Chemical Reaction Engineering 2 (Heterogeneous Reactors)
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Lecture 05
Shrinking Core Model Continued

Ya we have been talking about kinetic models for non-catalytic reactions and all the reactions we have also divided into over 6 categories A, B, C, D, E, F.

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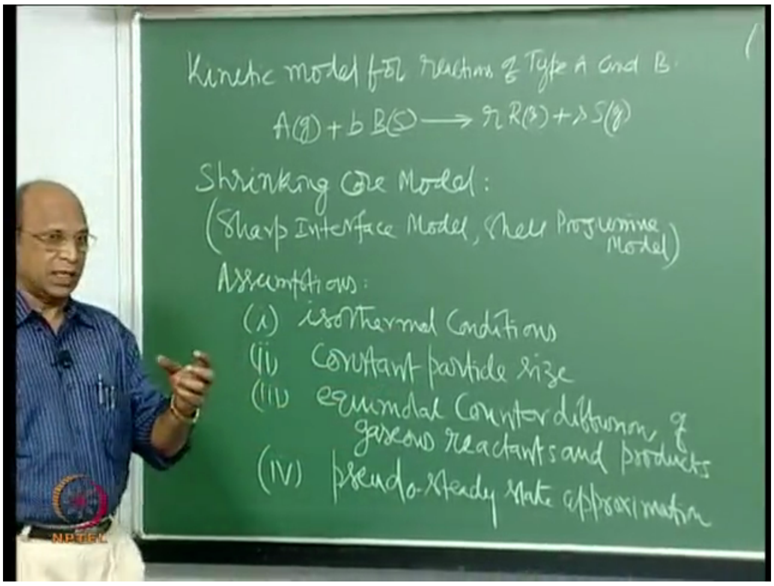

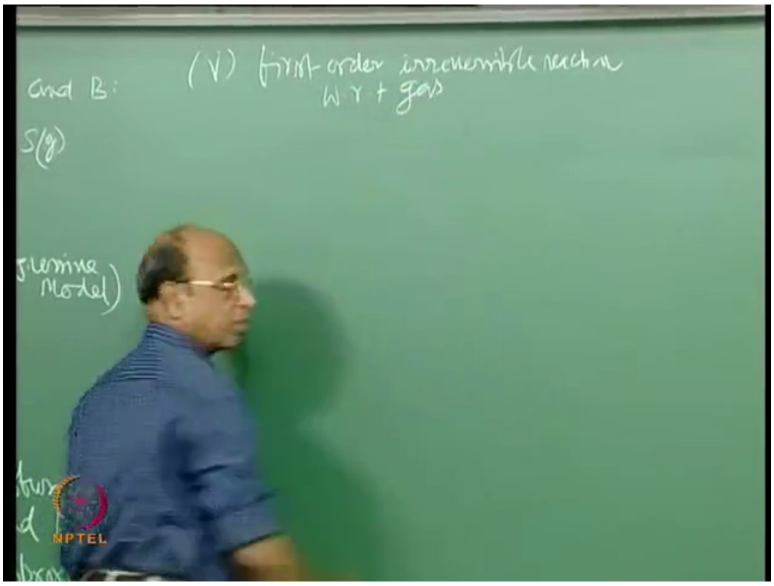

Now we will discuss kinetic models for reactions of type A and B that we will let here kinetic models for reactions of type A and B, I think I have to tell you few words for connection may be you can take this one as notes, okay. Ya type A reactions are type A reactions are the most common and are exemplified and are exemplified by reduction, comma oxidation and roasting of ores the general stoichiometric scheme is A g plus b B s solid going to r R g plus s S g that is the general stoichiometric scheme and you have to notice this one very carefully because A does not have a coefficient so if it has the stoichiometric coefficient you have to divided with that then make it as 1 and automatically b r S will be not exactly their own stoichiometry but divided by a small a this is s and this is, good.

Ya please continue this reaction scheme belongs to type A as we know we have discussed that already this reaction scheme belongs to type A as we know but can easily be applied to type B, type B in which no gaseous product is involved in the bracket s equal to 0 full stop there. Basically two types of models have been considered two types of models have been considered one which the solid is non-porous and one in which it is porous since full stop there since most of the pores are non-porous shrinking core model is widely used shrinking core model is widely used for developing the kinetic model for developing the kinetic model.

Now we are talking about shrinking core model you can also write this. This model can also be called as sharp interface model (let me also write that) interface model and also shell progressive model shell progressive model if you suddenly some other books other than Levenspiel or some other books then you will find sometime sharp interface model and shell progressive model you should not think that it is a different model.

You know broadly in chemical reaction engineering the way the subject is explained can be divided into two groups one is Levenspiel group, the other one is Schmidt group, right. So all Levenspiel group people will follow his notation that is why you know A plus B going to R plus S in many other books like Schmidt and Carbary they write A plus B going to C plus D, okay and ofcourse you would know or definitely you should have studied about the epsilon as the volume of increasing factor, okay ya that epsilon was introduced by Levenspiel whereas if you see Schmidt group like Carbary and other books it is not there.

So they write every time for gas phase reactions the number of moles and then find out mole fraction and find out partial pressure and then try to develop the kinetic model this difference also you should know because there are two approaches, epsilon is blind approach like our coaching centre you do not have to explain anything calculate epsilon, substitute there and then integrate if it is a design expression, okay.

Otherwise the other group every time you have to write the equation how may moles of A converted, how many moles of B converted the others form and then total moles, mole fraction, total pressure you will get partial pressure that you introduce and then that also can be used at the end both will be same in my reactor theory course I have I normally tell these two approaches and also tell that both will give exactly the same result.

But Levenspiel approach is direct substitution without thinking much, right but whereas there every time you have to use your brain but normally we do not like to use our brain every time that is the reason why that coaching, epsilon sticking some all that is easy for us, okay. So these are the other names for the shrinking core model. Then as you know definitely this is used for non-porous, right and what is our general procedure? Our general procedure is first to identify a single particle and then draw the profiles and after that write the equations for each profile mass transfer steps and reaction steps equate all of them and then finally you will get a rate which is called the global rate of reaction because every intermediate step where you cannot measure the concentrations are eliminated and finally it is expressed in terms of only measurable quantities.

So many times I am repeating this you know you should remember if someone asks what is global rate of reaction? What are the other names for this? Overall rate, observed rate, okay sorry ya measurable rate all this different books use different things but that is what is you know automatically comes for heterogeneous systems, for homogeneous systems does not matter both are same, okay good.

So now this model before drawing before drawing the figure picture we also should have some assumptions, right like any model. So the first assumption what we have is assumption 1 ya we have isothermal conditions, second one easy to understand constant particle size and third assumption you know equimolar ya equimolar counter diffusion of gaseous reactants and products and fourth one pseudo study steady approximation pseudo steady state approximation.

And the fifth one to make our mathematics simpler is first order reaction first order okay not only first order irreversible reaction irreversible reaction with respect to gas, okay good so these are the assumptions. And ofcourse this is easily understandable constant particle size you know during the reaction I told you one example where calcium oxide when it is reacting with (calcium) sorry SO 2 in the presence of oxygen, calcium sulphate where the particle slightly grows bigger because the molar volume.

So that is the reason why in many reactions this increase in particle size many time happens but right now it is mathematically slightly complicated that is why we are not considering that particular aspect but we assume that we have constant particle size, right then this equimolar counter diffusion because we have the gas phase going into the pores for the reaction to take place on the surface of the core, right and the products have to come out.

So if you take multicomponent diffusion again mathematically it is more complicated so to start with we can assume that equimolar counter diffusion for the products and gas so that assumption is clear. Pseudo steady state assumption is very beautiful assumption for gas solid reactions and I will explain that when actually we are deriving an equation for one of the steps that I will explain later.

And ofcourse first order with respect to gas irreversible first order and again to simplify the mathematics, okay if I do not have that again mathematics will be really complicated and we lose track of the physics what is happening in the problem that is why to start with we always start with simple assumptions so that you will understand what is going on ya Shekhar.

Student is Questioning: Can we say equimolar diffusions because A has only one mole and the product S has S moles. So then how can we say equimolar?

Ya that is why because it is not equimolar we are assuming here equimolar and then trying to do that, right if you are actually taking the actual number of moles we do not have to assume that, right. So that is why if it is one mole and then it is two moles effect may not be that much but if it is one mole that is seven moles definitely there is effect, right that comes in the form of you know your diffusion product diffusion that also I will tell you in one of the steps.

So this is the reason why to make the mathematics simple so that we will understand the physics that is the reason why we are going for these assumptions, okay otherwise in actual practise if you want to do we cannot (())(12:42). For example here I have not told implicitly one all particles are spherical for us but you can never see that kind of beautiful spherical particles accept when you are playing your marbles, okay marbles are beautiful spherical particles, other than that in chemical industry no one makes that kind of spherical particle this is ore please remember you are now digging out the ore and then you are using those particles you can never expect spherical particles but inspite of that we use the mathematical equations only in terms of spherical geometry because it is very easy for us to imagine how the symmetric diffusion is going through the this particle from all sides you know equal diffusion symmetrically. So that is why all these assumptions are to make our mathematic simple, right.

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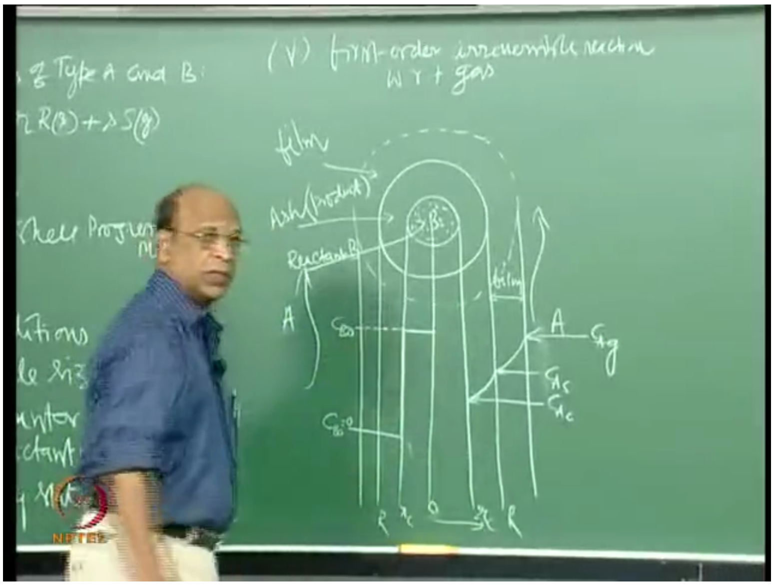

So our next step is now to plot the particle this is spherical particle and we are talking about after sometime it has already reacted so this is the actual particle and this is the product Ash layer I have been telling let me write that later ya okay this is film and this is Ash, Ash is nothing but product, okay let me also write once product, then we have here okay B reactant B and in fact what we have is here gas is moving A, A.

So now we have to plot the profiles so that is the centre, this is r c, this is capital R and this is the film so this is film again ofcourse film and here we have the centre as 0, r is increasing in this direction, I have here what is called r c, this is the core and here I have the capital R which is the size of the particle, right and this side also I will try to ya so this is r c, capital R and this is the film, good.

So anyway I do not have to ask you many times but I can simply draw this, this is C Ag and through this you may have a profile like this this is C As and now after some reaction as I told you we should have the this Ash layer or product layer must be porous, right otherwise there is no reaction if it is non-porous. So through the pores A again diffuses because this is a product which is (())(16:03) as far as reaction is concerned because it is irreversible, if it is irreversible then you have the problem again this product also will react with the the product gas will again react with the product layer and then you will have again some more reaction you know backward reaction (())(16:20) that is not there and most of the time for ore reaction that will not happen, okay so it is only irreversible reaction which is a good assumption, right.

So that is why it will not bother us then inside you have the diffusion as if it is porous particle simply reactant is diffusing. So this on this surface of this core we have C Ac because it is non-porous it cannot go inside reaction is taking place only like this and then slowly because of the reaction this core shrinks and then finally everything is converted and our aim here in in the kinetic model to find out what is the time required for 100 percent conversion of this particular particle, right.

So our kinetic model should give us that information then afterwards we will try to use that information in the actual reactor design, good ya. So this is one r c and C Ac, C As and C Ag now we have to also plot a profile for the solid this is very easy we have also discussed in the last class. So if I start with C B or C B not for example then I will have ya here it is 0 then only C B not here which is C B not ofcourse here I have to put dash dash ya this is C B not, right okay.

So with time only thing is this is becoming smaller and smaller but there is no decrease here that we have to remember, good okay. So that is all I think here if I say this one may be C B not equal to 0 somewhere so outside of this it is 0 here, here everywhere it is 0 except on this point, good. So now what are the steps we have to take to develop the model this is universal procedure for all heterogeneous systems we have to first draw this diagram I tell you this diagram is not that easy for you just to copy how you can copy easily but if you are developing on your own a new model you have to imagine what is the process that is going on, right and you have to identify what are the steps, right.

And for each step you have to write an equation then only eliminate all the intermediate concentrations that is universal procedure but the physics of this that phenomena in your mind that is more important to draw this picture as simple as possible that is why even though I am telling you many times it is not easy for you the moment I say that okay I have some other particle with two gases for example A plus B also going to A plus C and B B is the solid and I have A and another gas also C and if I ask you to draw that picture you cannot immediately draw unless you imagine the process, unless you have the clear understanding of the process, right.

So this is why most of the time in all these processes one should have the physics behind your mind that physics has gone long time back from our mind because our training (())(19:49) is always writing examinations so equations are more important for you but atleast now in the PG course and also in P.Hd level that imagination is very very important for us for anything, okay.

So the moment any process is told to you then the entire process should run in your brain as a movie and then you should be able to imagine that okay this is step 1, this is step 2 this is what happens inside and this is what happens outside all that once you have that understanding the next one to prove is mathematics you have to write and then prove that your idea is right or wrong that is what is all research about, right.

So if you are doing P.Hd the guide will give you the problem and you have to sit down that is what I was telling you know first six months if you give total thinking period for P.Hd scholars probably you will get very good quality work but ofcourse they should also use (()) (20:43) properly not for seeing DC plus plus and all that but if they are able to really think and after thinking you should be able to propose a hypothesis ya this is what is going to happen in my problem and just note down on a notebook and at the end when you are submitting just think how far you are right and if your intuition at that time and all also if your mathematics or if it is experiment if both are matching you have done wonderfully well, you became excellent research scholar or researcher later for life so that is the training actually what we are supposed to give, right but I think it is not happening in reality most of the time.

But individual students who have got that passion for research they will understand that so they will become an excellent people but most of the time education is by force unfortunately in this country or it is necessity I want this degree that is all whatever means you use you should finally get that, that is unfortunate really, okay.

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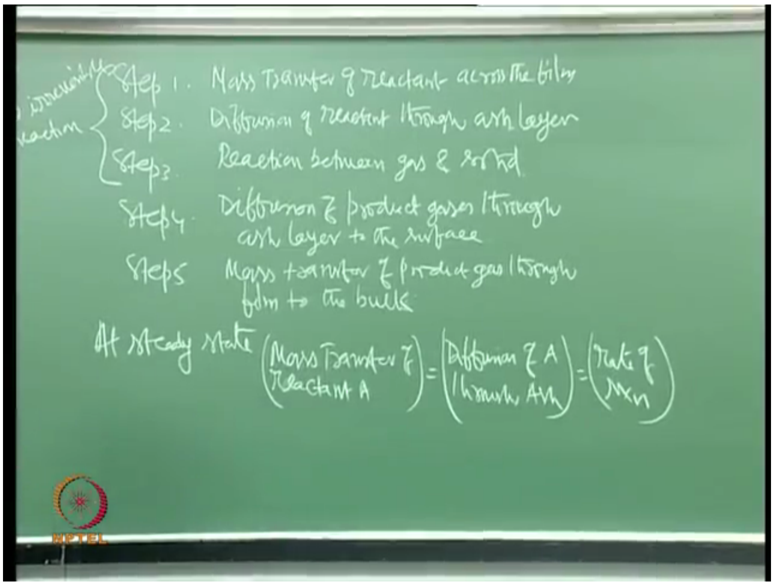

irreversible reaction

Step 1. Mass Transfer of reactant across the film

Step 2. Diffusion of reactant through ash layer

Step 3. Reaction between gas & solid

Step 4. Diffusion of product gases through ash layer to the surface

Step 5 Mass transfer of product gas through film to the bulk

At steady state $\begin{pmatrix}\text{Mass Transfer of}\\ \text{Reactant A}\end{pmatrix} = \begin{pmatrix}\text{Diffusion of A}\\ \text{through Ash}\end{pmatrix} = \begin{pmatrix}\text{Rate of}\\ \text{rxn}\end{pmatrix}$

So now let me write the steps, step 1 step 1 is mass transfer of reactant reactant through the film across the film, step 2 diffusion of reactant reactant gas only that is what I mean diffusion through Ash layer through Ash layer and step 3 reaction between gas and solid I am writing gas there but I think it can be also fluid, what Swami you were asking something? Step 3 is not adsorption everything is combined as reaction step, if it is a catalytic particle yes, okay what you are thinking is catalytic particle where molecule gets adsorbed and another molecule will come and sit side by side and then decomposition of you know surface reaction and then dissociation, then desorption all that it is for catalytic steps, this is for non-catalytic reaction even though things like adsorption first should happen and then reaction to take place with the solid, whereas in catalytic reactions the solid is not a reactant so that is why.

Ya step 4 is diffusion of diffusion of product gases through Ash through Ash layer to the surface that is the one and step 5 is mass transfer of product gas through film to the bulk to the bulk these are the 5 steps and we know very well that because it is irreversible reaction these two steps can be knocked out because they are not effecting our rate of reaction that is why simply so we have only these three steps, okay for irreversible reaction, good. Ya ofcourse if I have a type B again same model, right but only thing is there is no gaseous diffusion anyway these two steps will not be there the reason is there is no ya the product gas coming out so that is why the same model can be used, good.

So now at steady state all these three steps must be equal, right so at steady state (diffusion) mass transfer of reactant A equal to diffusion of A through Ash which is also equal to rate of reaction these three steps. Now we have to write in terms of an equation all these three, right.

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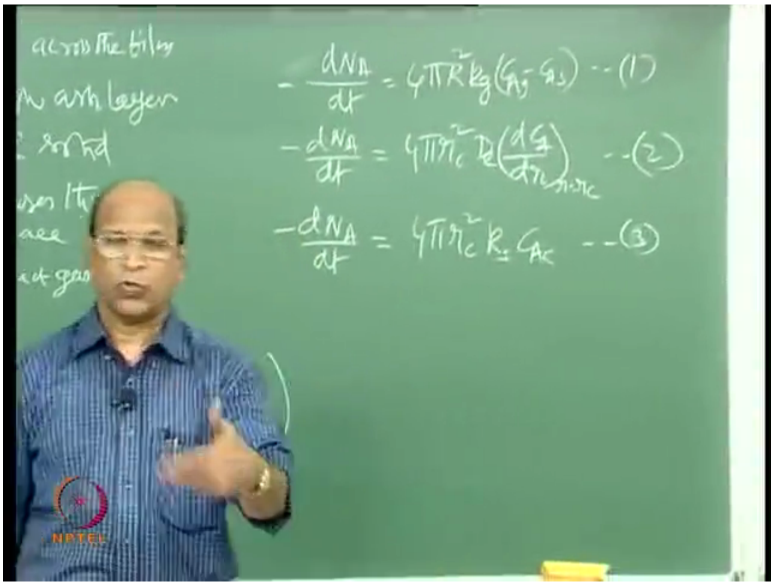

$$-\frac{dN_A}{dt} = 4\pi R^2 k_g (C_{Ag} - C_{As}) \quad \text{--(1)}$$

$$-\frac{dN_A}{dt} = 4\pi r_c^2 D_e \left(\frac{dC_A}{dr}\right)_{r=r_c} \quad \text{--(2)}$$

$$-\frac{dN_A}{dt} = 4\pi r_c^2 k_s C_{Ac} \quad \text{--(3)}$$

So the mass transfer step minus dN A by dt equal to 4 pi r square kg that is why this helps C Ag minus C As this is equation 1 ya this is also equal to minus dN A by dt second step second step is ya okay by the way what are the units of minus dN A by dt moles per time. So if I want to express that one as a flux I have to take one of those areas, okay. So now the multiplying by this area 4 pi r square so that is why it simply becomes rate rate of mass transfer that is why.

So now the other one is diffusion through the Ash layer that we can express anywhere inside you know I can express here, I can express also here, I can express anywhere but only thing what you need is a concentration profile and a derivative of that with respect to r, okay. So if I know that means it is nothing but Fick's law N A equal to you have or j i equal to minus d into dC A by dr or dC A by dz that concentration gradient I want.

So that is why we will write that equation and then try to think later how do you get that 4 pi r c square D e few sentences about D e I have to tell this is d C A by dr now there is a condition at r equal to r c otherwise I cannot take this area, if it is r equal to capital R still I can use no problem, right but this will be 4 pi r square, right okay good.

So the next one is rate of reaction equal to we have now 4 pi r c square that is where the reaction is taking place, okay and (k) k s surface reaction and C A C Ac here surface is the outer surface, okay but actual reaction is going on the core this is the core, okay I think it will be at also write here core that is the core so that is why please remember that this is where most of the time we will make the mistake even though it is simple things I say I am only trying to find out point out very very simple things because most of the students make simple mistakes and think that in the examination they have done correctly and then scold the teacher that he is not giving the marks, okay I mean this is the normal thing, okay good.

Ya these three equations what we have and what is the procedure now I have to C Ac I do not know, right and C As I do not know this contain C As and C Ag I know so C Ac C As I have to eliminate and then finally get the equation in terms of C Ag, right but ofcourse this is dN A by dt but you know this is extensive rate and intrinsic rate I have to have later this minus dN A by dt divided by 1 by 4 pi r square if I take then that becomes the intrinsic rate but based on outer surface of the particle, right.

So that is also important because in heterogeneous system most of the confusion is how do you express the rate by the way what is the rate here I think what should be the rate units here in this step chemical reaction rate units chemical reaction rate units dimensions normally what are those rate of reaction? Moles per time per I have to make intrinsic right but in this case I have already made it ya this is the rate in fact k s C Ac that is minus r A, right.

But now we have to multiply that one by area because my rate is based on unit area. So here it is not our unit weight of the particle or unit volume of the particle it is unit surface area of the particle, okay. So that is why one has to remember that and you know the moment we say that we have rate based on moles per based on meter square surface area the units of k s will be different they are no more it is first order reaction. In general the moment I say I ask you what are the units for first order rate constant what do you say? All of us will say time inverse, okay it is like L kg alpha betas you know always we remember that only, right because always first time we remember in the class only rate of reaction first order homogeneous so that is why it becomes time inverse but later in heterogeneous system it can be any you cannot, if anyone ask you what are the rate units for first order rate in a heterogeneous system you have to ask okay you tell me what is the rate based on either it is volume or weight or surface area or interfacial area, whatever that is why you have to be more careful about that.

So then here the most difficult thing is I cannot eliminate so easily this one C Ac and I do not have explicitly here what is C Ac or C As I need an equation for that this is the flux this is

Fick’s law and this D e is the diffusivity coefficient D e effective what do you mean by this effective diffusivity coefficient? It is not simple binary diffusion you calculate d Ab but this is happening d Ab is between molecules coming A coming this way, B coming this way but here this diffusion is through the pores and in that pore you also have ya (())(33:17) ya S gas coming this way and A going in the opposite direction but all this happening within the pores but these pores also having different dimensions, right pore size.

So if I have very large pores then I can say may be 100 times, 200 times the molecule size of the the gas then it is fine I have bulk diffusion I can happily consider that (())(33:44) was equivalent normal bulk diffusion but if they are very very small pores you should have heard of what are called what is called Knudsen diffusion Knudsen diffusion is when the mean free path is almost equivalent to your pore size mean (())(33:58) of the gas so then we have the Knudsen diffusion.

We have another diffusion called configuration diffusion so there are some pores where the size of the pores is almost same as the molecule size there it is like queue one mole will push one molecule will push the other molecule that will go inside, other molecule will push it is like exactly plug flow one behind the other. So all this I do not know what is the fraction, why because I cannot exactly find out the pore fraction of each and every the pores in the particle.

So all together I measure and that is called effective diffusivity there are methods how to find out effective diffusivity and this is very widely used even catalyst particles it is same even the catalyst particles you have the same problem because the pore sizes are not uniform, right ya. So that is why if you have one pore that is why Jewelite catalyst are very easy to characterize because the pores are almost uniform for for a given catalyst, whereas here when you are making the catalyst it is not that easy.

So that is why this effective diffusivity is a fitted parameter what we call that means you take the data and fit that D e value so that your experimental data and model will be fitting satisfactory, okay. So but still we call this one as Fick's Law, right (())(35:24) normally used only for gas gas most of the time or or liquid diffusing to the another liquid okay I mean inside the liquid phase that is what what we say even here effective diffusivity will come because of the various contributions from various diffusions, what you have to remember is bulk diffusion, Knudsen diffusion and configurational diffusion these three diffusion we will stop here.