Flow through Porous Media
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Lecture – 17
Transport Mechanisms (Adsorption/Pore Condensation)

I welcome you to this module of Flow Through Porous Media. What we are discussing is different concepts of Transport Mechanisms that are applicable when it comes to flow through porous media, other than regular viscous flow, a regular Darcy's law.

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CONCEPTS COVERED

So, in this context what we did is we mentioned that there could be, there could be let us say on one hand we have this viscous flow and this viscous flow is applicable more when we have larger pores. Whereas, there could be a Knudsen diffusion, there could be surface diffusion, there could be bulk diffusion. And then so, there are by various means these transport can also take place.

And in the last lecture what we showed is if you have a combination of viscous flow and Knudsen diffusion how that will affect. I mean we can still consider, still write it in terms of Darcy's law only the definition of permeability changes. Now, the permeability becomes effective permeability which is a function of pressure, we have discussed this in previous lecture. So, what I am going to do next is, let us look at, the pore size let us look at what all things can happen fundamentally inside a pore.

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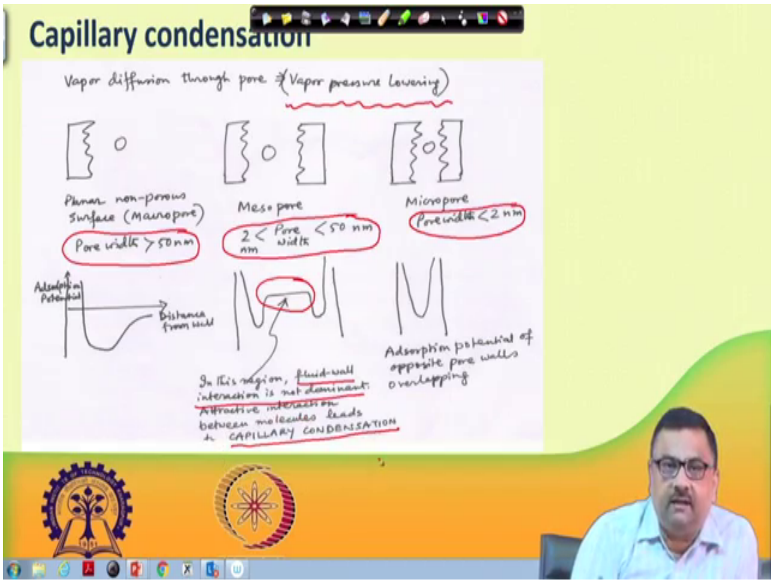

Capillary condensation

Vapor diffusion through pore ⇒ (Vapor pressure Lowering)

In this region, fluid-wall interaction is not dominant. Attractive interaction between molecules leads to CAPILLARY CONDENSATION

Adsorption potential of opposite pore walls overlapping

So, here we are talking about vapor diffusion through a pore, and there is a unique thing that happens inside which is known as vapor pressure lowering. So, we will be targeting that. What we have here is we have three different situations presented here, in one case it is planar non-porous surface, these are so called macro pore where pore width is greater than 50 nanometer.

The other case is that the definition of mesopore, where pore weight is between 2 nanometer and 50 nanometer and the third case is the micro pore where the pore width is less than 2 nanometer. So, here we can see a wall and the molecule and then there is not much effect on the molecule, and the wall is not affecting the molecule to any great extent, because the effect of wall would be far wall is far away from the molecule.

Here in this case the molecule can see both the walls, but it is still they are little apart and in this case the molecule is within the confinement of the two walls. See if one plots the absorption potential as a function of distance from the wall, here in this case the adsorption potential would be higher when it comes to near the wall. But, as it goes away from the wall that this potential tends to 0, I mean this adsorption potential the effect would be minimal.

So, this is the case when you have macro pore, when it comes to meso pore what one sees is that there is this wall has an effect. So, you can see this adsorption potential, this effect through adsorption potential, this wall has an effect and you can see this effect on adsorption potential. And in between there is a region which we are going to discuss now, and when you have in a micro pore the adsorption potential here it is we have an effect here and here also we have an effect.

So, this adsorption potential is affecting the molecule, if the molecule is sitting here this molecule is under the confinement of these two walls. Molecule is under the influence of these adsorption potential that is imposed, that the adsorption potential and the interaction of the two wall interactions they are dominant on this molecule. Now, let us come back to these mesopore here.

Meso pore in this case we have seen that in this location it is the wall interaction is there dominating, here also it is dominating in between what happens? So, in this region the fluid wall interaction is not dominant, fluid wall interaction is not dominant in this plateau region. So, we are talking about a plateau region and in this plateau region fluid wall interaction is not dominant, attractive interaction between molecules. Now, molecules they attract each other.

So, this molecule attractive interaction between molecules leads to a very well-known phenomena which is known as capillary condensation. So, I want to we want to build further on this what is this capillary condensation.

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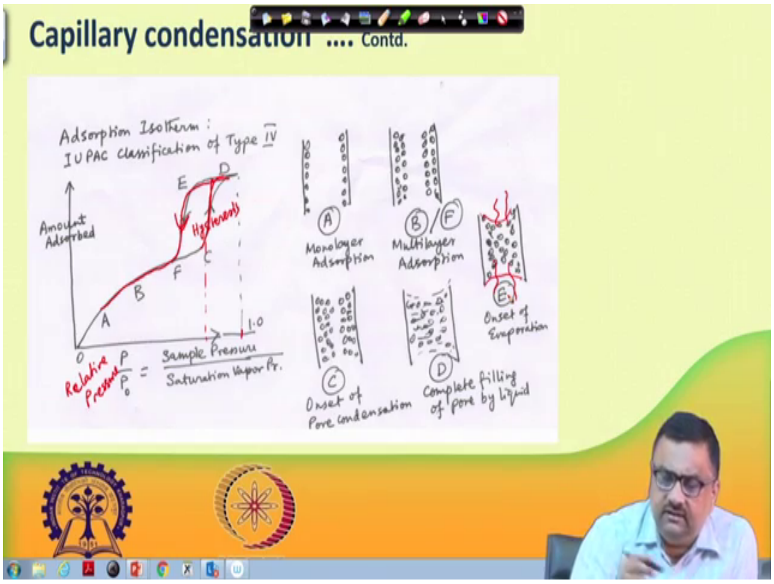

Capillary condensation .... Contd.

This picture here is this is known as adsorption isotherm, adsorption isotherm means it is plotted here, the y axis is amount adsorbed and x axis is P divided by P 0, which is known as sample pressure divided by saturation vapor pressure. So, what is a saturation vapor pressure? If saturation vapor pressure is existing in the environment. So, one can expect let us say water saturation vapor pressure has reached; that means, water will start condensing on the surface.

So, saturation vapor pressure is the so, when P by P 0 is equal to 1 this is the 1.0 value. So, when P by P 0 is equal to 1, we expect that liquid will condense on any surface. What we are going to see in this case is as I said in capillary condensation that inside the pore much before this P by P 0 is reached, I mean that is at a much less pressure the condensation takes place inside the pore.

Because there is some pool because of surface tension and that pool is instrumental in condensing inside the pore when because the pore radius is small, inside the pore the condensation takes place. So, let us see if I go by what is called adsorption isotherm, I said amount absorbed as a function of this ratio. This ratio is also referred as relative pressure, relative pressure P divided P 0. So, relative pressure P divided by P 0 is sample pressure divided by saturation vapor pressure.

So, now if we see that when sample pressure is sample pressure divided by saturation vapor pressure if that is 0 there was no adsorption, pressure is absolutely 0. As you increase the pressure there is so called monolayer adsorption, that is the regime that is the regime a which is shown in this figure here. So, monolayer adsorption; that means, if this is the pore one can see at the wall a mono layer of molecules will be seen here, as the pressure is increased further there would be multi. So, it started carving here.

So that means, it start a there would be multi-layer adsorption; that means, more than one layer of adsorption has taken place. So, that is the situation at B. Whereas, if it comes to C, you can see when it goes all the way to C then suddenly there is a straight line there is a jump in a straight line so, this part. So, this is vertically; so at this here the sample pressure is not changing much, sample pressure is not changing much, but the amount adsorbed is changing drastically.

So, at this time these multi-layer adsorption it has come up to this point they are now at C they are ready for onset of pore condensation and then and D, when it goes to position

D complete filling of pore by liquid takes place. So, all the molecules they condense inside the pore ok. So, there they are all condensing inside. So, it is basically liquid. So, mono layer multi-layer these layers are growing and at one point you find these layers are merging with each other and inside there is this liquid.

So, this is; so essentially the condensation takes place at a relative pressure which is much more, which is smaller than 1.0. So, it is condensing at a lower pressure than the way it would be if it is just a plain surface and not a porous medium. And then if you come backward now would decrease the pressure. So, it will follow, but it will follow a different track I mean if we decrease the pressure we would have expected that this will follow this line and then continue with this line, but instead the line that is followed here is a different line and then continue with this line and this.

So, this is basically, this is the condensation then this party we will call evaporation; that means, these molecules are now evaporating from the liquid ok. So, that is E is onset of evaporation and then F is similar to B; that means, now we are going back to the multi-layer adsorption state and if you reduce the pressure further it would be monolayer adsorption and continuing like this.

So, this is known as adsorption isotherm; now adsorption isotherm there could be different types. In fact, IUPAC classification gives different types of adsorption isotherms. It could be just simply up to this ok, then it would be simply a monolayer adsorption is possible then it could be mono layer plus multi-layer it could be that mono layer multi-layer adsorption is not there it starts from the condensation. So, there are various types possible, generally type IV is quite common I mean in case in case of a meso porous material this type IV is or meso micro porous meso micro pore combination you will see this kind of type IV isotherm.

So, IUPAC classification type IV isotherm will look like this and here this is referred as condensation and evaporation. Of course, one can see here that why these two lines are not same. This is in fact, referred as hysteresis, that it started with it went one way and when you came back it is not following the same path and that they are there are reasons for these; if we look at this picture here the condensation takes place because these layers are growing and then at one point they are touching with each other.

Whereas, evaporation take place if this is filled and then evaporation is taking place in this direction. So, these may not be they are not that the meniscus that they follow in the two cases condensation evaporation they may not be same. So, there are reasons why this hysteresis takes place.

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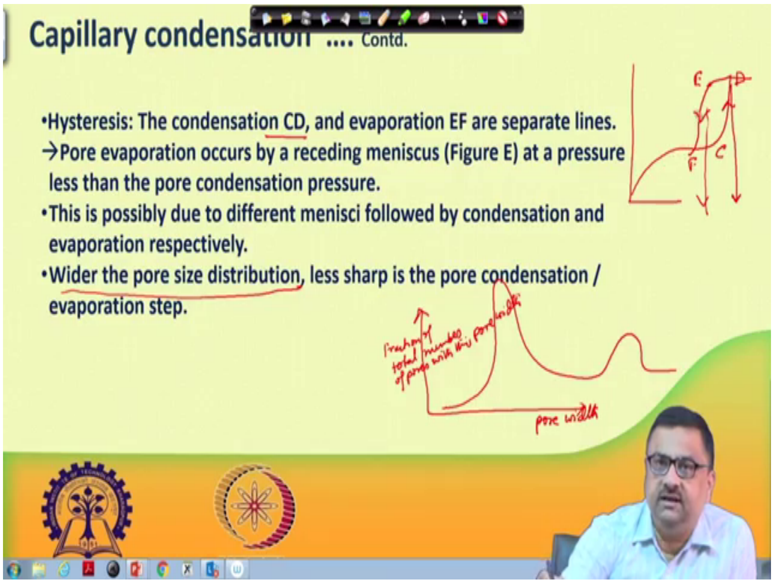

Capillary condensation .... Contd.

- Hysteresis: The condensation CD, and evaporation EF are separate lines.

→Pore evaporation occurs by a receding meniscus (Figure E) at a pressure less than the pore condensation pressure.

- This is possibly due to different menisci followed by condensation and evaporation respectively.
- Wider the pore size distribution, less sharp is the pore condensation / evaporation step.

Now, if we look at this hysteresis here is the condensation part CD; CD in that curve, I mean we are referring to this curve here we said that this and then. So, the condensation is the CD and this is EF, EF is the evaporation CD is the condensation. So, CD; condensation CD and evaporation EF are separate lines; pore evaporation occurs by a receding meniscus which is given in figure E there at a pressure less than the pore condensation pressure. So, pore evaporation so is essentially you are seeing that the pore evaporation is taking place at a less pressure than pore condensation. This is because this is added at some P by P 0 and this is at some other P by P 0 and they are different, this is possibly due to different menisci followed by condensation evaporation respectively.

Now, one thing you may note here that wider the pore size distribution; wider the pore size distribution. What is pore size distribution? We had discussed about these fraction of total pores, fraction of total pores total number of pores with this diameter, with this pore width if this becomes a y axis and this becomes the pore width. So, we can see that some pore width we will have a large number of pores, some are having like this.

So, if it is a very sharp pore size distribution; that means, all the pores are of a particular size whereas, if it is a flat distribution; that means, we have pores of different sizes present there. So, wider the pore size distribution; that means, when the pore sizes distribution is very wide then less sharp is the pore condensation evaporation step. So, then this this part will be more diffused, it will not be clearly visible I mean if you have a very wide pore size distribution.

Whereas, if you have a very sharp pore size distribution all the pores are of one particular size or at least near that size then one will see this behavior very clearly.

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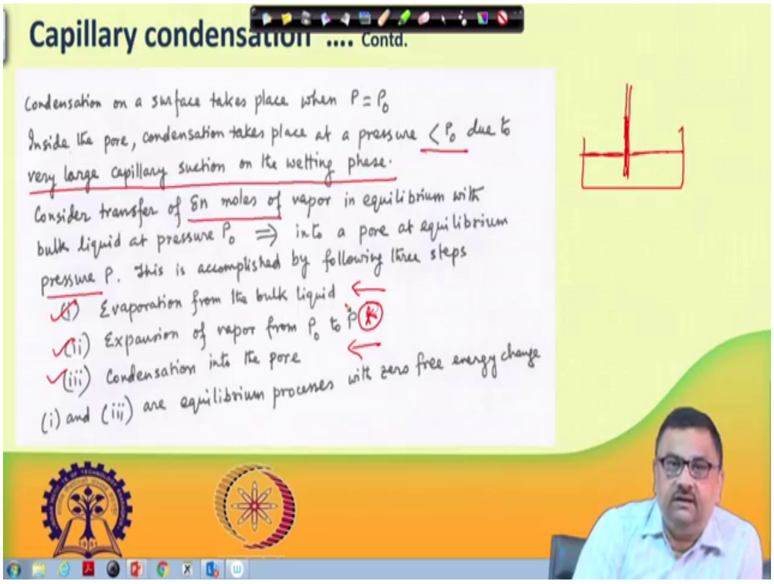

Capillary condensation .... Contd.

Condensation on a surface takes place when $P = P_0$

Inside the pore, condensation takes place at a pressure $< P_0$ due to very large capillary suction on the wetting phase.

Consider transfer of δn moles of vapor in equilibrium with bulk liquid at pressure P_0 $\Rightarrow$ into a pore at equilibrium pressure P. This is accomplished by following three steps

(i) Evaporation from the bulk liquid ←

(ii) Expansion of vapor from P_0 to P ⓚ

(iii) Condensation into the pore ←

(i) and (iii) are equilibrium processes with zero free energy change

So now, it could be pointed out here is that the condensation on a surface takes place when P is equal to P 0, that I already mentioned right. Condensation on a surface takes place when P is equal to P 0. Now inside the pore condensation took place at a pressure less than P 0 due to very large capillary suction on the waiting phase, that is the statement given here, that there is a capillary suction. Capillary suction means you have already you are familiar with this I think the capillary suction, that if you have a tube inserted in water and you find that there would be a capillary rise, water would be rising through this tube because of surface forces.

Because glass, I mean water tends to wet glass. So, it has a favorable contact angle. So, water tends to travel up. So, it is basically the it is this is capillary suction the glass capillary is sucking water into this capillary. So, that is why made the hydrostatic as per the hydrostatic head, as per the hydrostatics the level of water inside the capillary should have been here, but instead of that the level has gone up there.

So, this is a capillary, classical example of capillary suction. So, capillary suction here very large capillary suction is causing this condensation. Now, consider I mean how would put some theory into it, I mean what how what is capillary section, how much would be the capillary section? So, consider transfer of delta n moles of vapor in equilibrium in bulk with bulk liquid at pressure P 0 into a pore at equilibrium pressure P.

So, what that means, is why you would first of all a condensation take place in the, why a condensation will take place inside a capillary. So; that means, some moles of vapor which is in equilibrium with bulk liquid at pressure P 0 that has to be transferred into a pore at equilibrium with pressure P ok. So, then only this cap, and then only then only the condensation will take place. So; that means, it will be if this is this can be accomplished by three steps, one is I have the bulk liquid from there this delta n moles of vapor has to be evaporated.

So, one has to evaporate this delta n moles from the bulk liquid, then these have to be there has to be expansion of vapor from P 0 to P because P is less than P 0, P 0 is the saturation vapor pressure, but this condensation has to take place at a lower pressure. So, if you take it to a lower pressure there has to be expansion of that vapor. So, that expansion has to be accounted and then that vapor will condense inside the pore so, this condensation into the pore.

So, these are the three steps involved if you take delta n moles of vapor which is in equilibrium with bulk liquid at pressure P, and you expect that to condense inside the pore at a pressure less than P 0 or as a matter of fact at a pressure which is which is P. So, now these two one and three these two are the equilibrium processes. So, they have zero free energy change; however, this one has some free energy change to be considered.

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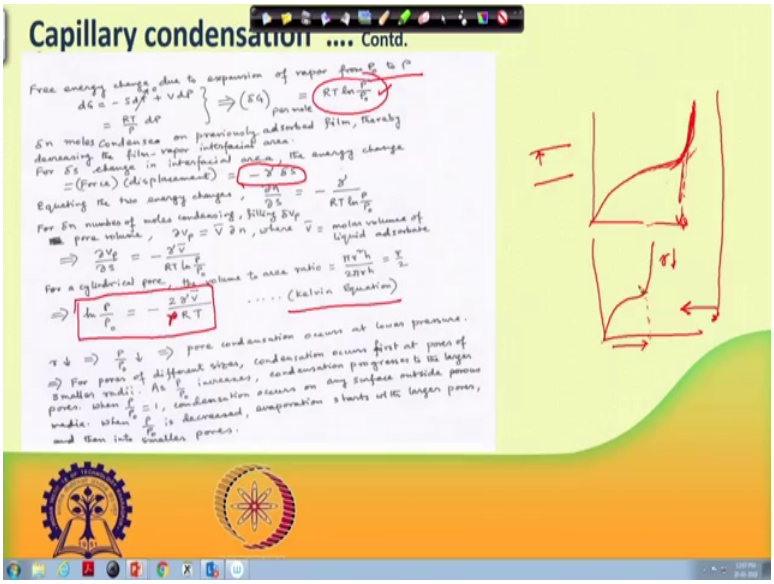

Capillary condensation .... Contd.

Free energy change due to expansion of vapor from P_0 to P

$$\left.\begin{aligned} dG &= -S\,\cancel{dT} + V\,dP \\ &= \frac{RT}{P}\,dP \end{aligned}\right\} \Rightarrow (\delta G)_{\text{per mole}} = \boxed{RT \ln \frac{P}{P_0}}$$

δn moles condenses on previously adsorbed film, thereby decreasing the film-vapor interfacial area.

For δs change in interfacial area, the energy change

$$= (\text{Force})(\text{displacement}) = \boxed{-\gamma\,\delta s}$$

Equating the two energy changes, $\frac{\partial n}{\partial s} = -\frac{\gamma}{RT \ln \frac{P}{P_0}}$

For δn number of moles condensing, filling δV_p pore volume, $\partial V_p = \bar{V}\,\partial n$, where $\bar{V}$ = molar volume of liquid adsorbate

$$\Rightarrow \frac{\partial V_p}{\partial s} = -\frac{\gamma \bar{V}}{RT \ln \frac{P}{P_0}}$$

For a cylindrical pore, the volume to area ratio $= \frac{\pi r^2 h}{2\pi r h} = \frac{r}{2}$

$$\Rightarrow \boxed{\ln \frac{P}{P_0} = -\frac{2\gamma \bar{V}}{r RT}} \quad \ldots\ldots \text{(Kelvin Equation)}$$

$r \downarrow \Rightarrow \frac{P}{P_0} \downarrow \Rightarrow$ pore condensation occurs at lower pressure.

$\Rightarrow$ For pores of different sizes, condensation occurs first at pores of smaller radii. As $\frac{P}{P_0}$ increases, condensation progresses to the larger pores. When $\frac{P}{P_0} = 1$, condensation occurs on any surface outside porous media. When $\frac{P}{P_0}$ is decreased, evaporation starts with the larger pores, and then into smaller pores.

So, now, if we look at here the free energy change due to expansion of vapor from P 0 to P that second step that will involve delta G per mole which is equal to RT ln P by P 0. What does what does this mean? See, this d G is written as minus Sdt plus VdP, since dt is 0 so no temperature change. So, it would be RT by P, if you take [FL] this is RT by P dP and then when you do an integration here delta G per mole would be RT ln P by P 0 ok.

So, now delta n moles condense on previously absorbed film. So, already I already have a monolayer adsorption or multi-layer adsorption, we have already have the this thing is that there is an adsorb layer. Now, there is a condensation taking place. So, what essentially condensation does is it decreases the film vapor interfacial area ok. Already the film was present and on top of that there was these vapor molecules in the gas phase.

Now, it since there is a condensation. So, that is causing the change in this area; so, previously adsorption from thereby decreasing the film ever intervention area. So, if somebody tries to find out how much is this energy change or how much is the work done for this, to this effect that would be equal to force into displacement and this can be written as for delta S change in interfacial area. One can write it as minus gamma which has a unit of Newton per meter which is the surface tension and then delta S is the change in area.

So, the product will be in Newton; product would be in Newton meter; Newton per meter into meter square. So, it would be Newton meter. So, for delta s change in interfacial area the work done to accomplish this change in interfacial area is given by minus gamma d s and that happened to be the energy change. So now, if one equates this energy change or minus gamma d s with this energy change. So, if we one equates that so one will end up with del n del s minus gamma divided by RT ln P by P 0.

So**,** now one may note here is that delta in number of moles condensing and if we expect the pore to be completely filled then for delta n number of moles condensing and filling delta V P volume, delta V P is the pore volume that you are filling. So, then delta V P would be simply V bar into delta n where V bar is the molar volume of liquid adsorbate. So, molar volume of liquid adsorbate multiplied by number of moles that has condensed; so, this becomes del V P is equal to V bar into delta n.

So, now in this case you may note here in this case instead of del n you are writing V bar into del V P. So, V bar has gone, sorry del n instead of that you are writing 1 by V bar into del V P. So, this V bar has gone to the right-hand side. So, you are writing del V P del s equal to minus gamma V bar by this quantity RT lnp by P 0. Now, for a cylindrical pore the volume to area ratio is volume of a cylinder pi r square h and the area is 2 pi rh.

So, this gives me the ratio as r by 2. So, if you instead of writing del V by del s, if you replace this del V by del s by r by 2. So, then you end up with this classical equation which is ln P by P 0 is equal to minus 2 gamma v bar, divided by r. This is r; r capital R T; this r is the radius of the pore gamma is the interfacial tension and V bar is the molar volume of liquid adsorbent. So, this gives me for a cylindrical pore at what pressure I can expect the condensation to take place? Suppose, I tell you that I have a pore which has a pore radius of this much r if I give you this information of what is this interfacial tension what is this V bar and what temperature we are talking about here.

So, convert that to absolute scale, r is universal gas constant. So, from there you can find out and P naught is the bulk property of that vapor at what is the saturation vapor pressure for that particular material that you one knows. So, from there you can find out what is the or you are not, you are just you are requiring P by P 0. So, from there you can find out at what pressure; at what pressure this is going to condense.

So, this is in fact, this particular. So, at what pressure this is this condensation takes place can take that this condensation will take place this is given by well-known Kelvin equation. And, this is that Kelvin equation ln of P by P 0 is equal to minus 2 gamma V bar divided by small r which is the radius of the pore, capital R universal gas constant and T temperature in absolute scale. So, now, couple of things we may note here at this time is that when r decreases when pore radius decreases P by P 0 also decreases.

So, what; that means, is I mean this is what we see from Kelvin equation. So, what this means is pore condensation occurs at lower pressure when r decreases. So; that means, we are if we are talking about another situation where the we are having a smaller radius of pore we can see the condensation happening at a lower P by P 0 at a lower pressure, this is with smaller radius. So, when radius is small this would be the case. So, essentially for pores of different sizes generally porous medium would be a mixed system right, you have pores of different sizes. So, for pores of different sizes condensation occurs first at pores of smaller radii because when you are increasing from low pressure when you are increasing.

So, at lower pressure the faster condensation takes place. So, and so that means, when this pressure is reached here the larger pore is still undergoing multi-layer mono layer multi-layer adsorption here, but smaller pore already started condensing, the condensation has started taking place in the smaller pore. So, as P by P 0 increases from 0 condensation progresses to the larger portion; so, first it is condensing at smaller radii and then it is progressing to larger pores. When P by P 0 is equal to 1 the end point, when P by P 0 is equal to 1 condensation occurs on any surface outside porous medium anywhere on table chair on our everywhere condensation will take place.

Now, when P by P 0 is now decreased from that side then evaporation starts on the larger pore first and then evaporation continues evaporation starts from larger pore first and then the evaporation will take place into the smaller pores. So, this is how we are putting these ok. So, this is how, this is how if in a porous medium in a porous medium we have a combination of large pores and small pores. So, what we would see first is as the pressure, see when I even when the pressure is increased slowly you find that there is condensation taking place inside the pore which pore, the smallest of the pores.

And then gradually the larger pores they are also the condensation is taking place and at one point when the pressure require being called the saturation vapor pressure condensation will take place everywhere even on the pore holder. But then again if you are decreasing the pressure, gradually you will see the evaporation taking place. So, moment you reduce from P by P 0 is equal to 1 you evaporation will take place everywhere, but not in the smaller pores. Then first the larger pores the evaporation will take place and then gradually the smaller pores also the evaporation will take place.

This whole process is known as capillary condensation and at least as long as we know Kelvin equation we have handle Kelvin equation. We can at least put get some numbers at what if this is the pore size I have at what pressure they are likely to condense. Now, what we will see in next I mean the next lecture what we will point out is that this particular mechanism, this capillary condensation is going to affect the transport process I mean suppose a vapour is transporting. So, we expected our you know common this thing experience we expected that it would the vapor would see molecules would simply flow like puzzle is flow and everything right.

But, essentially what would happen there is this condensation will take place inside the pore and this and it will follow a different transport mechanism altogether instead of a frequent diffusion for example. We expected molecules to diffuse by frequent diffusion it do not happen that way rather it will go through some other mechanisms. So, in this regard I think capillary condensation and some introduction to capillary condensation is important. I would briefly touch upon this capillary condensation in the next lecture when it comes to the transport how this capillary condensation will affect the transport process.

I think this is all I have as far as this present lecture is concerned. I will continue, I will touch upon this capillary condensation once again in the next lecture. Thank you.

Thank you for this lecture today.