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Lecture – 18 Transport Mechanisms (Adsorptions / Pore Condensation) Contd.

I welcome you to this lecture of Flow through Porous Media; what we are discussing before is different Transport Mechanisms. We saw that over and above the viscous flow that is given by Darcy's law or what we call in fluid mechanic is the Poiseuille's flow. Over and above that shear driven flow one can have diffusion contributing to the transport of molecules and because of these there could be some extra terms, there could be some extra non-linearity arising.

So, in this context we mentioned in the last lecture we discussed about capillary condensation; capillary condensation is a phenomena which is a phenomenon which is happening because of the surface pull, because of the surface forces the molecules are pulled together to condense at a pressure which is lower than the saturation vapor pressure. So, because of this the smaller pores it would be liquid existing whereas, in larger pores it would be it would be vapor.

So, now when it comes to transport of molecules, it this could contribute or this could affect the transport process immensely and that is what we were discussing. We have already talked about Kelvin equation that relates the radius of the pore with the pressure at which the condensation will take place, how much would be the reduced pressure at which the condensation will take place if the radius of the pore is given. So, Kelvin equation we have already discussed what is the origin of that and everything. Now, let us see how these capillary condensation; how these capillary conditions is going to affect the transport process.

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So, let us now focus on what we were; what we are discussing. See transport by of the process that we are talking about here is condensation vaporization; condensation vaporization. So, that is the that is the that is the transport we are referring to. So, here you can see we have two grains, this is one grain this is another grain in a porous medium and in between there is a gap which we call the pore or the void. And we expect the flow to take place through this gap, through this void to this pore.

So, now because of this capillary condensation; that means, though outside the pressure is less than saturation vapor pressure; that means, the liquid is existing in vapor phase, there is no chance of condensation, but inside the pore in particular the smaller pores there is a condensation happening and so if these pores will be filled with liquid that is what we learnt when we talked about capillary condensation. So, now, so there is there as I mean it is basically presence of liquid island, that is what we are talking about. So, this is that liquid island.

Now, when it comes to the molecules, molecule it has now two paths molecule has two paths these either it can follow this path A which is through the liquid another is path B which is through a larger pore let us say this pore is much larger; that means, the next grain is here. So, this pore cross sectional area is much larger compared to this cross-sectional area. So, this, so it can go through a larger pore by so this larger pore has not

there is no condensation it has not it is not filled with a liquid whereas, smaller pore is already filled with the liquid.

So, now, molecule has two paths; one is path B through which it can diffuse and which is which is basically Fickian diffusion the flux is minus d del c del x etcetera or the other way to do it is the molecule can go through the smaller one. But if it has to go through the smaller one, then it has to it has to undergo few things; one is these one is say let us say this is the pathway, this is this is the path. So, basically this part is expanded here.

So, these this vapor that is coming from this side; obviously, this is at higher pressure because we are expecting a flow here. So, upstream will be at a higher pressure, downstream would be at a lower pressure. So, at the upstream end the pressure would be higher. So, I expect P y P 0 to be higher relative pressure and add that pressure this. So, what was you are what was the curve we have? You remember the x axis was P by P 0 and in the y axis we have amount adsorbed.

So, there we have first mono layer, multi-layer and then it went like this, that was a capillary condensation right. So, this is the pressure at which the capillary condensation take, that is where the capillary condensation is supposed to take place. So, now, these pressure here this upstream side the pressure is higher, so upstream side P by P 0 is let us say this pressure or higher. So, there would be condensation.

So, moment there is a condensation; condensation means it has to give it has to get it has to discharge the latent heat; condensation means it has to so leave the latent heat. So, that latent heat; that latent heat is the amount of that latent heat is m v h f g; m v is the mass flow rate of vapor and h f g is latent heat of condensation. So, that amount of latent heat is going to this liquid phase and that latent heat will constant.

So, there would be then in that case a temperature gradient and because of this temperature gradient lambda being the liquid thermal conductivity A is a cross sectional area of the pore and delta T by delta L which is basically dT dx. So, ka dT dx, we know that the heat flux is given by q x is equal to minus k del T del x. So, now, the heat flow rate this is the flux, this is what is flux. So, the flow rate would be flow rate would be q x multiplied by A which is would be equal to minus. Or in fact, del T del T minus of del T we can del T del x minus of del T del x can be written as delta T by L.

So, these becomes k A delta T by L just like we had this in case of Darcy's law we had this k A delta P by L. Similarly there k was the permeability this k is let us put a subscript T which is the thermal conductivity. So, there by that same token, so this would be the total heat given because of the condensation and that heat has to transmit through this. So, now, at this meniscus when it at this meniscus the pressure is less because this is the downstream side of the pore; so, pressure is less.

So, pressure is less means we are talking about a pressure let us say here where the pore is supposed to have just adsorbed molecules, but not pore filling by capillary condensation. So, naturally these liquid will start evaporating at this I mean. So, it is like we had gone there was a condensation and then we are back to the evaporation because we are we increase this is at a higher pressure these are lower pressure. So, lower pressure means are coming down here.

So, there would be evaporation of molecules out from this end of the pore ok. And it for evaporation once again it needs a latent heat, because it is the liquid phase and from liquid to vapor you have to provide latent heat we all know water to boil water we will provide the heat. And that heat is that amount of heat required is m v h f g again and that is supplied by this lambda A delta T by L.

So, now this heat is again provided here and the evaporation takes place. So, if the molecules they choose to flow through path A this would be the mechanism that it is first it is. So, the process is known as condensation vaporization, so; that means, it has to condense fast and then it has to then the heat it has to provide the heat. So, that will travel to the other side and from this side continuously it will leave. So, from this side it will be accumulating. So, leave this pore will be filled with the liquid from this side you are providing the liquid and from this side continuously it is evaporating.

So, this method of condensation vaporization by this method here transport mechanism develops. So, now, if you give them a choice that; now if you give them give the molecules a choice it can follow path A it has to go through this mechanism or let us say a path B where it is simply Fickian diffusion minus d del c del x that that we have already talked about diffusion. So, if you look at generally the calculations and that are cited in this regard is this m v that is followed by condensation vaporization divided by m v Fickian, these two mass flow rate if you look at it is to the order of 10.

So, one can see that path A is preferred than path B. So, this is a counterintuitive because these paths or path way was larger, but still this is preferred, this is easier for molecules to travel. So, this is a method this is a process which we must make note of. So, we have already talked about this liquid island arises due to capillary condensation. We have already talked about vapor condenses at the upstream side as P by P 0 is higher on that stream side. We have already talked about this and delta T temperature difference across liquid island of length L.

So, this liquid island is of length L and the temperature difference is delta T. Now, for multi component vapor; that means, if it is if the vapor is consisting of different components which it not it is multi component means you can have a mixture; let us say we are talking about methane, ethane, propane, butane a mixture flowing through a porous medium. So, it is like there it is a gas mixture it is a vapor mixture right.

So, these are; so if I pick up a sample it has all molecules they are put together and they will travel through this porous media. So, in this case we call this a multi component vapor; that means, there are multiple components methane, ethane, propane, butane and they have different boiling point. So, at what point it will condense, at what point; so, what are the saturation vapor pressures they will be completely different.

So, now, if these molecules these mixture of molecules are placed here; these mixture of molecules are placed here and if they are supposed to travel by this condensation vaporization mechanism one will find that the lower boiling point component moves faster. Why? Because lower boiling point component; that means, it would be condensing also, boiling point means s it is a condensation temperature also.

So, that it will be condensing at a lower temperature. So, one a that is condensing at a higher temperature and one that is condensing at a lower temperature. For example, if we have methane, ethane, propane, butane we can say that the methane would be typically methane exists as a gas ok. Similarly, for ethane would be the it depends on what temperature you are holding it to. Whereas, as you are going to higher alkanes you will find that that would be mostly liquid under you know under standard conditions.

So, naturally you have the. So, one is; so which one is lower boiling component? The component that boils at a lower temperature and the component that boils at a higher temperature. So, lower boiling point component is the component that boils or that

condenses at a lower temperature. So; that means, it is lower boiling point components they move lower boiling point components move faster. Lower boiling component means that the component that is boiling at a lower temperature and this is this depends on the temp, on this depends on the see at what point is condenses other than the pressure; the pressure of the system it depends on the temperature also.

So, one, that the one that would have higher probability higher chance of forming these layer that would travel by, that would be traveling faster ok. So, that is; so in case of a lower in case of a multi component multi component vapor you will find that the lower boiling component will find it easier to condense and to vaporize easily. Whereas, higher boiling point components they are not; they are not condensable easily whereas, it is they are. So, this they will tend to remain in this place.

So, what essentially; that means, is if you give methane, ethane, propane, butane you will find methane or the lower boiling components these components they will travel faster. Whereas, the these components which will as such they boil at higher temperatures, so the so called higher boiling point components they will travel slowly ok, because this condensation and evaporation this process would be much easier for these components.

So, there would be; so one can see that there if when you travels through a porous medium there would be sort of a segregation some components will travel faster and some component will travel slower. So, these are some of the issues with this condensation vaporization process in a porous medium.

In fact, these condensation vaporization mechanism is also in case somebody, in case we look at the hydrocarbon production process there is a process which is known as thermal recovery which comes under enhanced oil recovery scheme. Thermal recovery or it goes under there can be steam flooding under thermal recovery you can have process known as steam flooding, there is another process known as in situ combustion.

So, in these processes whenever you increase the temperature you generate the vapor and that vapor would be a mixture of you know all the components a crude oil has. So, out of them one finds that the lower boiling components they are traveling downstream towards the production well whereas, the higher boiling components they tend to stack up. So, this is this tend to remain there.

So in fact, this is one good way to produce more cleaner components of the crude oil whereas, the heavier components are staying back. So, it is a method more of a it is a method more to fractionate the crude oil taking out the lower boiling component and leaving the high the leaving the more heavier components back in place. So, this is this these are some of the you know inventors of these capillary condensation that one must make note of. Other than these I must point out there are a couple of other mechanisms as such.

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These are see one I mean I must you know make note of these theory here, this is free volume theory which is transport of penetrate molecule through concentrated polymer solution. So, here this is also a this free volume theory it is when it comes to diffusion of molecules through polymers, polymeric membranes and similar materials. So, this is this theory has it has a good amount of; good amount of research material already accumulated on this subject free volume theory.

The theory says that movement of molecule under two simultaneous conditions. So, this movement of molecule can take place under two simultaneous conditions and these are referred here as 1 and 2. One the condition 1 is due to fluctuation in the local density a sufficiently large hole opens up next to the molecule. So, due to fluctuation in the local density a density a sufficiently large hole opens up next to the molecule, and second point is molecule has enough energy to break away from its neighbors.

So, what; that means, is there is always some fluctuation. So, suppose I have these molecules are stacked, I can think of molecules are stacked here; here like this and there is there are fluctuations and due to the fluctuations in local densities; due to the fluctuations in local densities suppose there is a large hole opens up next to the molecule. So, there is a hole opens up next to the molecule.

So, there are other molecules are located here and there, but here I can see there is a hole opening up. So, this molecule can move to this hole that is one possibility, but this can only happen the molecule which is here this molecule also has its neighbors and they are all tired up. These molecules should have enough energy to break away from its neighbors and move to this hole.

So, then we can consider a transport of a molecule. So, if this is happening on a continuous basis one can get a diffusion process or transport of penetrant molecule through a concentrated polymer solution that we mentioned here. The movement is completed only if another molecule jumps into the hole before the first molecule can return to its initial position; that means, these molecule will move to this open hole ok, but these molecule also since this molecule has enough energy.

So, there is a possibility this molecule can go back to its original position also because momentum molecule is here then this block this is again another open hole to this molecule. So, this molecule can also go back, but if this molecule is not going back instead some other molecule is occupying that position now, then we considered that truly this molecule has moved to this position and this molecule is now locked.

So, then do you consider this process to be complete and this. So, based on this idea, based on this concept theories have been developed and how what should be the transport rate of this penetrate molecule, what it would depend on? Normally, it will depend on concentration of polymer. So, what all other parameters are involved in this? So, there is a good amount of literature already developed in this area of free volume theory in connection with a transport of molecules through polymeric membranes or any polymer substrate. So, this is one thing I must point out at this time that I do not want to get into the theories here, but just for information that such type of theory is existing

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There is another concept which is known as dusty gas model that is also which combines advection and diffusion, that is also; that is also some good amount of literature has been developed. This dusty gas model is basically it is the application of kinetic theory of gases, the way this whole thing is conceptualized is that solid part of the porous media is conceptualized as large molecules, fixed in phase space.

So, if you look at kinetic theory of gases the molecules they are colliding molecules, they are exchanging they are energies molecules they are; so there are interactions between them. So, now, when it comes to putting it in a porous media, if the molecules are now placed in a porous media, so there would be solid walls right. So, tortuous path through is the molecule have to travel; so molecules have to travel. So, now, if one assumes that the solid part of porous media if this is conceptualized as large molecules fixed in space.

So, then there will be a part of the kinetic theory of gasses itself, only these are basically large molecules the solid grains that we are talking about and then these large molecules and they are fixed in space they are not moving. So, that is the only difference and now let the kinetic theory of gasses play out and overcome and based on these one can find out what would be the transport of penetrate molecule the rate will depend on what and what not. So, this is essentially dusty gas model and there has been a good amount of literature already established.

. So, these are basically the transport mechanisms that we have been we have talked about so far these are essentially all the transport mechanisms. Now, one two things you have to you have to keep in mind here I must point out; one is that these models that we have talked about so far these are basically one phase system. In down the line in later set of lectures we will be talking about two phase flow through a porous media, we have not touched upon that yet.

So, two phase flow means that I have let us say I have a pore here, let us say. So, these are this has nothing to do with dusty gas model this we will discuss, but just since we are we are trying to wrap up this list of transport mechanisms. I must point out at this time that there exists a good amount of literature, we will talk about it in much detail in later lectures, where there will be two phase flow. Two phase flow means suppose we have a pore here and then they through this pore I am here we are putting two phases; one is let us say a waiting phase and a non-waiting phase. If it is a water weight reservoir rock then we can talk about water as the waiting phase and oil as the non-waiting phase.

So, in that case we can see that the waiting phase would be occupying the space near the wall and the non-waiting phase would be mostly occupying the space near the center. So, because this is not this does not want to go close to the wall. So, because of this reason one can see that if you are injecting the waiting phase it could very well be traveling this way and going down or traveling this way and going down and leaving this phase intact. Whereas, now when you inject the in space you will find this phase will be travelling through this space only, leaving this other phase in place.

So, these are some of the; these are some of the concepts of two-phase flow that \ we will discuss. This is the that is also a so to say a transport mechanism, but they are by themselves they are a subject of their own. So, that is why we are not do we will talk about it in detail in later lectures. Another situation we have that is also another transport mechanism is when the porous media is deformable. That means, a porous medium who is porosity is changing. Suppose, I have this is the porous medium and then I have I am applying a pressure of delta P across this porous medium.

So, now because of this delta P; now suppose this whole thing is shrinking; the whole thing is shrinking let us say because of this delta P now after sometime this becomes the porous medium this as this as a shrunk this has been squeezed. So, naturally now when

we are talking about flow here, so I am having a flow. So, there is that this some flow rate is there. So, it is flowing, but at the same time this porous medium itself is getting squeezed. So, this part of the void space this part was also occupying some fluid and. So, that fluid is also coming out from the outlet.

So, this is with time these porosity is decreasing. So, you one has one is squeezing this whole set up. So, at the in that case there would be though it would be in fact, this is not a new transport mechanism as such this is again that same mass continuity you have to work with only thing is the porosity will change with time. So, that we have to look into, this is not a trans unique transport mechanism as such, but this is some application of continuity in a different way.

So, and this is this would be contributing to a different flow rate altogether. So, this is also something which we will discuss. As such I mean this is not exactly a new transport mechanism, it is the old transport mechanisms of that Darcy's law and everything, but placed in a different continuity equation. And, but; however, this two phase flow there are a lot of fundamental; fundamental physics we here we need to consider because the two phases the together when you place them in a pore they behave in a different way and they demand as I said lectures sessions on their own when it comes to flow through porous media.

So, that is all I have and so here I am trying to here, I am going to wrap up the transport mechanisms module and from next lecture we will start talking about the flow equations that particularly the viscous part once again. Because this is when it comes to macro porous medium this viscous part is most important. So, at this time I am closing this lecture on transport mechanism from the next lecture we will talk about the viscous part of the flow equations in a more in a better detail. So, that is all I have as far as this lecture is concerned.

Thank you.