillary condensation even when the channel is not completely formed or there is no multilayer formation. So, there is possibility of you know this chemisorption in that case. So, swelling could also be a reason reason why there is you know this hysteresis observed at low pressure. It could be also possible that there is some irreversible uptake of the molecules which in the which is present in the pores and this could actually violate the idea of the BET isotherm where there is no relation between interaction of the particles between themselves during the phenomena of adsorption.

Now, this cylindrical pores represents that you know the classical pore condensation model is valid in this case. So, pore fluid is actually fully occupy this entire pore region and the this desorption loop actually establishes the equilibrium phase transition. So, one can use the information during the desorption cycle for the calculation of the pore size etcetera. So, classical methods like this b j h etcetera can be applied there. Whereas, in the second, third and the fourth or the rest of the cases and the origin of the hysteresis could be of various reasons, there is also a chance of you know bottlenecking of the pores in this scenario.



Wider the pore size distribution, the less sharper is the pore condensation step.

theories for hysteries:
→ Diff. contact angles during adsorption & desorption.
→ Pore blocking
→ Adsorption → cylindrical meniscus Desorption → hemispherical meniscus

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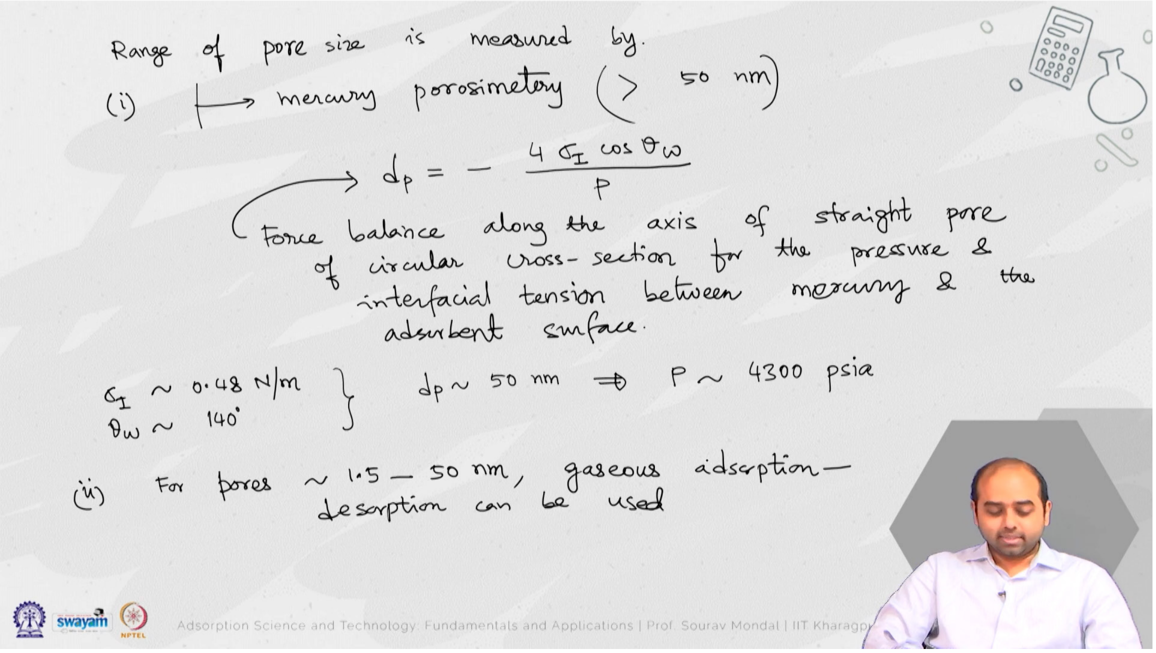
So, and the pore blocking phenomena could also be one of the reason for this hysteresis. So, in this case a further molecular approach something like DFT or something perhaps may be needed to understand the pore interaction in this method. So, the Kelvin based approach you know may not be appropriate in this scenario. So, the origin for the or the different theories that are applicable for the hysteresis, can be summarized is like there could be different contact angle during adsorption and desorption because please understand that during the desorption there is a partial liquid state which is present. Bottlenecking or pore blocking is one particularly important phenomena.

And the other one is also important that adsorption generally happens on cylindrical you know meniscus whereas, this desorption happens on the hemispherical meniscus. So, these are the different reasons for the hysteresis. Now, let us try to understand you know this how this idea of the hysteresis is actually is implemented or is actually used for the calculation of the pore size. Now, typically the sorry Now typically the pore size distribution or the pore size is analyzed from the you know this surface porosimetry or this surface calculations or surface energy calculations. This range of the pore size is measured, sorry is measured by classically by mercury porosimetry. So, what does this mercury porosimetry does and this is applicable only for pores larger than 50 nanometers. Why I will talk about now that typically the diameter in the case of the mercury porosimetry is calculated from the equation of the surface tension. So, the idea is that this is the surface tension equation theta is the wetting angle sigma is the surface tension divided by the pressure. So, idea is that that the mercury penetration in this case is happens you know as a function of the applied hydrostatic pressure.



Range of pore size is measured by.

(i) ⟼ mercury porosimetry (> 50 nm)

$$d_p = -\frac{4\sigma_I \cos\theta_w}{P}$$

Force balance along the axis of straight pore of circular cross-section for the pressure & interfacial tension between mercury & the adsorbent surface.

$$\left.\begin{array}{l}\sigma_I \sim 0.48\ \text{N/m} \\ \theta_w \sim 140^\circ\end{array}\right\} \quad d_p \sim 50\ \text{nm} \Rightarrow P \sim 4300\ \text{psia}$$

(ii) For pores ~ 1.5 – 50 nm, gaseous adsorption–desorption can be used

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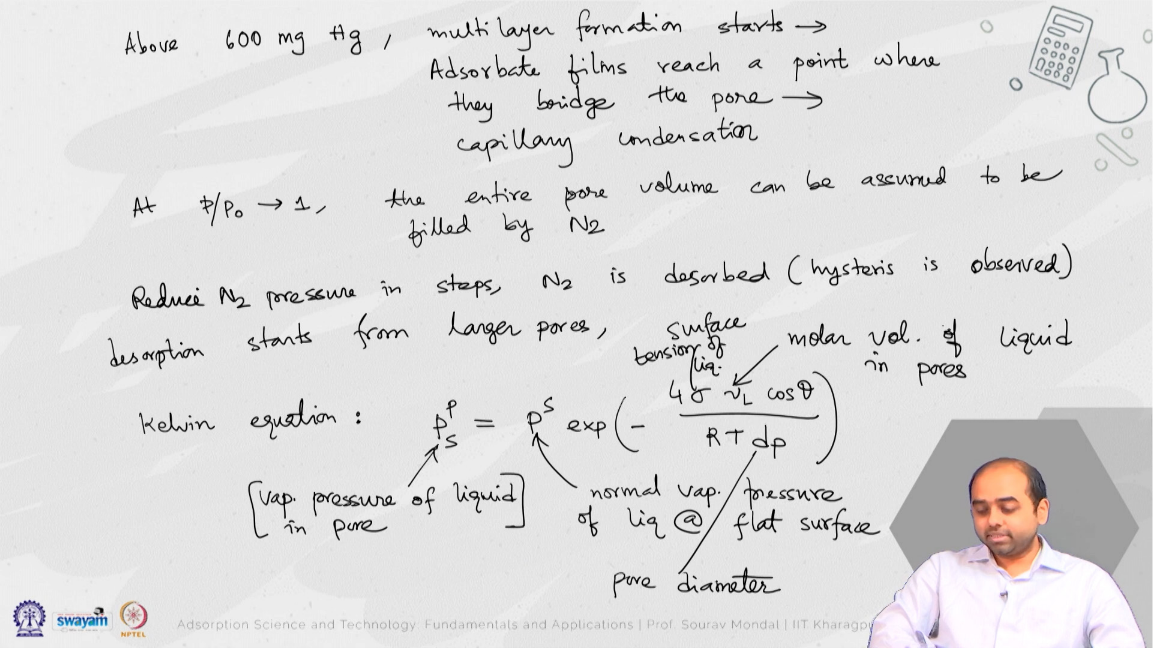
So, you make a force balance you make a force balance along the axis of straight core of circular cross section for the pressure and interfacial tension, tension between mercury and the adsorbent surface. So, based on this force balance only this equation is evolved. So, here sigma stands for the interfacial tension. Now, typically this interfacial tension for mercury is around 0.48 Newton per meter. And let us say if you consider a relatively hydrophobic surface the contact angle can be like 140 degrees or 120 degrees, but I am just giving you some idea about what is the issue with the pore diameter. Now, for this value considering a pore diameter of 50 nanometer you can see this gives a this hydrostatic pressure of around 4300. So, just to push mercury into a 50 nanometer pore the hydrostatic pressure would be in the range of almost you know 4000 psi which is significantly large value and you can understand any pores diameters less than 50 micron 50 nanometers the hydrostatic pressure would be unrealistically high. So, to avoid this situation or to you know make some you know possible experimentation in this kind of scenario normally this you know adsorption desorption method is used. So, mercury porosimetry is good for you know starting above 50 nanometers or typically from 100 nanometers or 0.1 micron and above mercury porosimetry is a very good technique whereas, for pores below this you know in the range of for pores.

In the range of 1.5 to almost 50 nanometer which is typically the range of the mesopores you know the gaseous adsorption and desorption can be used. So, what is the idea here? So, here this is an extension of the BET method and that is normally used for measuring specific surface area. So, what is generally done is that above you know this 600 mmHg this nitrogen pressure, the multilayer formation starts. formation starts and there is formation of I mean the adsorbate limbs reach a point. where they bridge the pore and this leads to capillary condensation.

So, almost at P by P0 tending to 1 the entire pore volume can be assumed to be filled. Now, when you selectively reduce this N 2 pressure in steps N 2 is dissolved and you see this hysteresis etcetera. So this desorption starts from larger pores So, why this option starts from larger pores is because the effect of the you know this pore size on the vapour pressure is very important and that is where you know this relation is used. So, this relation of the effect of pore diameter on the vapour pressure is through the condensed phase in the pores is given by this Kelvin equation. So, here this is essentially the vapor pressure of liquid in pore. Now, please note that this vapour pressure is actually observed when the pores start to evaporate during the desorption cycle after capillary condensation has achieved right.

So, that is the reason why this Kelvin equation or the pore size analysis is done from the desorption information because during the desorption phase the pores you know actually evaporate and equilibrium exist between the vapour and the condensed liquid at that phase. So, the vapour pressure during that state has to be used to calculate this pore diameter or the validity of this Kelvin equation is established during the pore evaporation phase. Now importantly as the this vapour pressure is reduced until the time this pore evaporation happens, we can calculate the different I mean calculate this VL or the molar volume. So, V L is actually the molar volume of liquid in the pores one can get a relation of the different you know pore vapor pressure of the liquid in the pore and the molar volume and for from there a range of the diameter or the pore diameter which exist in this particular sample can be evaluated. So, P s is of course, the normal vapor pressure of the liquid of the liquid at of course, flat surface or under normal conditions.



Above 600 mg Hg, multilayer formation starts →
Adsorbate films reach a point where they bridge the pore →
capillary condensation

At $p/p_0 \to 1$, the entire pore volume can be assumed to be filled by N_2

Reduce N_2 pressure in steps, N_2 is desorbed (hysteris is observed)
desorption starts from larger pores,

Kelvin equation : $p_s^p = p^s \exp\left(-\frac{4\sigma v_L \cos\theta}{RT\,d_p}\right)$

surface tension of liq.
molar vol. of liquid in pores
[Vap. pressure of liquid in pore]
normal vap. pressure of liq @ flat surface
pore diameter

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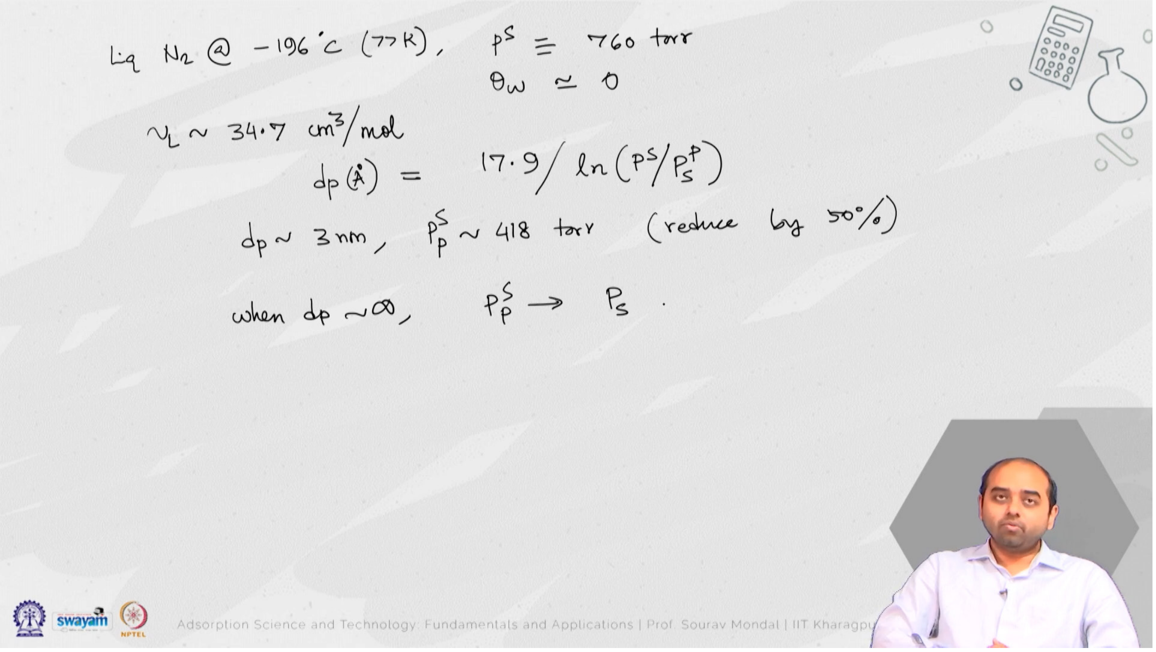
And sigma is of course, the surface tension of the liquid in the pore. So, you can you can see that for you know for particularly this Kelvin equation to be valid from where essentially this dp or the pore diameter is evaluated relies on the fact that There has to be pore condensation and during the pores this condensed liquid evaporation one can calculate what would be the you know this diameter using the Kelvin equation. Now, typically let us see for nitrogen what is the scenario. So, for example, liquid nitrogen at this minus 196 centigrade or 77 Kelvin this vapor pressure is 760 torr and let us say it is completely wetting. So, for theta w to be 0 and let us say for a particular molar volume of this one can work out what would be the, we put the numbers we can work out what would be value of this different pore pressures.



Liq N_2 @ $-196^\circ C$ (77K), $P^S \equiv 760$ torr

$\theta_w \simeq 0$

$v_L \sim 34.7\ cm^3/mol$

$$d_p(\text{Å}) = 17.9/\ln(P^S/P_S^P)$$

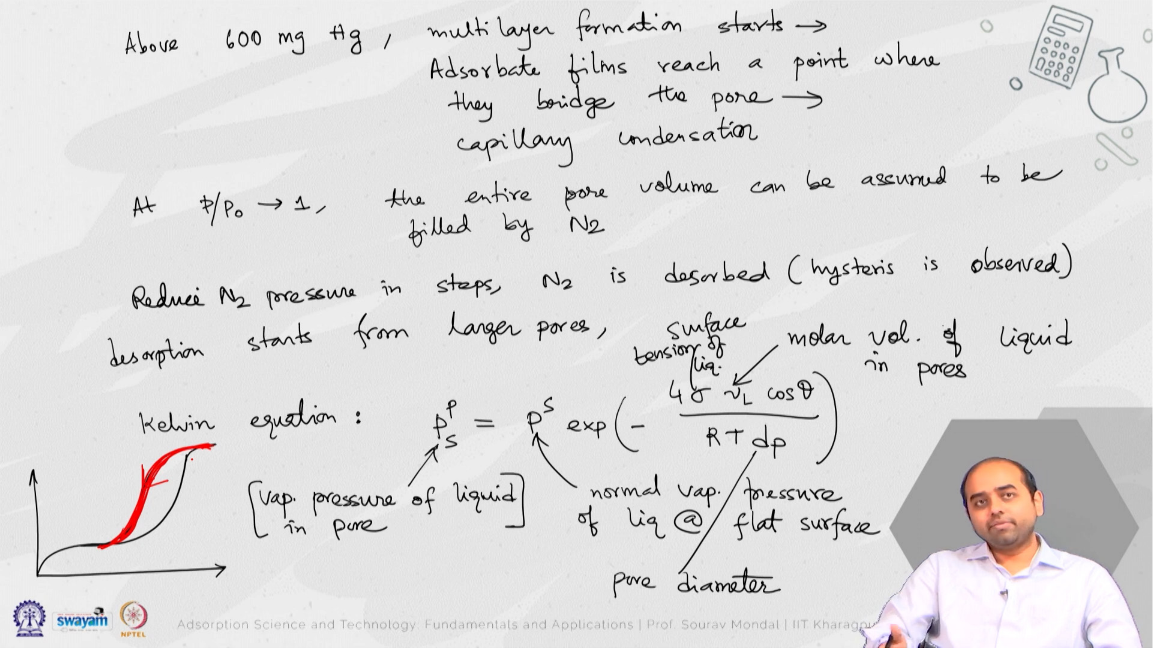
$d_p \sim 3\ nm$, $P_P^S \sim 418$ torr (reduce by 50%)

when $d_p \sim \infty$, $P_P^S \rightarrow P_S$.

So, from here you can get a chart about for different values of the vapor pressures what would be the dp. So, for dp 3 nanometers this turns out to be around 418 torr. So, that this is reduced by almost 50 percent. So, at I can see that when d p tends to infinity this pore vapor pressure approaches the vapor pressure of the flat surface. So, this technique nicely relates to the asymptotic limit when for large sized pores there is no difference in the vapor saturation pressure and this is particularly useful when you can see that less than 50 or you know 200 micron or so this difference can be nicely worked out.

So, from I mean I just want to give an idea that what is the value of the limiting pore size for which the difference in the vapor pressures is around you know you can work out yourself around 95 percent or something which can be measured and you can get a realistic idea about your pore size. Now one important point this is more of the equipment thing is that before Before the pore you know this pressure etc. is measured it is very important to work out or to calculate what is the you know this density of these particles and typically that is done from the amount of the you know this void fraction that is present in the molecules is something that also needs to be known because from there only you can work out what would be the specific pore surface area. So, calculation of the porosity or the particle porosity is also very important. So, typically the samples are degassed.

So, from the degassing one can you know remove any molecules or gases if at all that is present in the pores and after that helium is introduced into the sample. So, helium is not adsorbed. So, the amount of helium that fills the pores gives us the pore volume or the void volume in the sample. So, calculate or measuring the weight of the sample and relating the amount of the volume that this you know helium has been absorbed or filling the pores one can find out what is the pore volume of the sample and from there the true particle density can be worked out and that is an important information that needs to be used in the surface area calculation provided you know your diameter. So, this is how the diameter calculations or the pore volume calculations is actually done in this case.



Above 600 mg Hg, multi layer formation starts → Adsorbate films reach a point where they bridge the pore → capillary condensation

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surface tension of liq.

molar vol. of liquid in pores

[Vap. pressure of liquid in pore]

normal vap. pressure of liq @ flat surface

pore diameter

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I will also mention here that there is a correction to this Kelvin equation to take into the account that during the formation of the film or this you know the pore diameter that one calculates from here is based on the film that is produced over the pore surface area. So, this is one limitation and there are some correction factors to it that can incorporate and take into account of this feature. So, I want to reemphasize that once this adsorption desorption is done one calculates the different vapour pressures of the liquid is present in the pore during the you know this desorption cycle. So, if you recall this is the desorption cycle and it is in this phase it is in this phase where one should consider the vapor pressures or the pressures exerted by the adsorbed gas as the pore evaporates as in this phase only there is an equilibrium between the vapor and the liquid and that is what is used the information of that part is used in the Kelvin equation for relating the pore diameter to it. And this VL is the molar volume of the liquid that in the case of the nitrogen that is already very well defined.

So, I hope all of you get an understanding about how the pore size distribution is actually calculated. And this method of using the Kelvin equation is actually known as the BJH method of pore size analysis or getting a pore size distribution. Thank you everyone. I hope all of you like this lecture and found it useful. Thank you.