Flow through Porous Media
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Lecture – 16
Transport Mechanisms (Combined Mode)

I welcome you to this lecture on flow through porous media. What we were discussing before this transport mechanisms. What we said that initially we studied Darcy's law and found the characteristics of permeability and porosity for these porous medium and then we said viscous flow may not be the only way transport can take place, one can have the other transport mechanisms operating there. For example, diffusion, we said that molecules because of their own Brownian motion they will travel from higher concentration to lower concentration and that can lead to some kind of movement of molecules from one end of the porous medium to the other.

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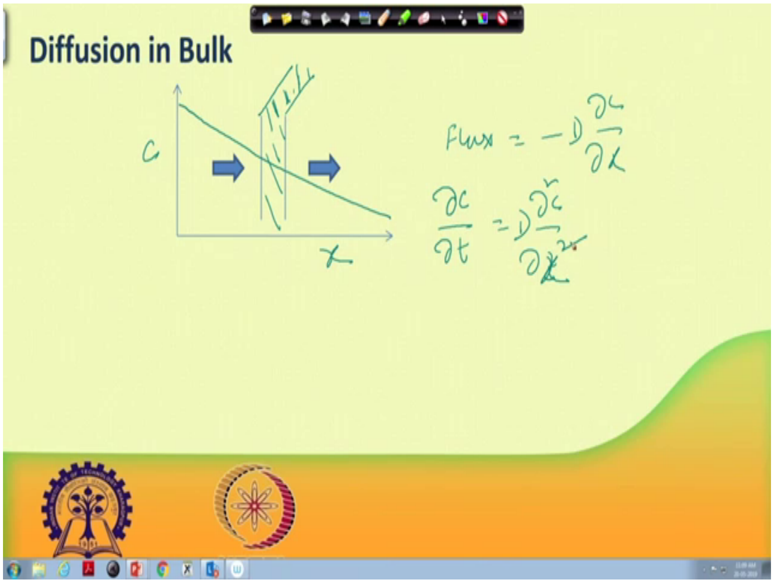

Diffusion in Bulk

$$\text{Flux} = -D\frac{\partial c}{\partial x}$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

So, now we were in the last class we discussed about these essentials of these diffusion process. So, when it comes to diffusion, we have been found that the flow can or the movement the molecule can take place from higher concentration to lower concentration. So, and this can be characterized or this can be theorized using so, called Fick's first law and Fick's second law what we found is the flux, that can be written as the flux is equal to minus D del c del x if x is in this direction and c is the concentration and also what we did in the last class is that we have considered accumulation. In this differential element, how much is the change in concentration happening, because of flow in minus flow out and from there one can arrive at Fick's second law which is given by this equation.

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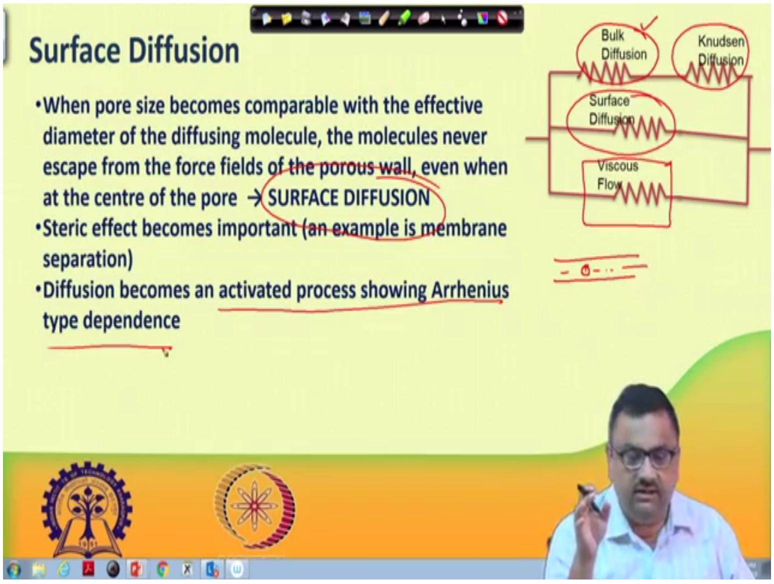

Surface Diffusion

- When pore size becomes comparable with the effective diameter of the diffusing molecule, the molecules never escape from the force fields of the porous wall, even when at the centre of the pore → SURFACE DIFFUSION
- Steric effect becomes important (an example is membrane separation)
- Diffusion becomes an activated process showing Arrhenius type dependence

So, now these are the things we had studied in the last class what we are going to do next is we are going to apply this to the surface diffusion. What we mentioned there is that there could be various transport mechanisms by which the movement can take place one is so called Bulk diffusion, another is so called Knudsen diffusion, another is surface diffusion and of course, the viscous flow which we followed by Darcy's law.

So, now if the; so, we have talked about bulk diffusion and we said that Fick's first law and Fick's second law they are applicable for bulk diffusion. The wall of the pore wall does not come into play there, simply the molecules they will move because of a concentration gradient from higher concentration to lower concentration. Now, when pore size becomes comparable with the effective diameter of diffusing molecules. This we mentioned that if the pore size is this much and the molecule is this much though molecule is at the center line of the pore, but still for this molecule is under the influence of the wall.

So, then the diffusion that takes place through this pore that is not necessarily bulk diffusion rather the wall effect comes into play there. So, that is why it is articulated here as follows when pore size becomes comparable with the effective diameter of the diffusing molecule, the molecules never escape from the force fields of porous wall even when at the center of the pore. So, this is referred as surface diffusion.

So, this surface diffusion here couple of things one needs to remember that when surface diffusion happens this is slightly different from bulk diffusion, because bulk diffusion molecules are free to move. So, it has it is own intrinsic diffusivity which controls the movement of the molecule.

So, here in this case steric effect becomes important and the second thing is diffusion becomes an activated process showing Arrhenius type dependence. This Arrhenius type dependence we have seen for reaction rate constant. Reaction rate constant we generally we say reaction rate they have this Arrhenius type dependence on temperature etcetera. So, here this diffusion; this surface diffusion it is slightly different from bulk diffusion in the sense that it has it becomes an activated process. So, these are; so, this is what is surface diffusion in this case.

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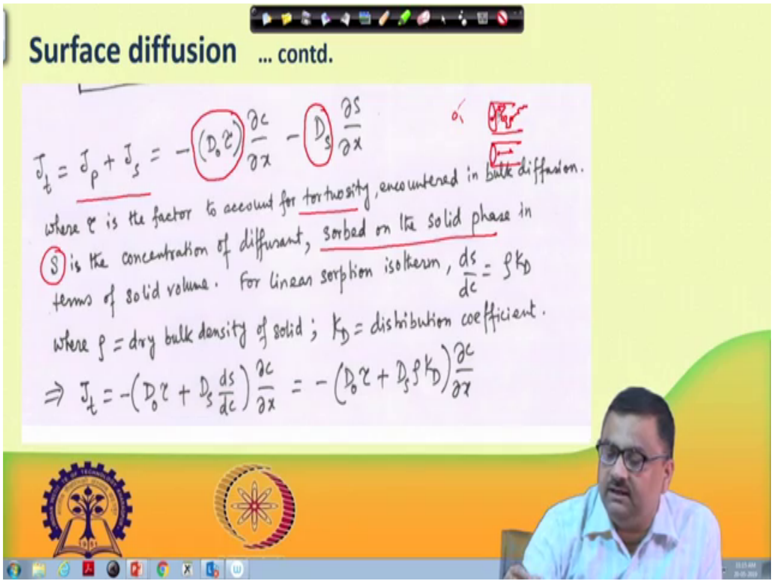

Surface diffusion ... contd.

$$J_t = \underline{J_p + J_s} = -(D_0 \tau)\frac{\partial c}{\partial x} - D_s \frac{\partial s}{\partial x}$$

where τ is the factor to account for tortuosity, encountered in bulk diffusion.

s is the concentration of diffusant, sorbed on the solid phase in terms of solid volume. For linear sorption isotherm, $\frac{ds}{dc} = \rho K_D$

where ρ = dry bulk density of solid ; K_D = distribution coefficient.

$$\Rightarrow J_t = -\left(D_0 \tau + D_s \frac{ds}{dc}\right)\frac{\partial c}{\partial x} = -\left(D_0 \tau + D_s \rho K_D\right)\frac{\partial c}{\partial x}$$

Now, if we want to put some theory behind the surface diffusion; the surface diffusion in this case or the surface diffusion will always be occurring alongside bulk diffusion. There would be some diffusion which is happening through the center of the pore and some diffusion which is under the influence of the pore wall. So, total flux in this case is given by J p plus J s one is surface and another is pore diffusion.

Now, here you can see we have given two diffusivities one is surface diffusivity, another is D naught into tau. This is the diffusivity; see tau is the factor to account for tortuosity because in case of bulk diffusion molecule is free to move. Inside a pore when it travels suppose, I think of a pore through which a porous media through which this molecule is traveling as against the same cross sectional area pipe through which the molecule is traveling.

So, when it comes to inside porous medium, these molecule has to travel through a zigzag path right because some parts it is already blocked. So, it has to find some other pathway. So, naturally it is length through which this molecule has to travel is becoming higher and how higher is that tortuosity is the factor that gives you an idea how much it would be the pathway would be increased. Whereas, if it is through a fly pipe without any porous medium, without any solid present there then the molecule can travel on it is own ok.

So, here it is forced to move through a pathway which is tortuous inside the porous medium. So, one has to account for these by multiplying the bulk diffusion which is applicable for in the bulk with a factor which is tortuosity factor. So, tortuosity factor would be less than one and so the diffusion in this case, the diffusion coefficient would be reduced because it is taking a tortuous path. So, this is one the diffusion so, called bulk diffusion through poor network and the second one is the surface diffusion ok.

So, surface diffusion was assigned some diffusivity let us say we call it D S, D subscript S. So, here S in this case here we are writing del c del x the concentration gradient, but here we are not writing c, here we write s; s is the concentration of diffusant, sorbed on the solid phase in terms of solid volume. So, what was concentration? Concentration is so much of mass present in the bulk divided by the volume ok. But here this volume so, here it is the concentration of diffusion sorbed on the solid phase.

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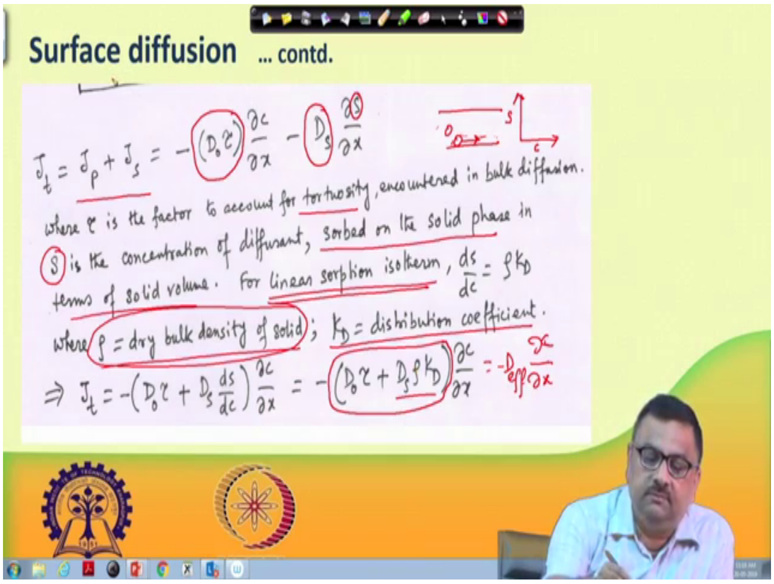

Surface diffusion ... contd.

$$J_t = J_p + J_s = -\boxed{(D_0 \tau)}\frac{\partial c}{\partial x} - \boxed{D_s}\frac{\partial \boxed{s}}{\partial x}$$

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$$\Rightarrow J_t = -\left(D_0 \tau + D_s \frac{ds}{dc}\right)\frac{\partial c}{\partial x} = -\boxed{\left(D_0 \tau + D_s \rho K_D\right)}\frac{\partial c}{\partial x} = -D_{eff}\frac{\partial c}{\partial x}$$

So this diffusion, the diffusion that is taking place; the diffusion that is taking place because of this method known as surface diffusion. So, here we have if this is the pathway. So, molecules they are getting sorbed here on the surface and diffusing. So, what we need to know is how; what is the concentration of these sorbed molecules per with in terms of solid volume. So, the concentration means some weight divided by volume.

So, in this case this S is concentration of diffusion sorbed on the solid surface divided by the solid volume in which it is adsorbed in which it is sorbed. So, you can see this definition of s; s is different from c, c is bulk concentration. So, now, for linear sorption isotherm; if one assumes linear sorption isotherm; that means, linear sorption means that if you plot the amount adsorbed versus concentration in the bulk.

So, if you increase the concentration here; if you increase the bulk concentration of molecules automatically this s; the sorbed the concentration that the concentration of molecules that absorb per unit solid volume where it is sorbed. So, that also increases if these molecule number of molecules decreases. So, here also it decreases. So, there exist some kind of an equilibrium there. So, you are talking about linear sorption isotherm which says that ds dc, if you increase the concentration bulk concentration c then automatically some the sorbed concentration also increases.

So, that ds dc is given by rho into kD, where k D is the distribution co-efficient. Distribution co-efficient means how much is going into the sorbed phase, against how much is remaining in the bulk phase and rho is the dry bulk density of solid ok. Basically this two ratio of the concentration is the distribution coefficient that is our distribution co-efficient is defined how if you are talking about two phases how much this; what is the concentration in one phase against the concentration in the other phase. But you have to multiply this by the dry bulk density of solid.

Because in one case you are working with bulk phase another in case it is the solid phase. So, one has to multiply this rho. So, naturally you one can write this in this case the total flux as minus D naught tau, tau is the tortuosity coming from the bulk diffusion. And then D S now instead of del s del x they have written it as ds dc del c del x net result is the same, and then it is instead of ds dc it is replaced by D S rho k D.

So, instead of ds dc you are writing the rho k D replaced this ds dc. So, these becomes the expression for flux. So, if you write the expression for flux this way then these becomes the effective diffusivity right because you need basically a minus effective diffusivity del c del x. So, these becomes the effective diffusivity when surface diffusion is present. This quantity this one within bracket is the effective diffusivity when surface diffusion is present.

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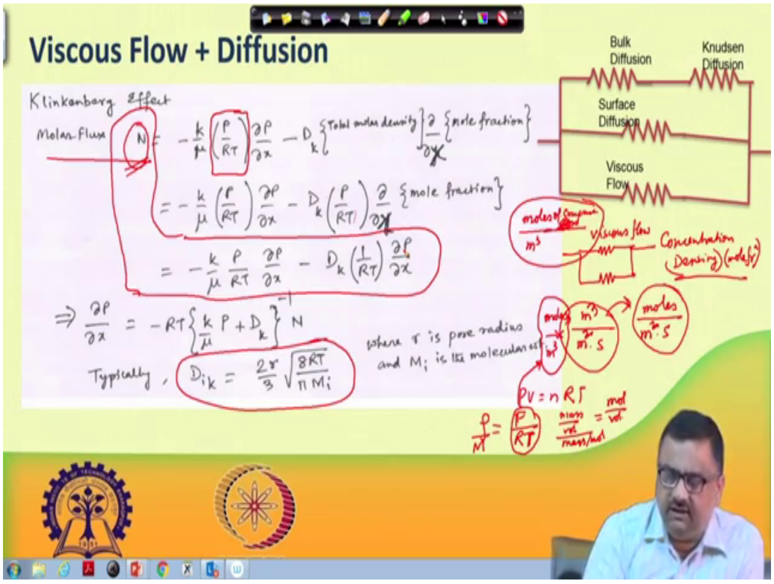

Viscous Flow + Diffusion

Klinkenberg Effect

Molar Flux $N = -\frac{k}{\mu}\left(\frac{P}{RT}\right)\frac{\partial P}{\partial x} - D_k\{\text{Total molar density}\}\frac{\partial}{\partial x}\{\text{mole fraction}\}$

$= -\frac{k}{\mu}\left(\frac{P}{RT}\right)\frac{\partial P}{\partial x} - D_k\left(\frac{P}{RT}\right)\frac{\partial}{\partial x}\{\text{mole fraction}\}$

$= -\frac{k}{\mu}\frac{P}{RT}\frac{\partial P}{\partial x} - D_k\left(\frac{1}{RT}\right)\frac{\partial P}{\partial x}$

$\Rightarrow \frac{\partial P}{\partial x} = -RT\left\{\frac{k}{\mu}P + D_k\right\}^{-1} N$

Typically, $D_{ik} = \frac{2r}{3}\sqrt{\frac{8RT}{\pi M_i}}$

where r is pore radius and M_i is the molecular wt.

$PV = nRT$

$\frac{\rho}{M} = \frac{P}{RT}$

$\frac{\text{mass}/\text{vol}}{\text{mass}/\text{mol}} = \frac{\text{mol}}{\text{vol}}$

So, now with this background let us see we are looking at another combination now, the combination is something like this. Suppose I have a situation, where surface diffusion is not important ok we have two types of flows happening simultaneously in a porous medium. This is a situation when the radius of the pore; diameter of the pore the characteristic dimension of the pore that is small with reference to the mean free path that lambda of the molecule. So, it will happen when we are working with a low smaller pore size porous medium and the fluid that is flowing is likely to be gas where the lambda is more.

So, generally when this lambda and the pore diameter D lambda is the mean free path that length there and D is the diameter of the pore. When these two are comparable then we assume that we have to consider a Knudsen number we have to consider the Knudsen flow and. In fact, there is something called lambda by D is called Knudsen number and there are some threshold numbers available when these Knudsen one has to consider this Knudsen diffusion.

So, when it comes to these Knudsen diffusion; generally this knudsen diffusion also is given as one can write these Knudsen diffusion as minus D del c del x. And these Knudsen diffusivity D for a species i typically, this is the equation that is followed for Knudsen diffusivity where r is the pore radius and M i is the molecular weight, R is universal gas constant T is absolute temperature. So, all other parameters are known. Typically this is given as the diffuse Knudsen diffusivity of a particular species.

Now, suppose we have a case where we are having two types of flows happening simultaneously; that means, on one hand you have viscous flow and on the other hand you have these Knudsen diffusion. So, you have a situation where this is what is governing. So, in that case the molar flux N; molar flux N would be written as minus k by mu del p del x. Now mind it what was minus k by mu del p del x that is the volumetric flux or so called superficial velocity as we used in Darcy’s law.

So, minus k by mu del p del x is the volumetric flux; volumetric flux means so many meter cube per meter square second right, that is what the volumetric flux is. Now this volumetric flux has to be if I talking about molar flux. What is molar flux? Moles per meter square second. So, how are we converting this meter cube per meter square second to moles per meter square second. If we want to convert this we have to multiply this meter cube by meter square second with something called moles per meter cube. Moles per meter cube then only we will have meter cube and meter cube they will cancel out and then we will have moles per meter square second.

So, now moles per meter cube is what, moles per meter cube is you remember in case of ideal gas law when we write P V is equal to n R T at that time we have written the density is given by PM by RT that is our standard physical chemistry formula, rho is the density. P by RT, P is the pressure, T is the temperature in absolute scale and R is universal gas constant and M is the molecular weight ok. So, this is this density is given in mass per volume.

So, then this if we divide this by M so, if I write this rho by M then we will have this M will go out. So, then what would be the unit in this case? The unit would be in that case mass then it would be we are dividing it by molecular weight. What is molecular weight? Mass per mole so; that means, we are dividing it mass per volume, we are dividing it by mass per mole. So, essentially this is what mole per volume. So, that is why if we this P by RT is basically moles per volume that is moles per meter cube.

So, essentially what we need to do is we have to multiply the volumetric flux which was the this our superficial velocity. We have to multiply this by P by RT then only we can get moles per meter square second which is basically N. So, since we are writing it as molar flux instead of volumetric flux we have to multiply by this P by RT term; of course, the tacitly here we assume it is an ideal gas. And then we have so, this is the viscous flow part. So, one arm is viscous flow and parallelly we have another one another flow another mechanism is operational which is minus D del c del x which is this D is the Knudsen diffusivity and then you have del c del x.

So, instead of that we can write moles per meter cube and del del x of the mole fraction. Basically, it is like these the concentration; concentration can be written as the density multiplied by the mole fraction right. So, that is how the Knudsen diffusion is defined here. So, in this case you have here now if you expand this instead of total molar density you were writing it as P by RT ok.

So, this is the total molar density; total molar density means so many so what is exactly happening here. Concentration we are writing a total molar density means moles per meter cube and mole fraction means, if you have two components present. So, what is the fraction of one of the component; so, when you multiply it by mole fraction. So, it gives me the mole when you multiply after you multiply this by mole fraction this give me moles of that particular component divided by meter cube. So, these becomes the concentration in this case.

So, that is how, then this is why the minus D del c del x is the split into minus D total molar density into mole fraction del x of this. This total molar density is taken out as P by RT outside and del del x of mole fraction one is continuing here. So, in this case now if somebody is going at giving it back to this pressure term here, when this pressure goes inside this P by RT you leave this 1 by RT as it is outside and P when it is multiplied by mole fraction that gives the corresponding partial pressure of that particular component.

So, P into mole fraction gives me the partial pressure so, this is now the del p del x in this case. So, minus D P by RT del del x of this; so, this becomes a governing equation for the molar flux ok. This is how this is how the N is defined it. So, in this case now one can take out these del p del x outside; one can take out these del p del x outside and then it becomes minus. See if you take del p del x out then this thing becomes N divided by this whole thing right.

So, del p del x you are taking common and then leaving this del p del x on one side the other side will have N divided by this. So, you can break it up and you can write it in terms of this expression.

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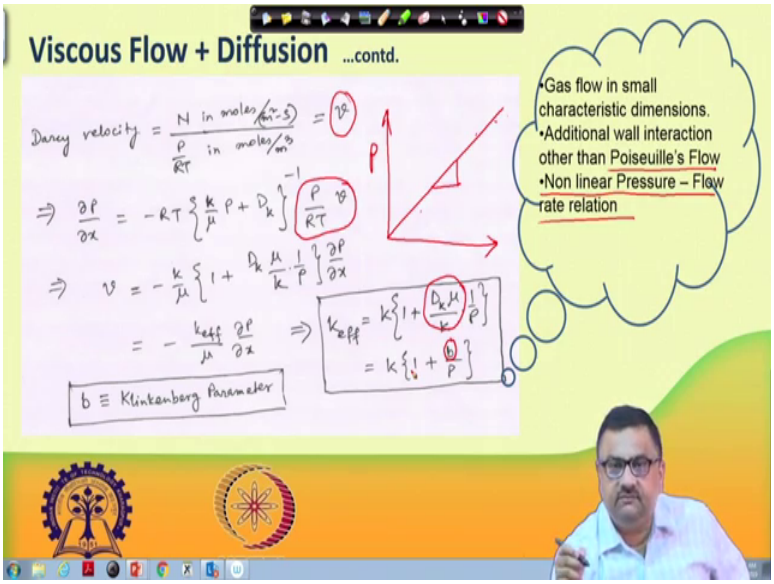

Viscous Flow + Diffusion ...contd.

$$\text{Darcy velocity} = \frac{N \text{ in moles}/(m^2\text{-s})}{\frac{P}{RT} \text{ in moles}/m^3} = v$$

$$\Rightarrow \frac{\partial P}{\partial x} = -RT\left\{\frac{k}{\mu}P + D_k\right\}^{-1}\frac{P}{RT}v$$

$$\Rightarrow v = -\frac{k}{\mu}\left\{1 + D_k\frac{\mu}{k}\cdot\frac{1}{P}\right\}\frac{\partial P}{\partial x}$$

$$= -\frac{k_{eff}}{\mu}\frac{\partial P}{\partial x} \Rightarrow \boxed{k_{eff} = k\left\{1 + \frac{D_k\mu}{k}\frac{1}{P}\right\} = k\left\{1 + \frac{b}{P}\right\}}$$

$$\boxed{b \equiv \text{Klinkenberg Parameter}}$$

- Gas flow in small characteristic dimensions.
- Additional wall interaction other than Poiseuille's Flow
- Non linear Pressure – Flow rate relation

Now, the Darcy velocity is written as N in moles divided by P by RT in moles per meter cube, we have already any moles per meter square second. So, molar flux divided by molar density. So, that gives me the superficial velocity this we were already discussed. So, in that case one can write instead of N the one that we had this expression just now we had this expression for N here.

So, instead of this N here we can write it in terms of superficial velocity and so, this is that superficial velocity. So, instead of N we are writing it as v into P by RT. So, this instead of N we are writing this here and then we write v as then we take P P by RT to the other side and these becomes the expression for the superficial velocity and essentially this. So, it becomes minus 1 by mu into this quantity del p del x and on the other hand we know that superficial velocity is given by minus k effective by mu del p del x.

So, essentially the effective permeability becomes equal to k into what we have here in this second bracket. So, we have written it here as k effective is equal to k into 1 plus D k mu by k into 1 by p. So, this becomes the k effective or in other words we can write this as k into 1 plus. Now this whole term D k mu by k we can replace this by b. So, this is this is what we it is replaced by. We had written it in terms of b. So, then this becomes k effective becomes k into 1 plus b by P. What is the implication? b is known as Klinkenberg parameter and this equation is referred as Klinkenberg equation.

So, what does it mean? We have been all the time talking about these pressure versus velocity or pressure versus flow rate and it is a straight line it should be a straight line all points that we aligned along a straight line passing through the origin etcetera. But, and what is the slope that gives me the permeability that that gives me the information permeability. Now what it this say is permeability is not constant permeability will vary with pressure. So, permeability is essentially not a constant term it varies with pressure.

So, this is the finding this is. So, permeability can vary with pressure only if you consider if you bring in these Knudsen diffusion into the if you put in Knudsen diffusion into the viscous flow term. So, now, this kind of variation one see one find in gas flow in small characteristic dimensions, gas flow in because gas flow means mean lambda is higher and so in small characteristic dimension means D is lower. So, lambda and D they become comparable. Second thing is additional wall interaction other than Poiseuille's flow and this is.

So, we have already considered Poiseuille's flow in Darcy's law, but the here we are bringing in additional wall interaction which is other than Poiseuille's flow and here we have non-linear pressure flow rate relation. So, because we are not having k as constant k becomes 1 plus b by P ok. So, this becomes; so, this one must make note of in this case.

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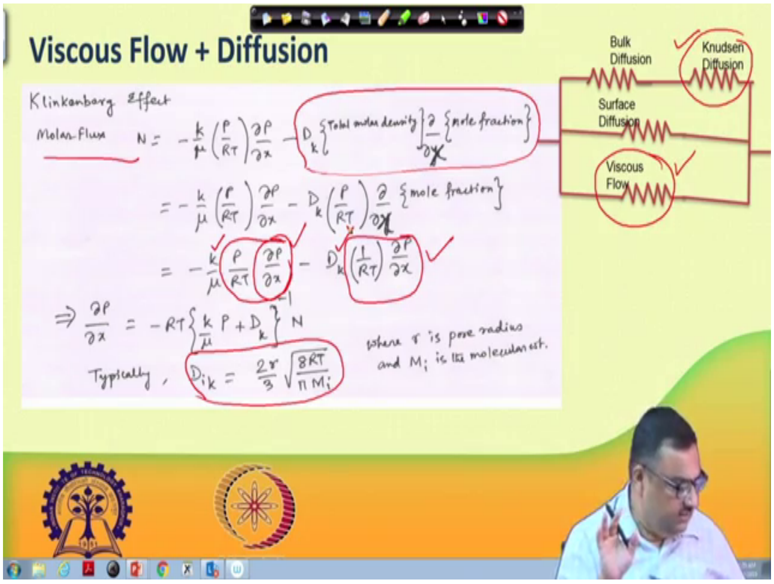

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$$\Rightarrow \frac{\partial P}{\partial x} = -RT\left\{\frac{k}{\mu}P + D_k\right\}^{-1} N$$

Typically, $D_{ik} = \frac{2r}{3}\sqrt{\frac{8RT}{\pi M_i}}$

where r is pore radius and M_i is the molecular wt.

I must point out here is that we have essentially let me quickly revisit what we have done here. We have assumed here in this case the viscous flow yes and Knudsen diffusion yes and we have considered them in parallel.

We have taken their that the total molar flux as sum of the viscous the Poiseuille's flux that is arising from Poiseuille's flow and the flux that is arising for because of Knudsen diffusion ok. So, Knudsen diffusion it depends on some kind; it depends on the Knudsen diffusivity of course, and Knudsen diffusivity is given by this term. And there has to be a gradient and that gradient essentially if you see at the end of the day what we put as gradient is 1 by RT del P del x that began the gradient.

So, it is basically here also we have a gradient, here also we have a gradient here because of molecules they have a concentration and because you have this side you have higher pressure that side you have lower. So, automatically there would be a concentration gradient of molecules and that is driving the flow. So, you have these two gradients being present here in this case here or rather here the in this case the gradient is this and here in this case this and here outside you have k by mu term and here you have the Knudsen diffusivity term.

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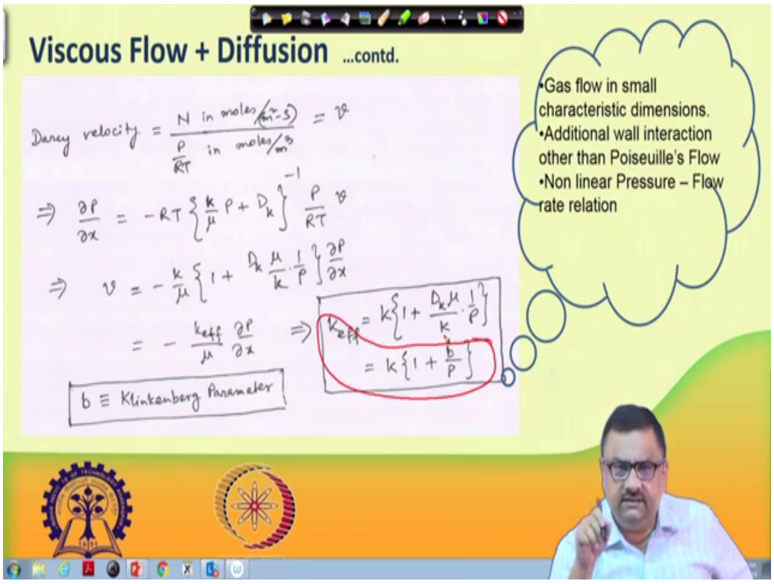

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$$= -\frac{k_{eff}}{\mu}\frac{\partial P}{\partial x} \Rightarrow \boxed{\begin{aligned} k_{eff} &= k\left\{1 + \frac{D_k \mu}{k}\cdot\frac{1}{P}\right\} \\ &= k\left\{1 + \frac{b}{P}\right\}\end{aligned}}$$

$$\boxed{b \equiv \text{Klinkenberg Parameter}}$$

- Gas flow in small characteristic dimensions.
- Additional wall interaction other than Poiseuille's Flow
- Non linear Pressure – Flow rate relation

So, by combining these two fluxes what we end up doing is we are getting this final form which is known as Klinkenberg equation. And this leads to a non-linear permeability and this type of flow becomes important when somebody is for example, in reservoir flow when one is working with shell and one we were working with a gas flow. So, then one needs to consider these permeability non-linear permeability or permeability which depends on pressure. So, this is the origin of this Klinkenberg equation.

I am going to stop here as soon as this particular lecture is concerned, I will continue working on further on these transport other what other transport mechanisms that could be important in this context that I will continue with this we in the next session thank you.

Thank you very much.