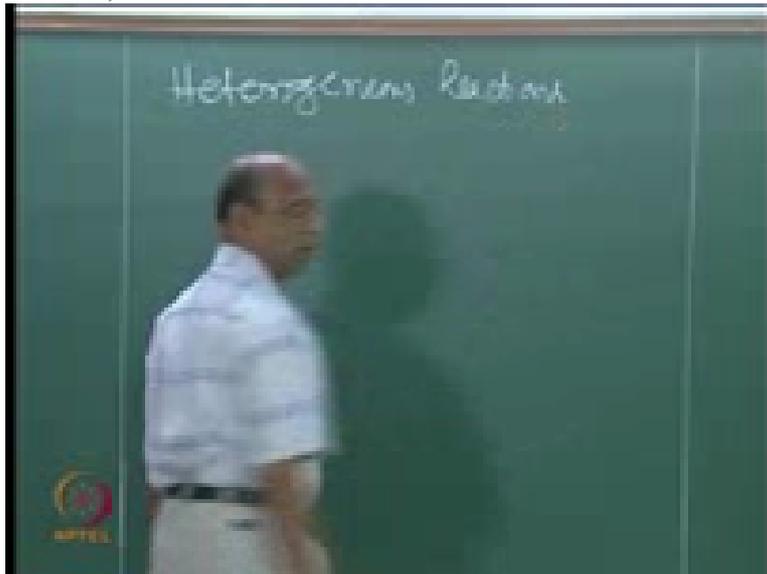


Chemical Reaction Engineering 1 (Homogeneous Reactors)
Professor R. Krishnaiah
Department of Chemical Engineering
Indian Institute of Technology Madras
Lecture No 20
Kinetics of Heterogeneous Reactions Part 2

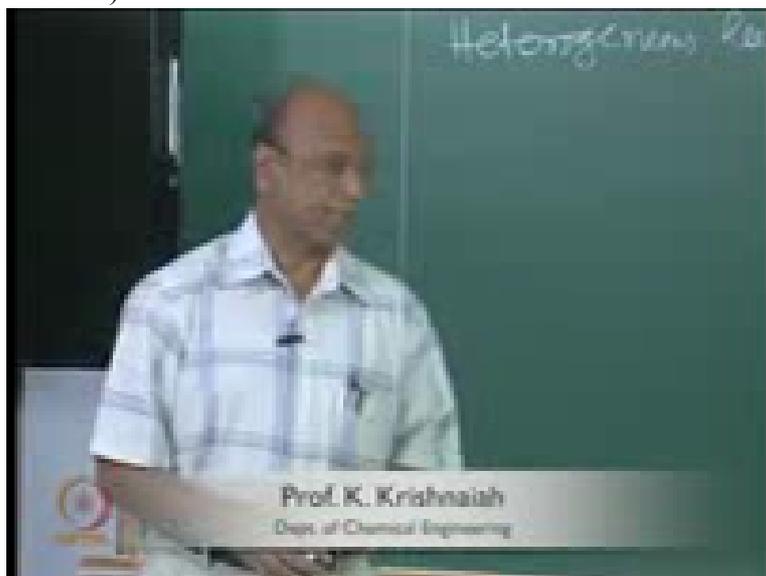
Heterogeneous reactions we have been talking.

(Refer Slide Time: 00:20)



Heterogeneous reactions yesterday we started this, and I just, as I told you, I just wanted to give 1 or 2 examples so that you will know what is the difference between heterogeneous reaction and homogeneous

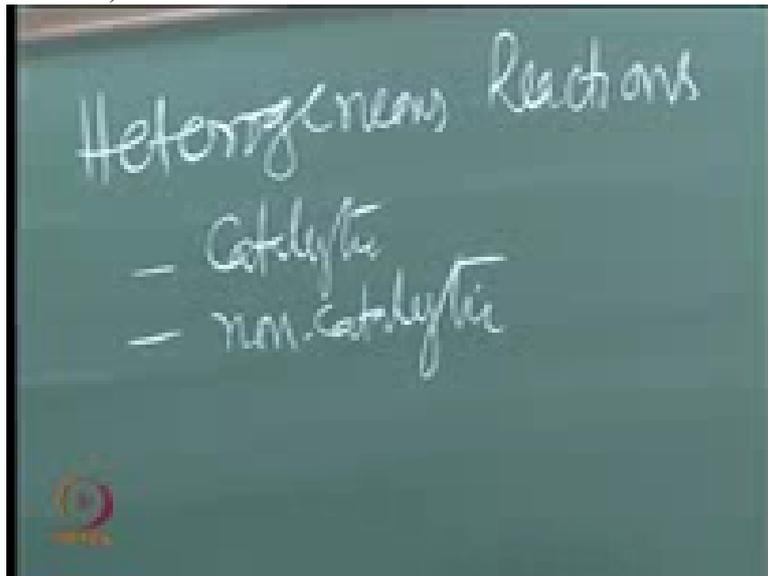
(Refer Slide Time: 00:32)



reaction and we go deeper into homogeneous reactions because that is needed for this Reactor Theory course, Ok.

So in heterogeneous reactions, yesterday we discussed about catalytic and non-catalytic, Ok. So the idea here

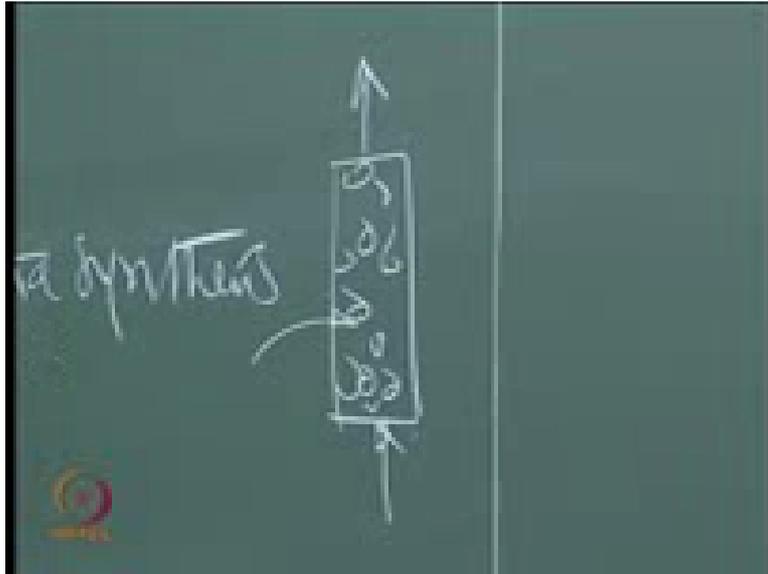
(Refer Slide Time: 00:53)



is that how do I develop a rate equation for heterogeneous reaction if it is a catalytic reaction? And also non-catalytic reaction, I mean the rate, how do you develop for non-catalytic reaction? So that is the idea.

So we have taken catalytic example as ammonia, right? Catalytic reaction ammonia synthesis. That is what is the example we have taken and this ammonia synthesis as we know already that is not a new process, that is old process. So we have taken a packed bed, Ok. So then this is coming out, this is entering; somewhere here I have taken for my

(Refer Slide Time: 01:43)



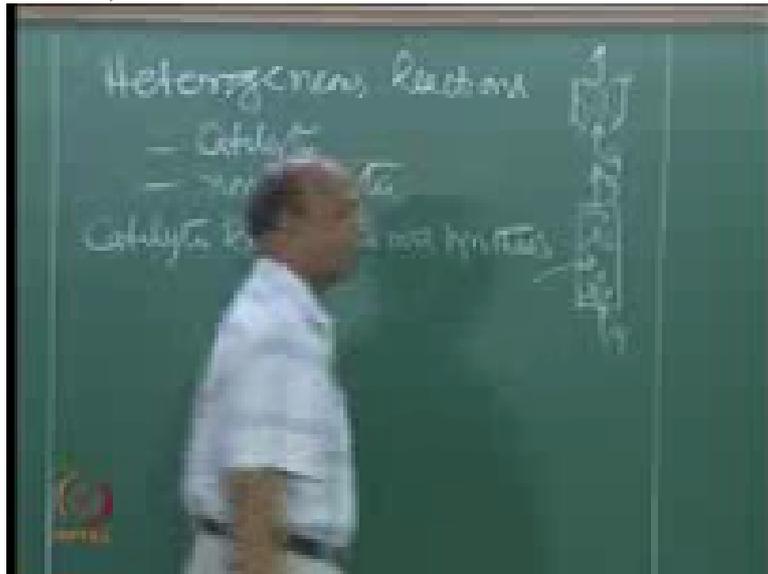
kinetic equations. Ok I have to take a single particle.

This is true. You know even if I conduct this ammonia synthesis, catalyst as iron, right, fluidized bed also I can take. In fluidized bed these particles will not be stationary. Not like pack. They will be moving. Yesterday also I have demonstrated no, how particles move. So they will be moving. So even when they are moving I can pull out one particle.

What is happening around that particle? You know this is the original system. So for all heterogeneous systems you should have that thinking of no, some thinking about the process. If it is fluidized bed, Ok, so what is happening? Particles are constant. Around that you have the flow of reactants. Ok. So then what are the steps that are required? Right. That we understand.

Fluidized bed also now we understand. Fluidized bed will be something like this where gases are entering, gas, gas, gas, liquid also can be same. So here are the particles. This is the catalyst. And then it comes out.

(Refer Slide Time: 02:51)



This is fluidized bed. So when we are making these particles float with the support of you know, either liquid or gas, you are able to follow me, no? Fluidized bed?

Because most of the chemical engineers must know what is fluidized bed, right? I think Arya; in your waste water treatment also fluidized beds are widely used, right? So I think in chemistry they may not be 100 percent knowing that, I think someone has to help them.

So you take this, for example sand. It is easy to imagine.

(Refer Slide Time: 03:25)



Sand, all of you would have seen? I think that. Do not tell me that you have never seen sand. Ok, yeah. You have seen sand no? Ok.

(Refer Slide Time: 03:32)



So sand you just take in a cylindrical column where you have a distributor plate at the bottom. Ok, now send the air, for example. Air you cannot see but we know we can feel. Right, when you put sand, starting you know,

(Refer Slide Time: 03:46)



air is touching you but you cannot see it, right, yeah. So then you are sending air or some other fluid also but air is easy for us to imagination, this air when it is going through the perforation, it will push the particles and then it also moves through the particles to go, right?

If I am using

(Refer Slide Time: 04:04)

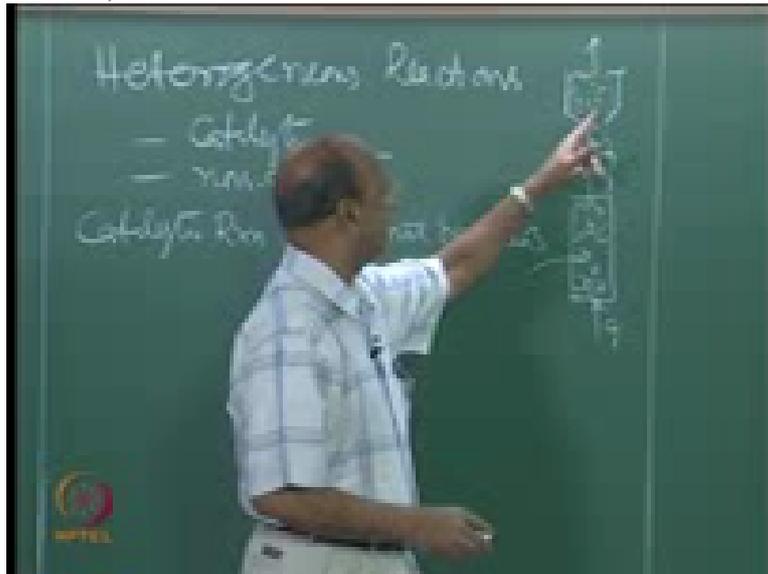


very, very small flow rates then air has just the capacity to move through the particles. And now slowly increase that velocity. I am just telling particularly for these chemistry people and those who have not been exposed to that. So slowly I am increasing that flow rate here through this. Before that you have sand just filled up in that. That is theoretically a packed bed.

Why a packed bed? That is a packed bed because particles are not moving. Then slowly introduce the air. Then at very low velocities those you know, the gas will go through the perforations and also through the particles, between the particles not through the particles, means not inside the particles. Ok, around the particles.

And we have in a packed bed the what is called voidage, porosity of the parti/particle, of the bed. So through that it goes. So you keep on increasing, you keep on increase the flow rate a little bit, little bit by little bit. So initially when it is very, very small then it will only move through the particle. But when it has sufficient velocity

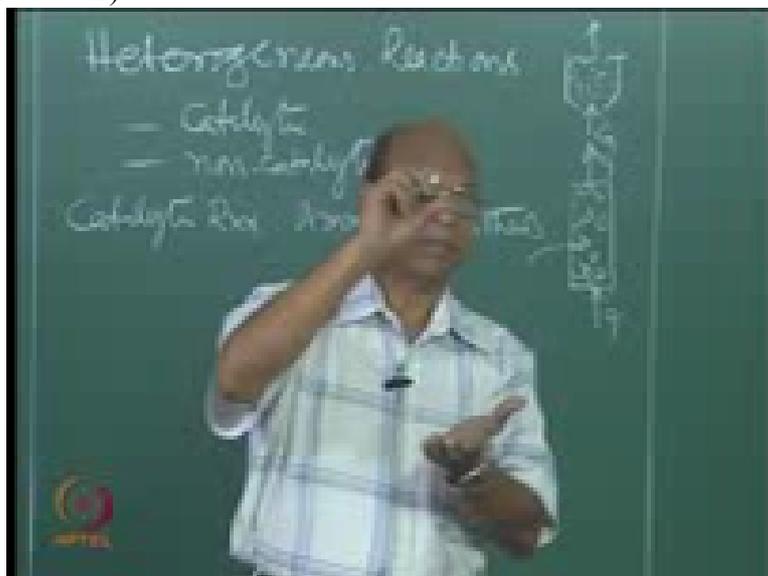
(Refer Slide Time: 05:11)



then it starts moving the particle. That is the first time. Ok.

So that means the particles will try to get adjusted on its own when the, when there is such a velocity where it is able to move the particles a little bit. You slightly increase even above that. Then the entire particles also will be floating. And when I look at one particular particle then this gas is sufficient, gas velocity is sufficient to keep that particle under suspension,

(Refer Slide Time: 05:41)



Ok.

(Refer Slide Time: 05:43)



Theoretically you can also be fluidized with you are going by motor bike very, very high speed. Correct, no?

(Refer Slide Time: 05:48)



Because what is happening is the drag force of the air which is acting on your body? Right. If you have not properly hold it and then you know legs are not firmly on the pedals then you may be fluiding. That is what I am telling. Or afterwards you may be pneumatically conveyed. That means

(Professor – student conversation starts)

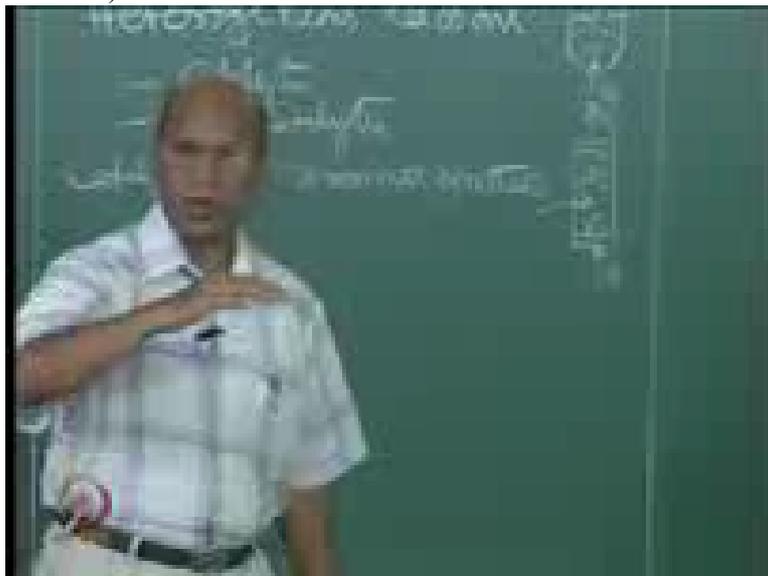
Student: (laugh)

(Refer Slide Time: 06:11)



Professor: (laugh) You will travel with the air. Ok that is also, same thing happens here. Sometimes you float

(Refer Slide Time: 06:18)



and afterwards you will be travelled.

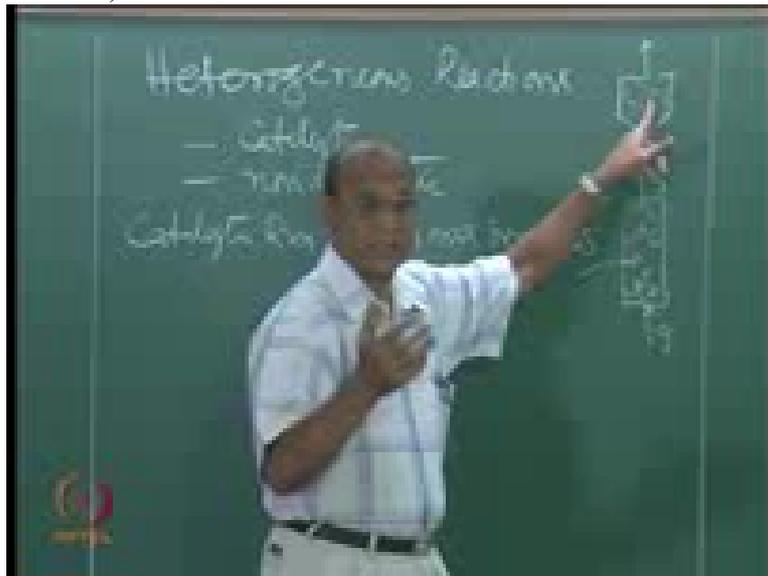
(Professor – student conversation ends)

So here also all these particles are just suspended in air stream. Ok, That, you know we have many, lot of dust is now there in the air. You can see them on your cycle or if you have car or if you have all your furniture and all that, and if your room is opened, the windows are opened, then you can see. After one day you and touch it, there is lot of dust.

So those particles also practically fluidize, right? If they are not moving from place to place. When it is moving from place to place then they are also pneumatically conveyed and finally it will go on the, unfortunate that it will enter your room because there is no sufficient amount of breeze there to go away so then they settle. Ok that is what what we are talking.

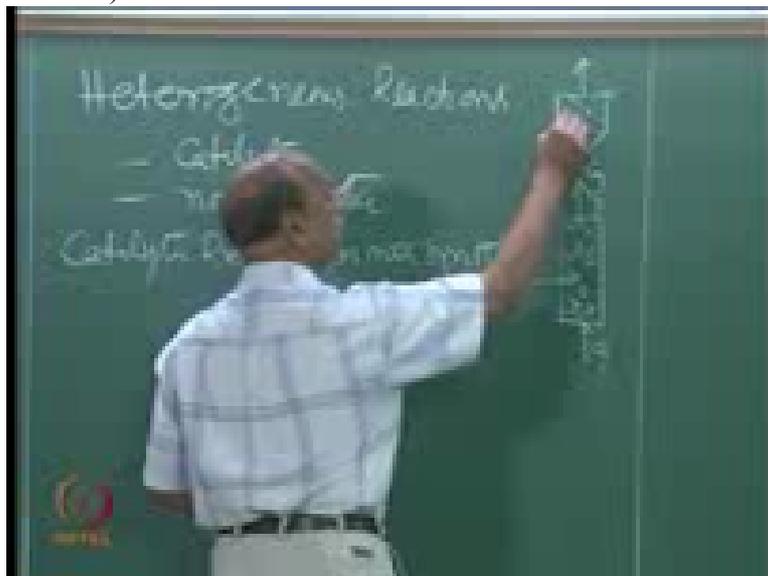
And even this catalytic reaction, the solid particles are catalysts.

(Refer Slide Time: 07:07)



And the gas which I am telling here is ammonia plus, not ammonia, hydrogen plus nitrogen, together mixture. Ok you may send it in stoichiometric quantities, or whatever. So that is the one what you are talking. Even here I can simply pull out

(Refer Slide Time: 07:21)



a particle. Not only this.

We also have what are called rotary kilns. Have you heard of them? It is a kiln, big tube, cylindrical tube, it will be slowly moving. You put now, this side the solid particles, right and opposite side you can also put nitrogen and hydrogen. The particles may be slowly

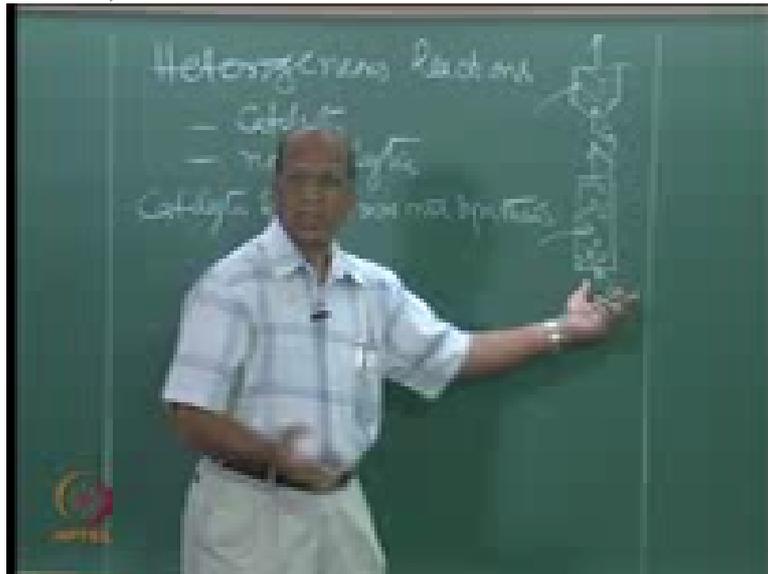
(Refer Slide Time: 07:44)



coming and you are taking back and again introducing them, to take back and again introduce them. That is also a possibility. No one does that, Ok. But that is also a possibility.

Why? All these things are possibilities but these are difficult possibilities than packed bed. Packed bed is the simplest. This also can be used. There is also another reactor also called moving bed reactor. You take the packed bed and put a hole here, not distributor. Distributor has small holes where the particles cannot fall. Only air can enter or, or nitrogen and

(Refer Slide Time: 08:19)



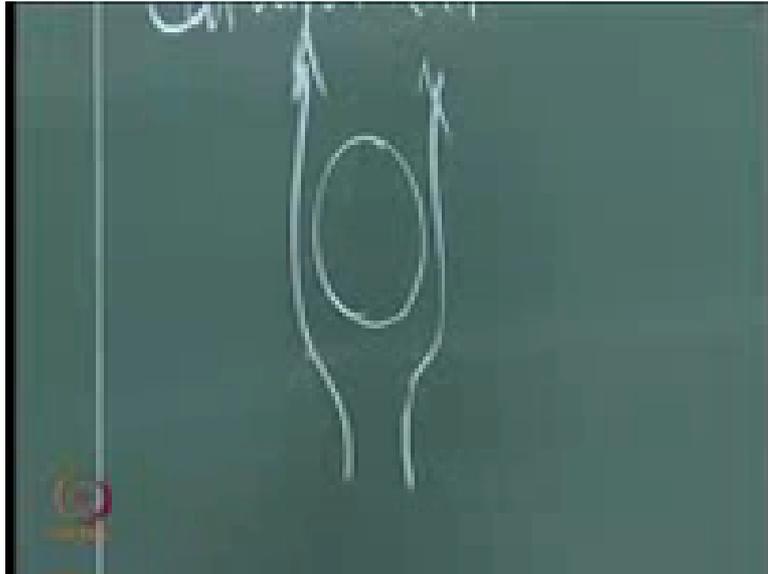
hydrogen can enter.

So now you can put big holes there where the solids can slowly come down. So then you are also sending in the opposite direction, the gas. Now the entire bed is moving. That is why it is called moving bed. Ok, understood no? These, these are not generally difficult, Ok. So that moving bed also, when I want to develop a rate expression for catalytic expression I will pull out one particle again. Right?

See the chemical reaction rate will not change in all these systems. What will change is the physical rate. That means how mass is transferred to the surface. But in all these things what is our imagination? We have a particle, ok. Yesterday I have drawn horizontally but now I will show, more truly I will just draw this.

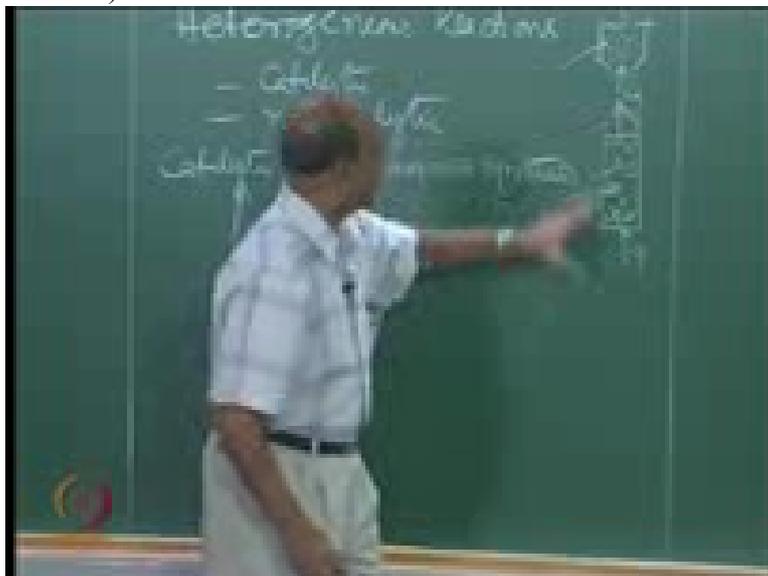
So this is how, if I pulled

(Refer Slide Time: 09:15)



out, because I pulled out one particle. Why I should pull out one particle? Because let me imagine that what is happening in this one particle. Same thing must be happening to all the particles. So if I develop this equation and this equation, yeah is valid at any point where you pulled out and because

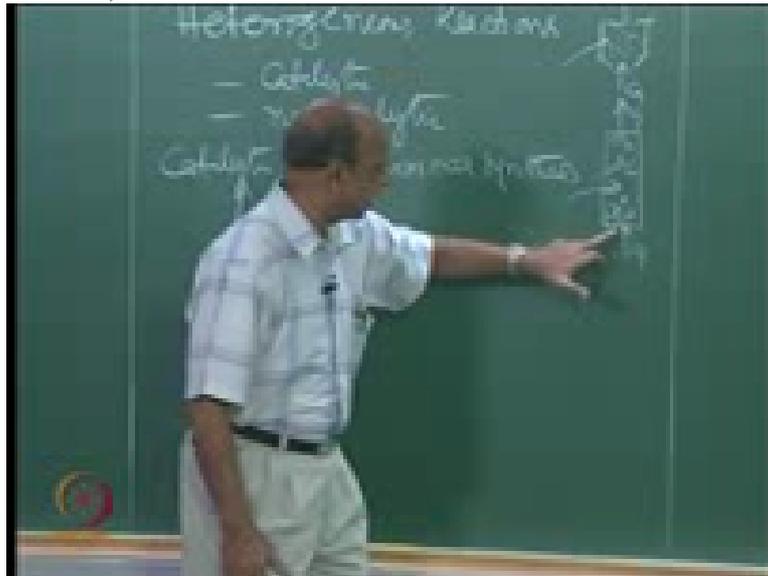
(Refer Slide Time: 09:32)



it is a packed bed, there is change of concentration from this place to this place, then I can integrate.

Because this is a distributed parameter system. That means the concentration is changing from this end

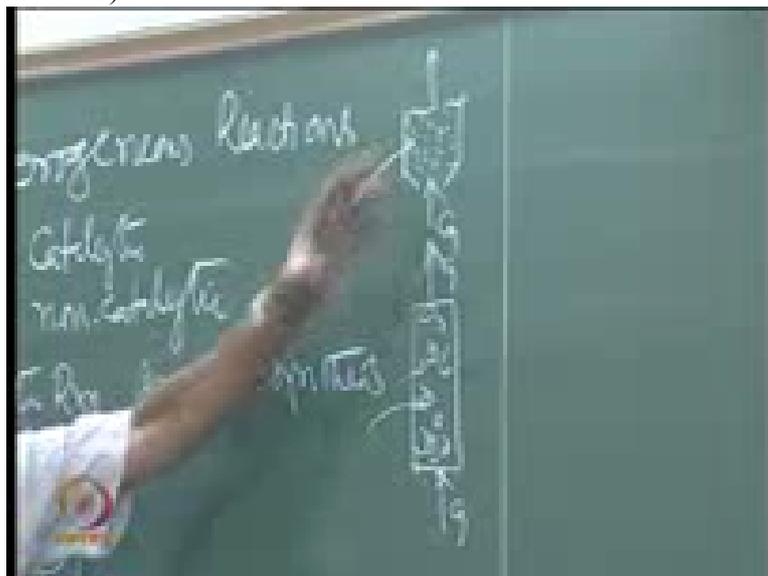
(Refer Slide Time: 09:43)



to this end. Whereas here it may not. Better not talk, you know, about fluidized bed. Fluidized bed is one of the most difficult reactors to be modeled, to be constructed, to operate. It is not that easy. But still very, very efficient one. But why it is efficient also, I will discuss if you take the course next semester but right now I think we will only just mention the names, Ok. Good.

So that is why

(Refer Slide Time: 10:08)



in all the systems, whatever reactor you choose, whatever system because you know we have many, many possibilities for the reactor, heterogeneous system. So now if you see this particular bed,

(Refer Slide Time: 10:19)



right, there are 2 phases. And in our diagram we have contacting pattern, right?

So now we have to talk about, for each phase what is the contacting pattern? When you are talking about homogeneous reaction there is a single phase. So you are only talking about contacting pattern of that particular phase whether it is in perfect mixing or whether it is perfect plug flow or whether it is in third one. Perfect mixing is in mixed flow. Pooja? Plug flow already we told. Do not forget batches.

May be L K G information but still, because that is what first we learnt, no? Batch.

(Refer Slide Time: 11:01)



So we have only 3 contacting patterns, whether it is batch or plug flow or mixed flow. Plug flow, mixed flow are continuous,

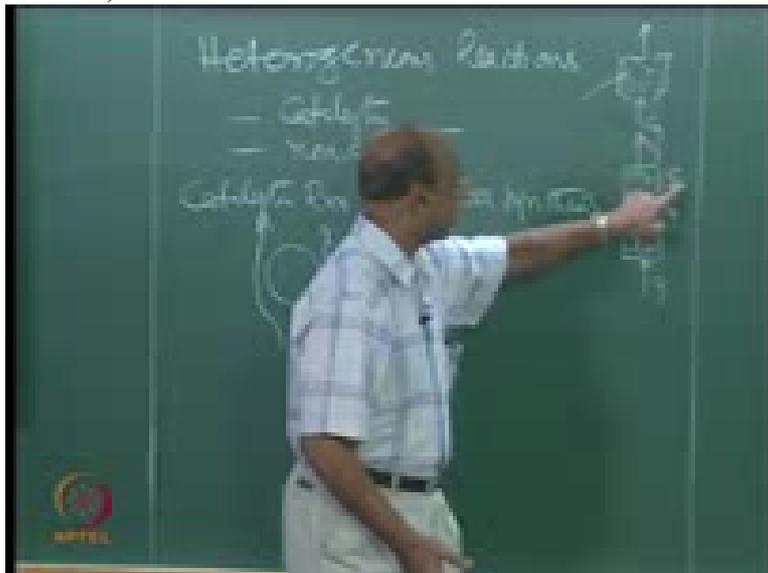
(Refer Slide Time: 11:08)



Ok. And whereas batch. But you have to now identify for each phase here, how they are moving? That is very important again for us.

So when I talk about this packed bed, I have solid phase and gas phase, these two no, non-catalytic gas solid reaction. So now I have to tell what is the contacting pattern for

(Refer Slide Time: 11:30)



solid in packed bed? Now only 3, just imagination, we have only 3, batch, plug flow, mixed flow. Batch, why because solids are not moving. They are there, Ok. So that is why, so this is batch.

And what about gas, how is it moving? It is plug flow. Why? I can tell, I mean when you look at the packed bed, fluid mechanically also you can prove that, most of the time your plug flow, the velocity profile will be flat, if you are operating properly with Reynolds number. No book gives the connection between Reynolds number and plug flow.

Only K K gives that connection, that is why please remember when you are operating packed bed it should be in the turbulent Reynolds number. What is turbulent Reynolds number? That Reynolds number for turbulence in a packed bed?

(Professor – student conversation starts)

Student: Greater than 500

Professor: Greater than?

R; 500

Professor: 500, do not tell 40000 and all that. 40000 also will

(Refer Slide Time: 12:27)



be, but I think starts from 500 onwards, Ok, good, excellent. You remember that.

(Professor – student conversation ends)

Yeah, so that is why

(Refer Slide Time: 12:33)



that, even though it is batch I cannot write any equation for a catalyst particle because, as far as conversion is concerned, because reaction is taking place only within the, it is taking place on the surface of the catalyst and inside the catalyst but what I am converting is my entering reactants and then the products will come out.

So that is why, yeah

(Professor – student conversation starts)

Student: We can call that homogenous?

Professor: How can you call that homogenous?

Student: Because

(Refer Slide Time: 13:34)



the solid does not react, the catalyst does not react. You can consider it to be a 0:13:38.6.

Professor: Yeah, any answer for that? I will make you fight. I will be referee.

(Refer Slide Time: 13:49)



Yes Sir, possible?

Student: No Sir

Professor: No?

Student: That is actually wrong.

Professor: That is actually wrong. Why?

Student: Actually it takes place

(Refer Slide Time: 13:58)



on the surface of the iron particles.

Professor: Yeah, so?

Student: Without iron there is no reaction at all.

Professor: Ok, he says that you also take that as one phase, as everything together?

Student: Mass transfer

Professor: Yeah, who said that? Anupriya no?

(Refer Slide Time: 14:15)



Yeah slowly getting the fundas also clear.

Student: (laugh)

(Refer Slide Time: 14:17)



Professor: Yeah, important thing is there is extra mass transfer

(Refer Slide Time: 14:22)



that is coming.

(Professor – student conversation ends)

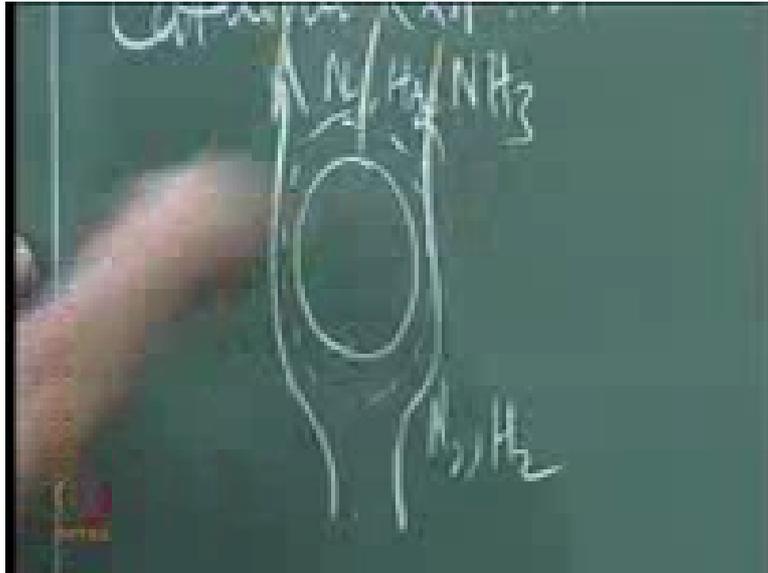
Whereas when you talk about homogenous, it is a good question what he has asked, others also may have this confusion no, number of times, when we talk about homogenous system there is no external mass transfer coming into picture.

Actually, that is the definition of homogeneous, and heterogeneous. In heterogeneous system you need mass to be moved from one phase to the other phase. Here mass is moving from gas phase to the solid phase, if there is no solid, there is no reaction. Correct, no?

It is not reacting with solid. It is reacting in the presence of solid because that is a catalyst, right? So that is why you cannot now say that you have a heterogeneous, homogeneous system. It is heterogeneous because necessarily, here this is what next one I was trying to tell you no, yeah.

So this one I have a film around this, and the, yeah here I have nitrogen and hydrogen going and here I have N_2 , H_2 and also NH_3 ,

(Refer Slide Time: 15:27)



because that has reacted after this particle contacted there and then this is coming out and now this N_2 and this H_2 without contacting this, if it is going out, then there is no reaction. So for the reaction to take place, this N_2 and H_2 have to diffuse through the

(Refer Slide Time: 15:45)



film. Then it has to go to the surface. If it is only non-porous iron, non-porous iron, then the reaction is occurring only on the surface. But this mass transfer step is must. Then the reaction rate that is happening on the particle.

So the reaction that is taking place on the particle, we call it as chemical reaction, chemical reaction rate and then this mass transfer step we call it as physical rate step. That is why you have in that diagram, under kinetics, physical and chemical both together.

So now for heterogeneous both are required. So that is why, when I write this simple equation later you will know what kind of rate expression you get. I do not want to complicate it, because so that first we have to understand the basic things and then we can extend. You know next one is only algebra, that is all. If you understand these concepts next thing is only algebra.

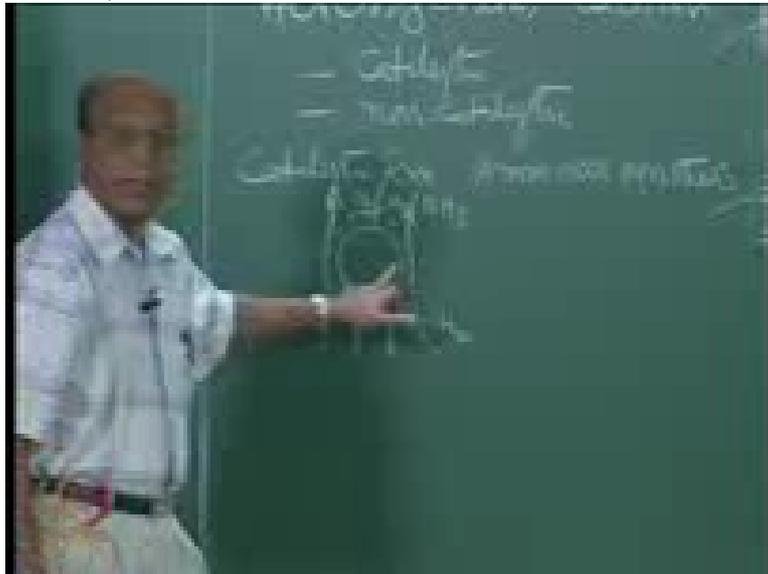
That means equation will be more complicated. So you have to use, spend more time for actually finding out the rate. That is all the difference. So that is why we have now, Abdul you understood now no, why we cannot call it as homogenous, yeah.

But actually when you again take next semester, this course on chemical and catalytic reaction engineering, there what actually he said is also right. Under some conditions we will take the entire system as pseudo homogenous packed bed, pseudo homogeneous packed bed. There are particles but I do not feel the particles under certain conditions, Ok.

That conditions I cannot discuss because I think we have to talk about homogeneous systems more for understanding. So that is why you have that information also. And most of the time, the models we are using for packed bed is what he has suggested. This is homogeneous, pseudo homogeneous models.

There are class of models where, models means writing, trying to write equations, Ok trying to write phenomena in terms of equations. That is all modeling. That is why phenomena is important. That is why I am telling you so many times, take the particle out, and then imagine that there is a flow around that. Then you have the step 1 as mass transfer through the film, through the surface

(Refer Slide Time: 18:00)



and if it is non-porous then I have only one step that is reaction occurring on the surface.

And after reaction, there is no use of that reaction if NH_3 , N_2 , H_2 all are there on the surface without coming out, correct no? I do not get any product. It is sticking only to the surface. But that cannot happen by nature because ammonia, reaction is taking place, the reaction is taking place on the surface. Ammonia is produced there. At the point of production you have concentration of hydrogen more. Not hydrogen, ammonia more.

So at the outlet, not outlet, outside in the bulk concentration of ammonia is less. So it is natural phenomena. You cannot stop it, right? So whether you have a good smell or a bad

smell, if it is released from your body, you cannot stop it. Because that is nature. God will take care of it. He will spread it uniformly, happily, Ok.

So that is why when I have scent and all that, everyone will enjoy, not only me. Why? It is not my greatness. It is greatness of the nature because whatever scent I have, that concentration is not there with Gopinath, equal concentration. So if there is exactly same concentration,

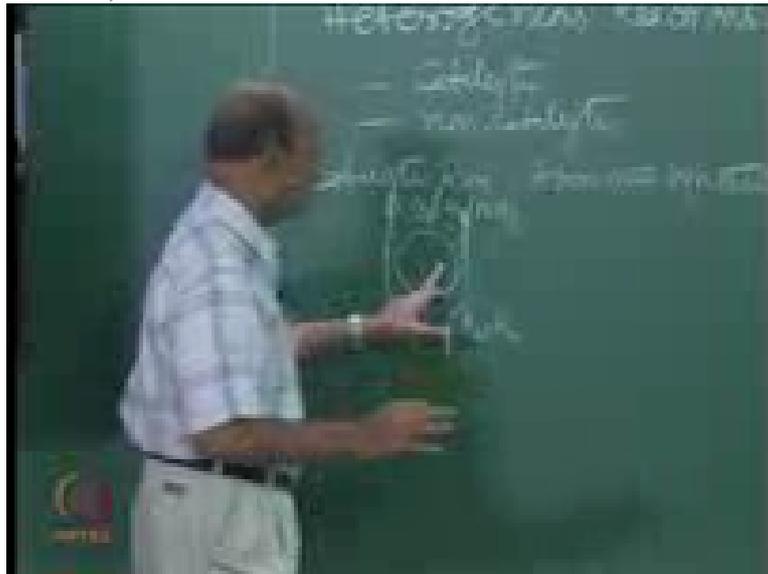
(Refer Slide Time: 19:09)



no I will keep my smell with me and he will keep his smell with him. Because concentration, there is no gradient, it cannot move.

So that is the reason why, ammonia after formed here, it will come out. That is what what you are seeing at the outlet here, Ok. So that is what is the entire phenomena that is taking place. Now to write the equations,

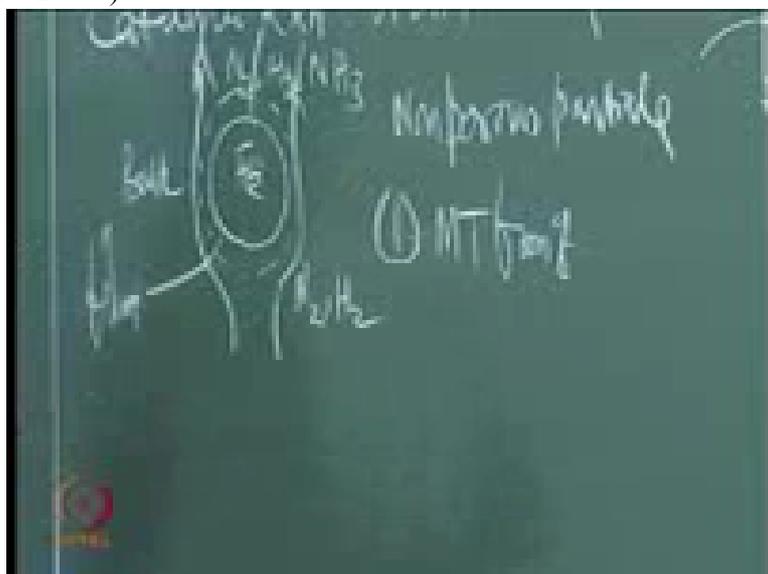
(Refer Slide Time: 19:30)



let us list now for non-porous particle, non-porous particle, what is step 1?

Step 1 is mass transfer M T from bulk to, this is bulk, this is bulk and this is film, Ok that is film. And this one is F e, catalyst, non-porous catalyst. So now all these three we have now. M T of, yeah whenever you are

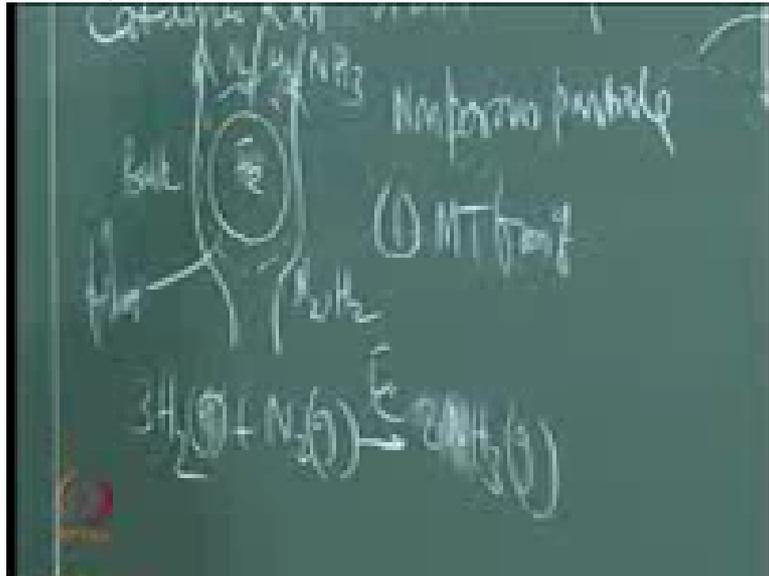
(Refer Slide Time: 20:06)



writing mass transfer, I have been telling you, this is the difficult thing in mass transfer, when you go to fluid mechanics also, everything put together you will write no, momentum transfer, right? And in heat transfer also, entire whatever number of phases you have, the entire thing you talk about, what is the total heat that is contained.

But when you come to mass transfer only, you have to identify each and every species. Right, so that is why when you are writing here, if I am calling my hydrogen is limiting reactant, because normally that is what is used as limiting reactant, so that is my A. N₂ plus, Ok, sorry let me also write this, H₂ gas, better write N₂ gas giving me in the presence of F e, 2 N H₃, correct? 2 N H₃ gas, this is 3, yeah, 3 H₂, that is balanced, Ok and in the presence of F e. This is

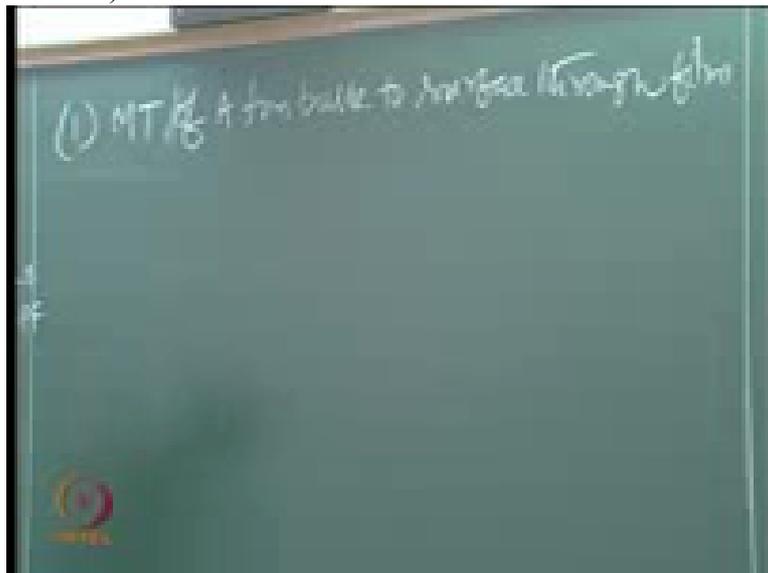
(Refer Slide Time: 21:07)



the reaction.

So my A is this this, limiting reactant. You can also also choose N₂. That is not a problem for us. But that is my A. That is why if I write here, I think I better write here then, 1 is M T of A, A you can write here, this is B giving R, Ok corresponding numbers and all you can take, M T of A from bulk to surface through film. That is step 1. Right, correct no? Mass transfer of

(Refer Slide Time: 21:52)



A from bulk to surface through the film.

Then second step, because it is non-porous particle, that is what we have taken, non-porous particle, right, reaction, you see I am simplifying things here. Next semester it will be more complicated. So whatever is happening I am not, you know, actually if you look at the molecular level, hydrogen will go and get adsorbed on the surface.

Then N_2 fellow is also coming because it is gas phase and it is stoichiometrically mixed and then you are sending it, right? So N_2 also will get adsorbed. And again how deep you go depends on our mind only. But as engineers we are not going that deep. So what we just imagine is hydrogen got adsorbed there, nitrogen is also getting adsorbed there.

They somehow decompose through the intermediates and those things will come together and then you have NH_3 form and because of the concentration gradient, NH_3 leaves, that is desorption of the product and then it comes out through the film and then finally joins the bulk, Ok. That is one.

But in fact if you go to the mechanism for which that Ertl I told no, E r t l, Ertl Nobel Prize, he got Nobel Prize for sending, for exactly proving this mechanism experimentally. It is not that easy the way I told you. Hydrogen something it will happen, nitrogen something will happen, I think energy, there are so many beautiful things what he has explained in his actual mechanism on the surface how the molecules are behaving for the reaction to take place.

He has mathematically proved and experimentally found out the same thing what is happening, what he has proved that mathematically That is why he got Nobel Prize. But as engineers we are not doing that. Our thing is Ok, I need hydrogen, I need nitrogen. Both of them went to the surface. Something happened between them, got the product and then I am happy to have that product, right?

But if you are a scientific engineer, Ok, engineer also can be scientific then you will go deeper and deeper and then look at the molecule what is happening. That is why you have the nanotechnology and all that. Because we think that we have understood all chemical engineering.

Then now you know engineering is macroscopic and science is microscopic or nanoscopic. You have to go to even nanoscope level. And then try to find out what is happening. And this nanotechnology, entire thing started only with that because it is exactly no, one simplest example how on this planet life is coming out?

If you take any mammals, sperm and egg, what is the shape? We do not know. Shapes we know but inside that cells and all that you know, shapeless, only cell. So with time, with reactions, with conditions changing slowly it can be a bull, or it can be a man or a woman or it can be a monkey, all these things. But what is the starting point? Only that very, very small minute thing. What a wonderful creation!

That is why, humans of course, we can, when they get pregnant and also how the body, baby is growing, all that nowadays you also see in the Youtubes and all that. At various, 3 weeks, 5 weeks, 10 weeks like that. You know what is the nature is trying to do? It is using the nanotechnology to build up by adding more and more, more and more, finally to bring to a shape.

That is what exactly we are trying to do in nanotechnology. We go to the atomic level and then now try to arrange those atomic levels

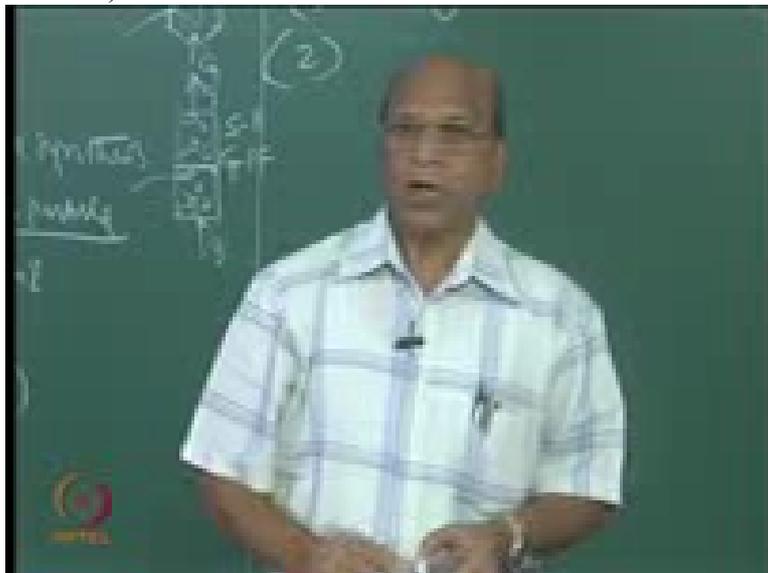
(Refer Slide Time: 25:28)



and to a particular shape, to a particular product. Nature has already done this. Otherwise you and me would not been here, discussing C R E, if nature had not done that. So that is what is the meaning of nanotechnology. Please remember.

I do not know. All of you would be happy to take nanotechnology; happy to do research in nanotechnology may be without understanding the basics. Ok. So

(Refer Slide Time: 25:52)



and what we thought was, I gave you the example, you know, when Malaysia when I went, that girl beautifully told me that Sir, you bring hydrogen, you bring sulphur, you bring O 4, that is what is wanted, you know, in nanotechnology level.

I will simply pull out one hydrogen molecule, simply pull out some O 4, you know sulphur, then put them together, Ok, Abdul take it. This may come after may be 200 years, 300 years later in, in you know,

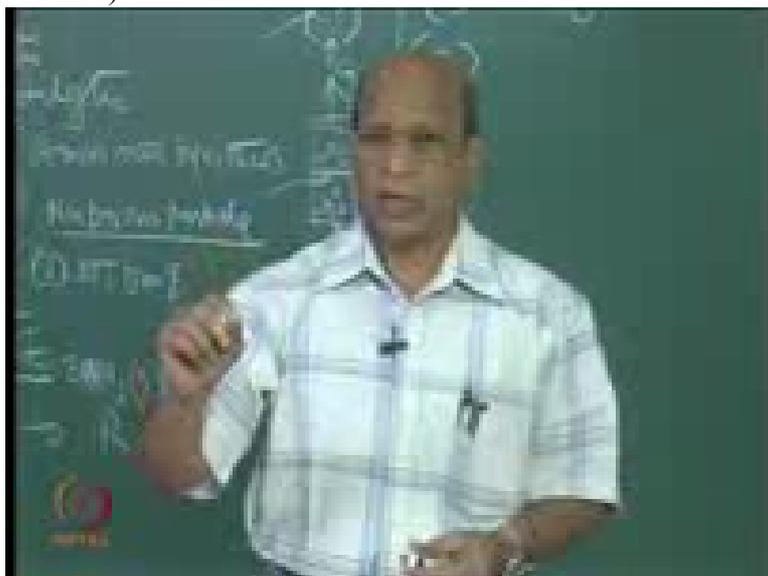
(Refer Slide Time: 26:19)



hospital. When you go for a particular disease, I can guarantee you will have much more diseases at that time, Ok, because we are not following the nature here. We are only following ourselves, Ok.

So then you know the doctor will go and then

(Refer Slide Time: 26:32)



he will not write any prescription. He has a lab. You know, now you have already seen in some movies, where, now this dragging has come in cell phone and all that, you know, pull, like this, like this, like this, you will get all the messages.

Earlier there was a movie called Minority Report. So there if you see the computer, like this, like this, like this, like this, you know all structures he puts, all he brings this way, this way, this way, this way and then finally you will get a structure.

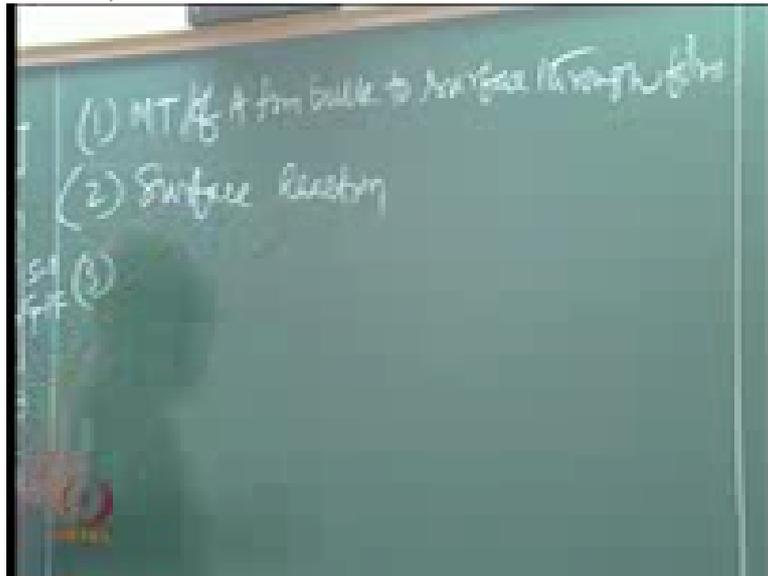
That may be what may be happening in every doctor's room. He may be taking all molecules stored, entire periodic table, pull this, pull this, pull this, pull this Oh this is medicine, take. Finished, Over. That is what is nanotechnology. So when we are talking now at present as chemical engineers we are not talking about that particular thing, that is adsorption, then we have the decomposition after adsorption and all that, molecules decomposing.

Then we have surface reaction, that means the molecules, the intermediates coming together and then reacting and then of course, producing the products. Then you have the product coming out, right? So those steps we are not talking. To make the simple thing, to make the point what is the difference between heterogeneous and homogeneous, that is the main thing now.

That is why step 2 is surface reaction. This surface reaction contains adsorption, desorption and surface reaction again, you know, surface reaction is between the intermediates and all that. Ok all that we are not talking, good. Yeah. Then what is the third step?

Actually before this, there is another

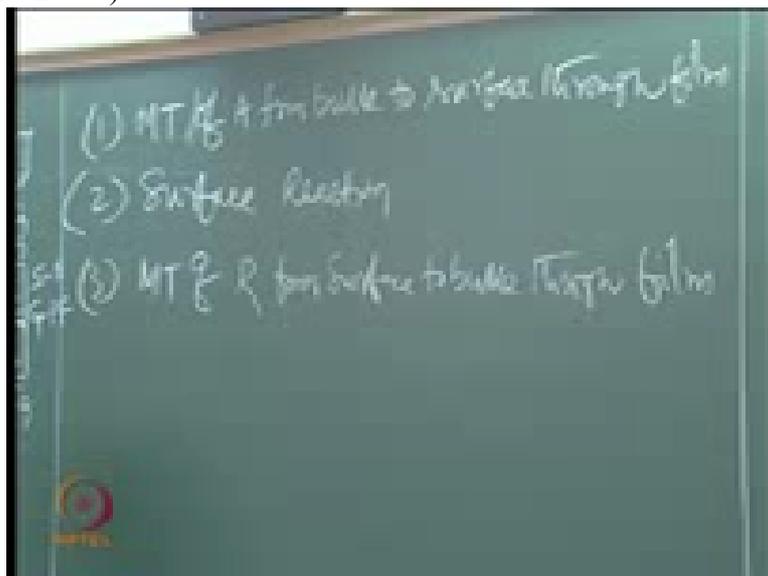
(Refer Slide Time: 28:01)



step if it is a porous particle. If it is a porous particle, other thing is, Ok, something will get, go to the surface, external surface but there is a lot of internal surface that is available as pores so that will diffuse into the pore. That is another mass transfer step; diffusion is a mass transfer, right? So that step also we are not taking. That is why, simplify to have non-porous particle, where yeah, non-porous particle. This is one. What is the third step now?

Now mass transfer of product, if I say, R, yeah, R is the product, mass transfer of R from surface to bulk through, again film. Simplest assumption is Ok, one molecule is going

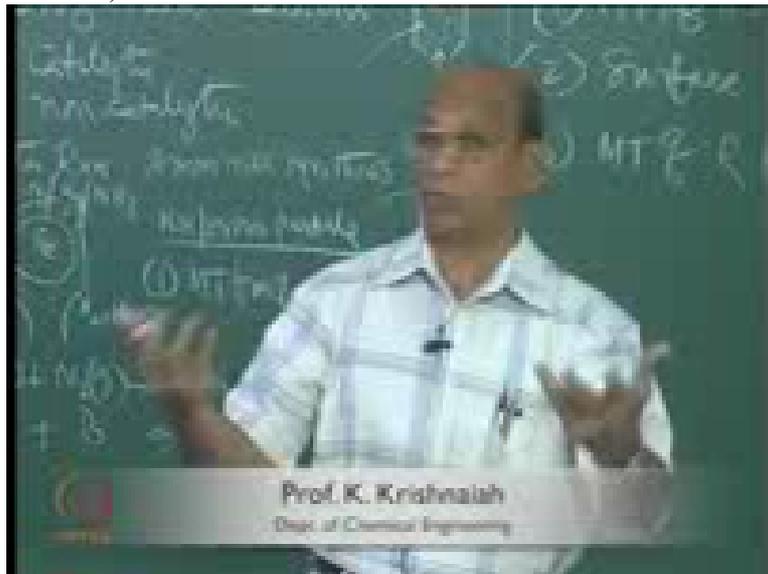
(Refer Slide Time: 28:49)



into the, through the film to the surface, getting reacted, another molecule is coming out. Then we have some kind of adjustment between these two. Then you will have a rate expression for mass transfer.

That is what what you have studied in your film theory. That is what. I think something is coming in this direction, something is coming, equimolar

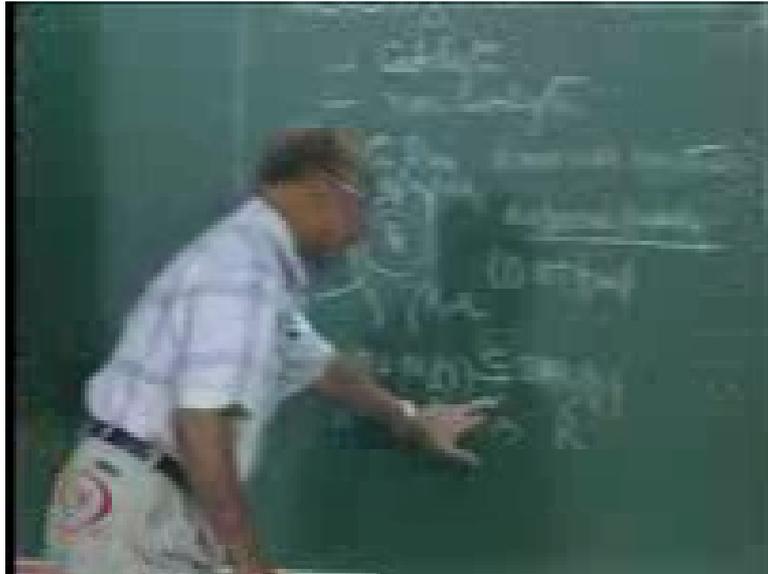
(Refer Slide Time: 29:06)



counter diffusion we will say and then you know what is the equation what you have to use, simplest one. And we are not using here diffusion equation, even though there is a connection between diffusion and mass transfer. I do not know whether that connection is known to you or not.

Ok, so, that is why now I have to write these 3 steps. But right now I am imagining that my reaction, this one is not even, because I am simplifying many things. Just to make the point. Now even

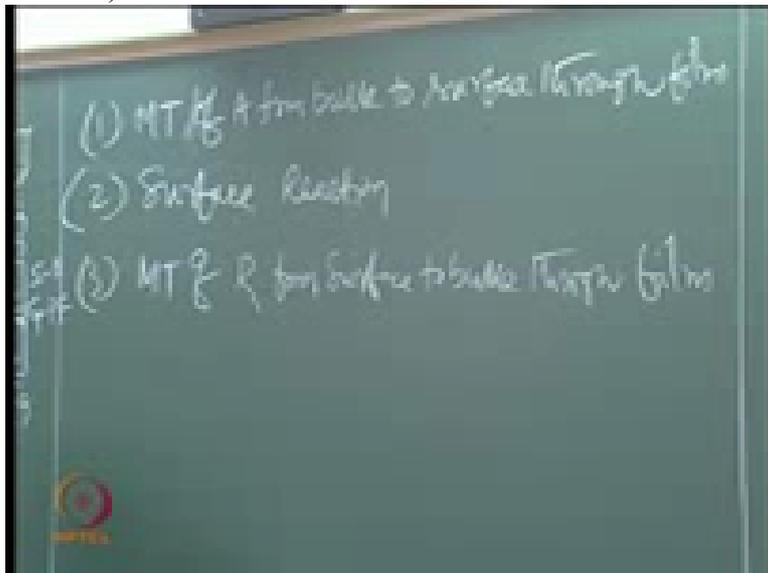
(Refer Slide Time: 29:32)



this reaction is not reversible, Ok. It is not reversible reaction. I mean, do not think that ammonia is not reversible. I am just simplifying that this A plus B going to R is not a reversible reaction.

So what are the steps that will eliminate if I say that the reaction is not reversible? Because at steady state all these three steps must be

(Refer Slide Time: 30:00)



equal for the reaction to happen and also for the products to come out, right. But even these three steps I can still further simplify if I say that the reaction is not reversible reaction.

Where is mass transfer of unreacted A and B coming? In the three steps. I am talking about these three steps. Product is coming out from the surface of reaction. Second step is reaction. First step is reactant transfer through the, which step you can eliminate; one of the steps can be eliminated. If I say reversible reaction, what is the meaning of that? That means the product is

(Professor – student conversation starts)

(Refer Slide Time: 30:33)



Student: Again converted back.

Professor: Yeah, so right, that means the product is also

(Refer Slide Time: 30:37)



affecting the rate. The moment I say irreversible reaction, then product does not have any effect on rate. Which step you can eliminate now? Excellent. Right.

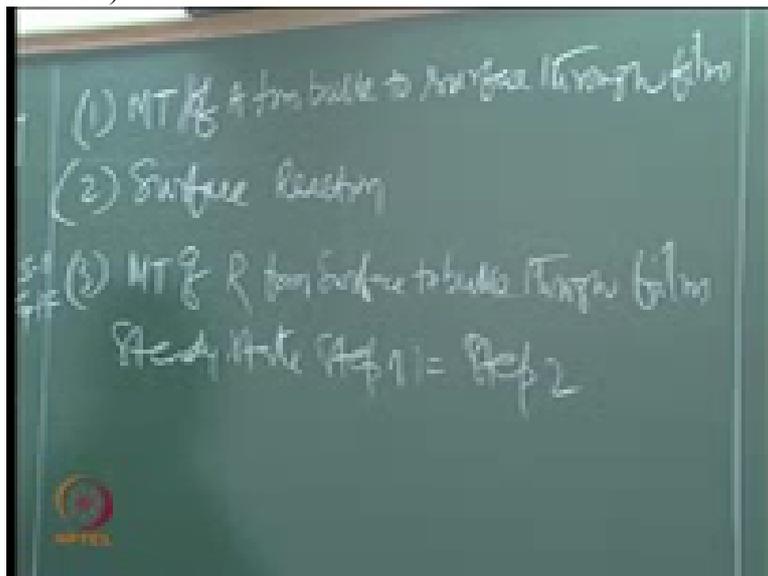
(Professor – student conversation ends)

That is why the thinking I say, expanding the brain a little bit, delta x, delta x, delta x so by the time the course is over, that head will become this much. Ok, that is good, that is what we want. It is not the physical increase, Ok. The knowledge increase.

That means, you know this is what is the problem. You are not able to think beyond what the teacher tells. So that is very simple only. Now you see, reversible reaction, what is the effect now? Definitely the product also will affect the rate of reaction. So I want to simplify mathematics. So that is why I say that now, let us assume now we have reversible, irreversible reaction.

So that means the product does not have any effect. So that means this step also can be ignored. Now under steady state, steady state, step 1 equal to step 2. Correct no? The other one also is there, but that is not participating in the reaction and when I want to develop an equation, this is the mass transfer step, so many moles are going.

(Refer Slide Time: 31:50)



Under steady state condition, so many moles per unit time must react, correct no?

And they have to come out. But they are coming out in third step but it is not changing the rate.

(Professor – student conversation starts)

Student: Why are you not considering the third equation?

Professor: Yeah, because what is the idea of writing all these three steps?

Student: 0:32:11.5 going on

(Refer Slide Time: 32:12)

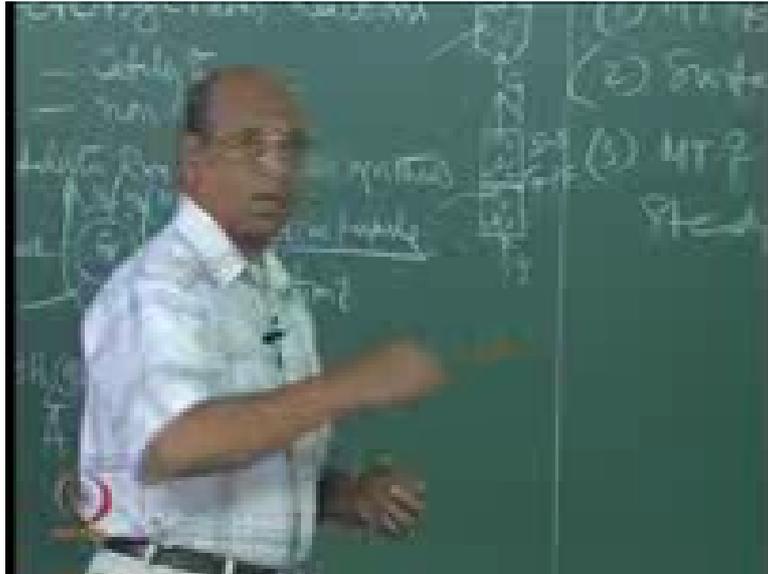


Professor: How to develop a rate expression.

Student: Yes, develop a rate expression

Professor: How to develop a rate expression. Now by assuming irreversible

(Refer Slide Time: 32:19)



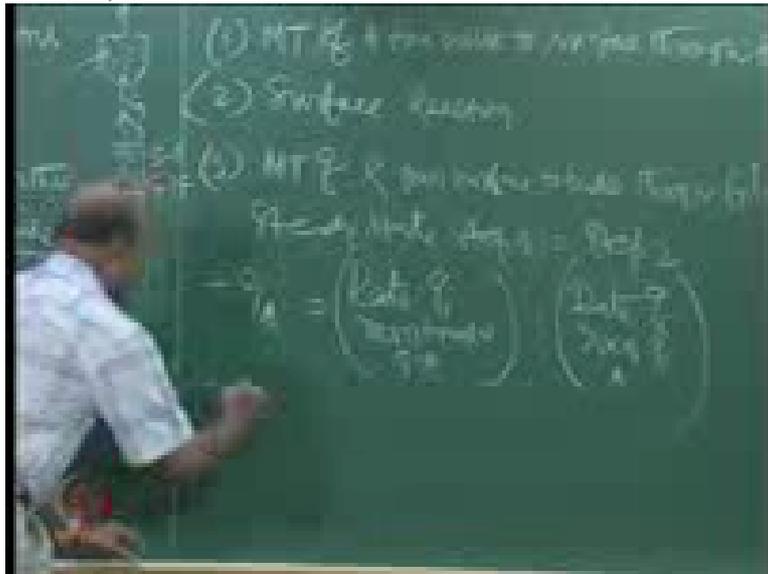
reaction, my rate expression is not affected with the third step. Why?

(Professor – student conversation ends)

Why because rate is not changed by the product. It formed, but again you know in the reversible direction that will again decompose to some reactant. That is what the reversible thing no? That is not there. That possibility is not there. So that is why first 2 steps itself is enough for me.

So now steady state, rate of mass transfer, let me also write, rate of mass transfer of A must be equal to rate of reaction of A on the surface. Rate of reaction, because these two I can now say that it is minus r_A . So now what is the equation?

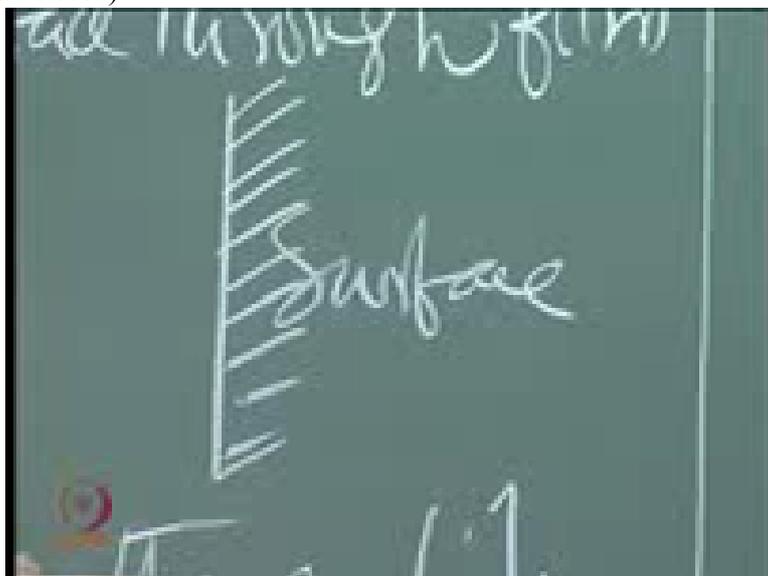
(Refer Slide Time: 33:08)



This is minus r_A . What is the equation for rate of mass transfer of A?

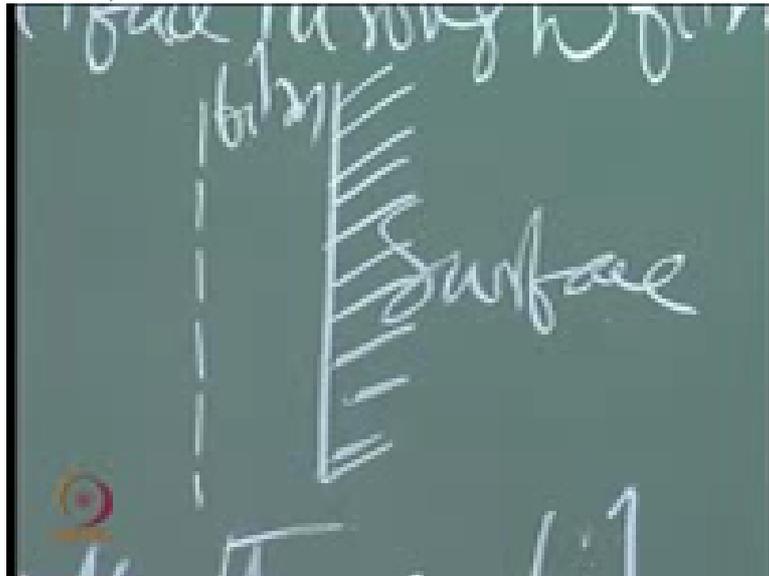
It is simple film theory. Film is there, through the film, mass is going, you know to reach the surface. So what is the equation you use? Mass transfer equation. So that can be k_g into, yeah, one more step I have forgotten to tell you, this can be now imagined as like this, this is the surface of the catalyst. This is the surface of the catalyst,

(Refer Slide Time: 33:40)



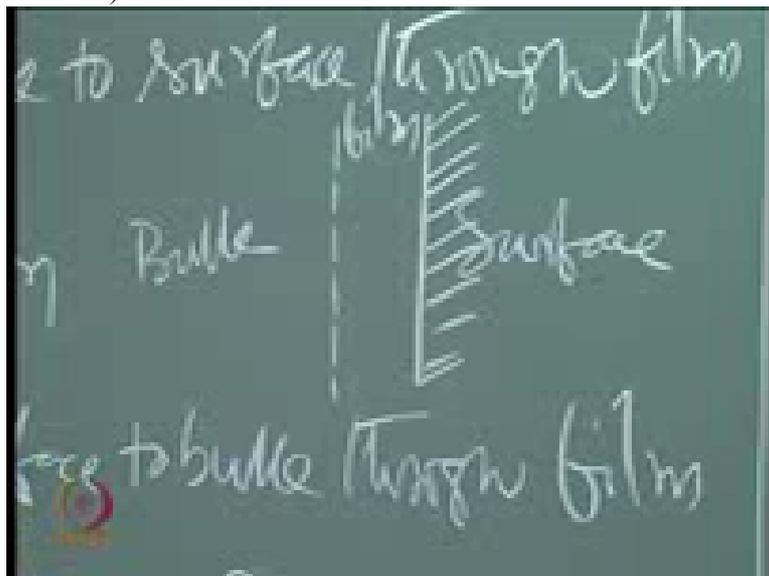
Ok. So then this is the film, correct no, this is the film. Now

(Refer Slide Time: 33:50)



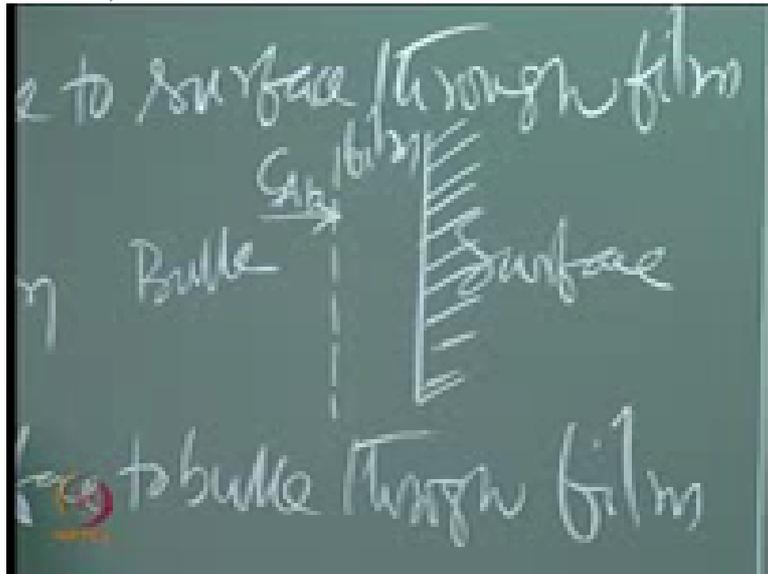
outside I have bulk, right.

(Refer Slide Time: 33:54)



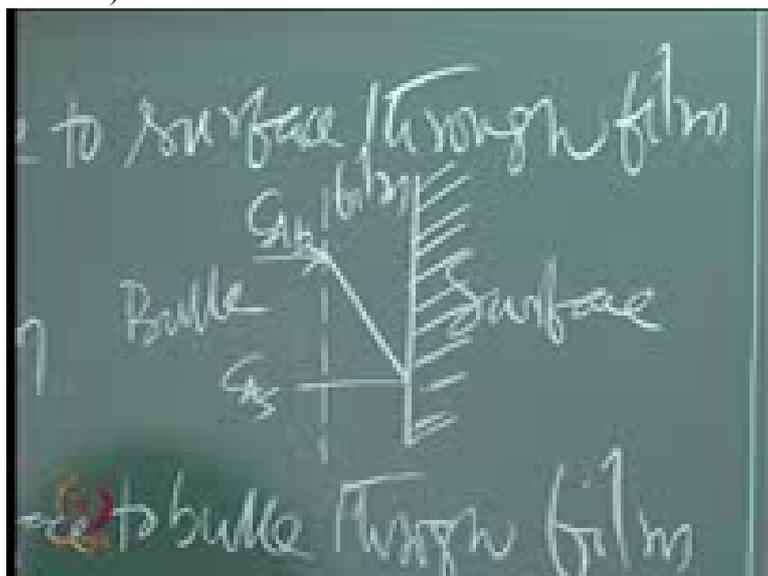
So if I want to draw the concentration profile, this will be C A b, or Ok, C A b

(Refer Slide Time: 34:04)



that is $C_A b$, Ok. Now definitely there is some concentration gradient inside the film. So now if I show that that will be something like this. What is this one? This is $C_A s$.

(Refer Slide Time: 34:21)

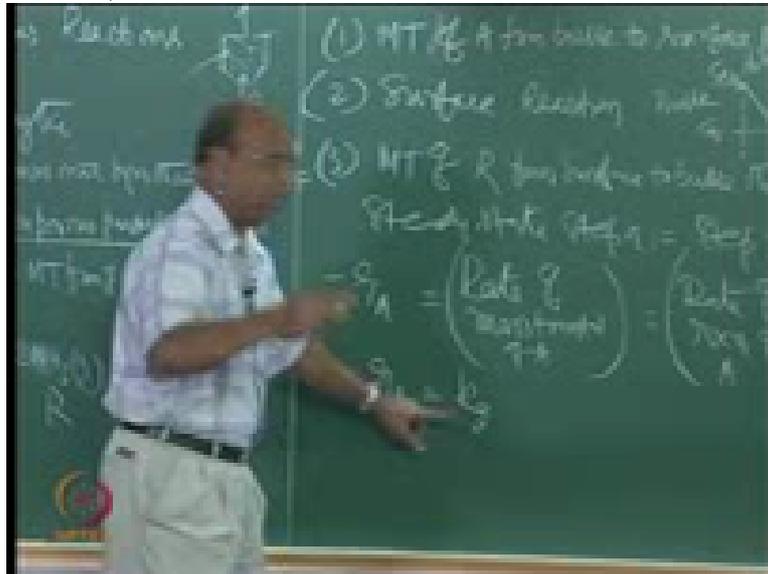


So drawing this concentration profile will make me, the things will become very easy to write the equation.

I know now that I have to write an equation through the film. And I also know the concentration on the surface and also concentration in the bulk. So that is why, and I know that the, this mass transfer rate also equal to reaction rate that is why I am interested in reaction rate that is why I have written minus r_A . I can also write that one equal to N_A . Ok, but I am interested in rate of reaction.

So that is why we write here minus $N_A k_g$, that is the proportionality constant, mass transfer coefficient,

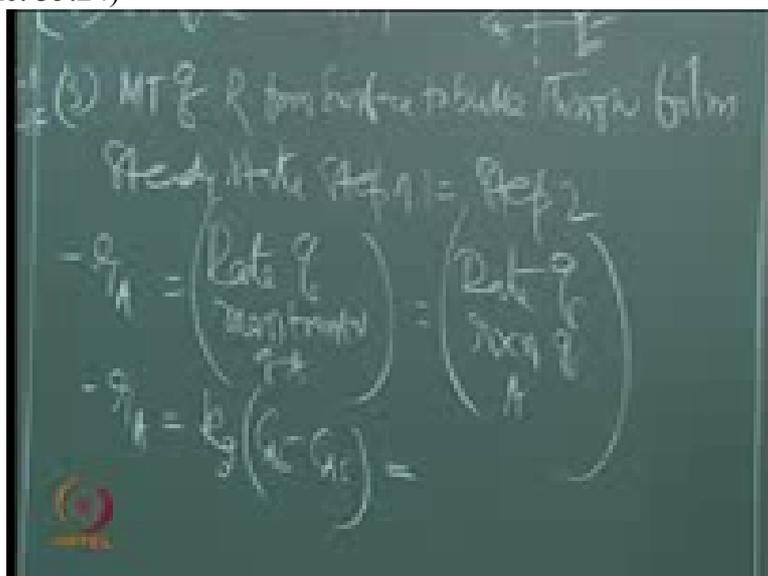
(Refer Slide Time: 34:54)



then $C_A b$ minus $C_A s$, right. Ok. Now this must be equal to rate of reaction. Rate of reaction means you should have an equation for rate of reaction.

That is the pure chemical step. This is pure mass transfer step. Because now you are taking both of them into account, that is why in heterogeneous system that is the extra step. This physical step, this mass transfer step,

(Refer Slide Time: 35:24)



you will not see this in homogeneous. Why? Because mass is available all through without again transferring from one place to the other place. It is there.

If you have A molecule there may be 10 B molecules. If there is B molecule, there may be 10 A molecules. So that is why, for anytime for the reaction to take place, sufficient number of A, sufficient number of B is there.

But here, it is not there. Unless it is transported to the surface, there is no reaction. Even though catalyst is capable of converting anything that comes there, there is no reaction. So that is the reason why this extra step that is coming,

(Refer Slide Time: 35:57)



because there must be some transfer from one phase to the other phase in any heterogeneous system where mass transfer also plays a role, right?

And I have the film thickness so big, no mass is going inside the surface. So then what will be the rate of reaction? It will be very, very less. That means it is affecting no? What is that effecting? Mass transfer is affecting. Physical step is affecting. That is why in that diagram, we write chemical and physical. That is what is the exact difference between heterogeneous system and homogeneous system where mass transfer will not come into picture, good.

So what, again I have tremendous assumptions here. What now I assume is

(Refer Slide Time: 36:41)

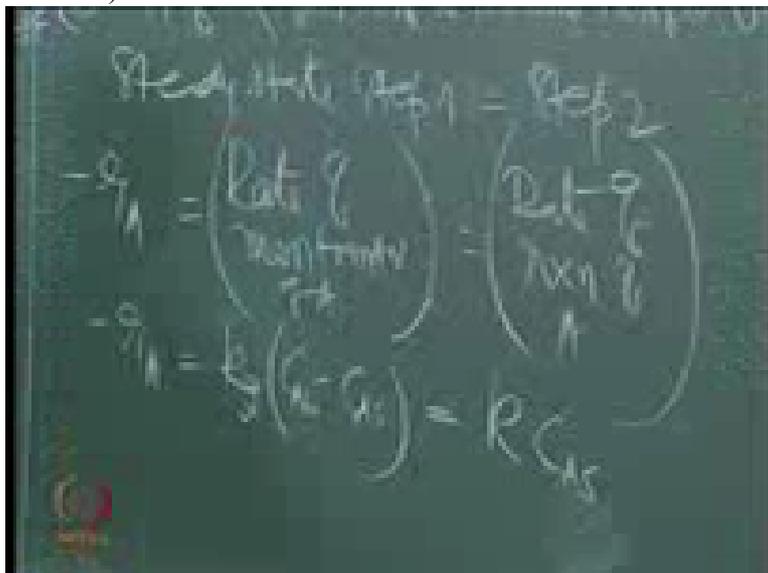


for easy mathematics, I will have first order. This is rate constant k and $C A s$. Please remember reaction is occurring on the surface, here. Reaction is taking place on the surface. That is why it is $C A s$; it is not $C A b$. Ok, good. And the assumption here is I have first order rate.

This is first order, directly k into $C A s$. I can also have second order. I can have any complicated order. This may be again m plus $C A s$ but this concept is same, equating that is same, Ok, good. Now that, I do not want to complicate right now.

So now this is the equation what I have.

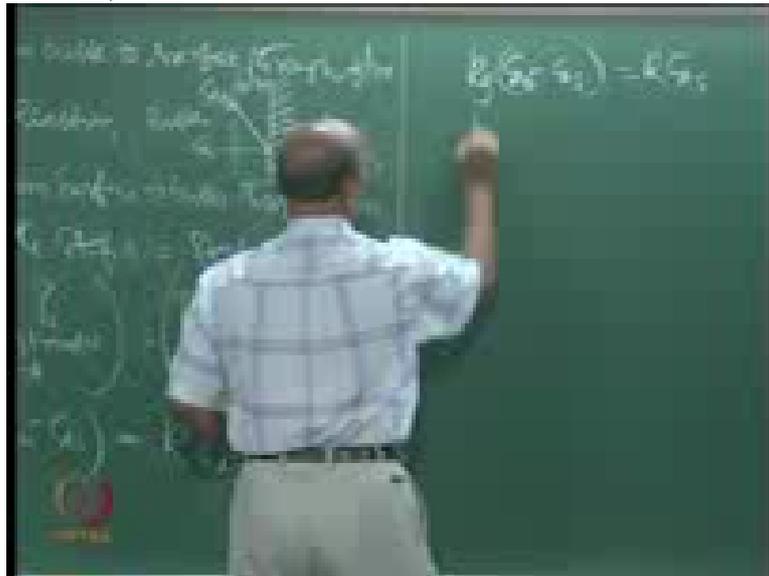
(Refer Slide Time: 37:24)



As engineer again I tell you that you know we should know how easily one can do things. For me which composition measuring is easy? Which concentration measurement is easy? C_A b.I do not have to go to the surface and then find out what is the concentration of C_A s.

That is why from this I can now eliminate C_A s. I can now eliminate C_A s. So at steady state when these two are same, then now we can, you can eliminate. So minus r_A , Ok first let me do this, $k_g C_A b$ minus C_A s equal to $k C_A$ s. So I am writing

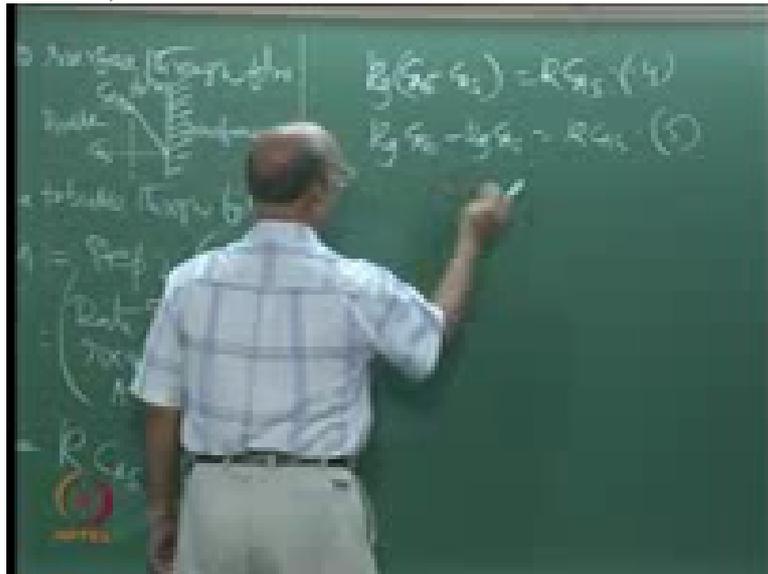
(Refer Slide Time: 38:05)



all spoon feeding steps.

C_A b minus $k_g C_A$ s equal to $k C_A$ s, C_A s. Ok. from there I think I have not properly putting the, Ok, from here I think this is 1, this is 2, this is 3, 4, 5. From 5 can I say that

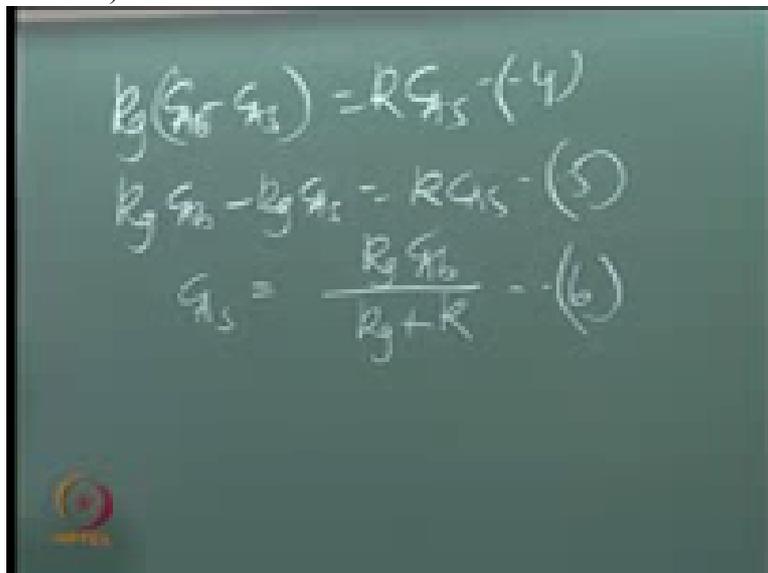
(Refer Slide Time: 38:30)



I have an equation C_A equal to $k_g C_A$ by, yeah, K_g plus K . So this is equation number 6.

So now, still my problem is not over. That means I should now

(Refer Slide Time: 38:51)



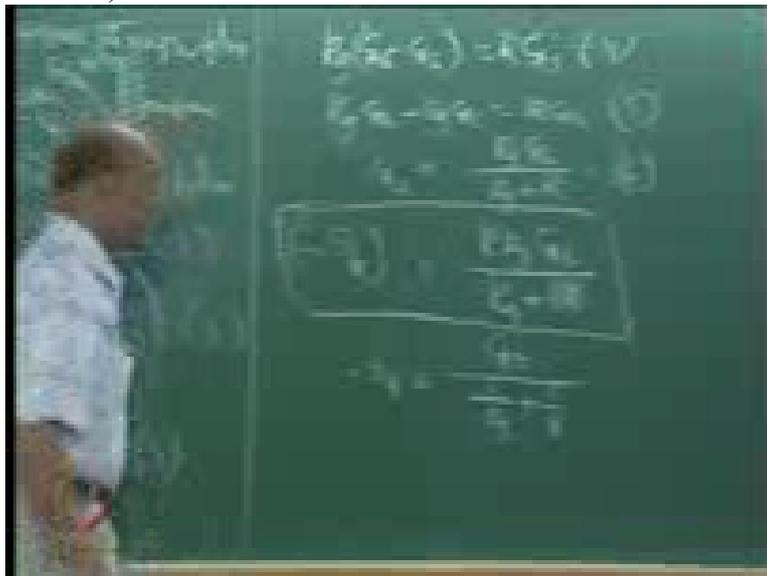
find out what is minus r_A . Right, how do I find out? I can either substitute that, the idea is that C_A I should not have in my equation. Why? If C_A is there, I have to go to surface and measure the concentration, right?

But without that I have to express the rate in terms of only C_A , bulk concentration where simply I can take the bulk gas and now try to find out what is the conversion there, or what is the concentration there, Ok. So that is why.

Now, so I can now use this equation or this equation because this is also equal to this or that. Now substitute easy one. Always humans go for easy resistance. So this is the one I can take. Now substitute for this k_g , for this C_A , equation 6. So then what you have?

You will have minus r_A equal to $k_g C_A$, k_g divided by $k_g + k$. So this is the rate expression for it. And this also can be nicely written as minus r_A equal to, why nicely means just to get 1 by k_g by 1 by k .

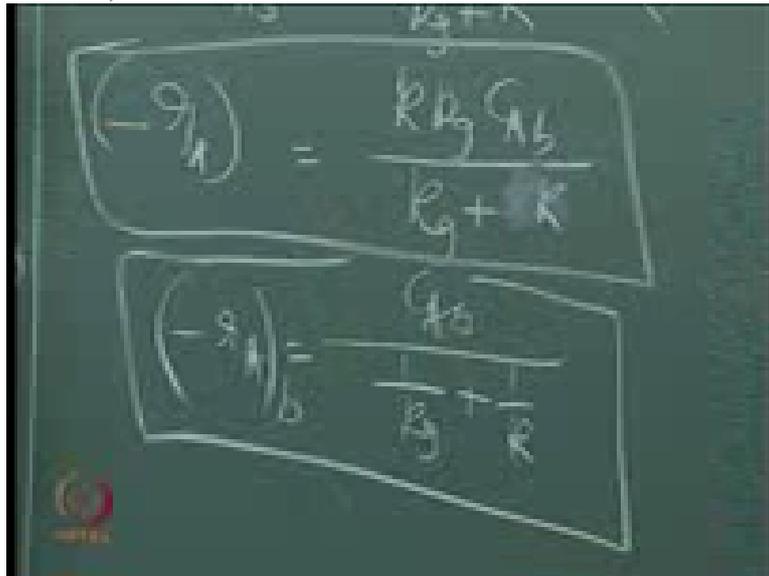
(Refer Slide Time: 40:07)



So this is the rate expression. Ok, now I also asked you this question in zeroth test, what is the bulk rate of reaction? Or overall rate of reaction? Ok? In heterogeneous system that will come.

This is called bulk rate. Why?

(Refer Slide Time: 40:31)

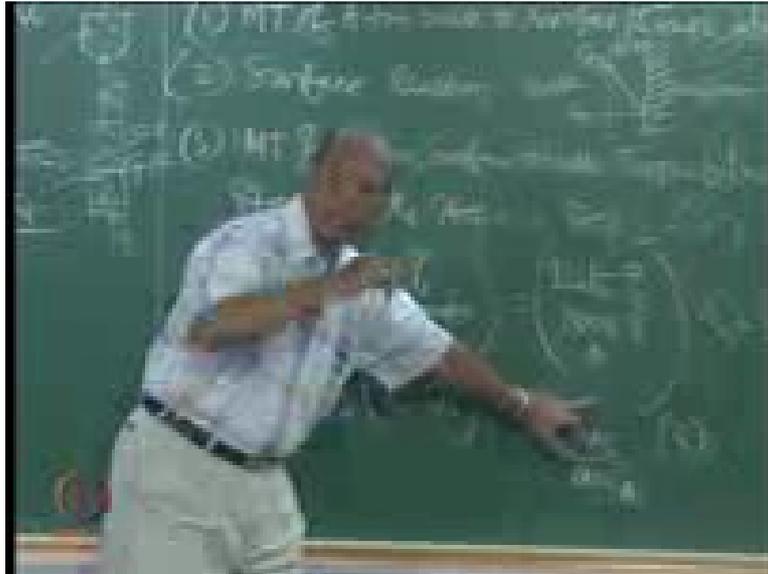


Because now this rate expression is only based on bulk concentration, bulk condition, Ok. So the name of this is either bulk rate, bulk slash overall slash observed, observed, any other name, Rahul, remember? Yes global, yeah so many names, global rate of reaction, yeah.

So that is the name given to heterogeneous reactions because all heterogeneous reactions, the method is same. All heterogeneous reaction. Now I can tell you now that if I have a complicated equation then I will have here M plus, do not write that, I am just telling you, yeah. This is the equation. This side it will not change.

But I told you mathematically it will be more complicated. Now I have to find out anyway C A s. So whatever form, you can also have simply

(Refer Slide Time: 41:43)



quadratic equation $C A s^2$, then you have the quadratic equation $C A s^2 + C A s + C A b$ these are constants anyway. Then you have to solve a quadratic equation and get what is $C A s$ and substitute $C A s$ in, yeah, in any equation, either this equation or this equation. That is what is the overall picture, approach to all heterogeneous systems, approach to all heterogeneous systems, Ok.

One more thing also I have to tell you here is, this equation is a wonderful equation for the discussion, for discussion. So I think you know in heat transfer you should have heard what are resistances, right? Here also $1/k$ is a resistance. $1/k$ is a resistance.

That means, Ok so I say that I have, at very high temperature, at very high

(Refer Slide Time: 42:38)



temperature I want to simplify that equation, special cases. Ok, as special case as

(Refer Slide Time: 42:48)



when mathematically telling k tends to infinity. That means

(Refer Slide Time: 42:54)



I have very high temperature and we know that when we have very high temperature, Ok, k will be very, very large because exponential increase.

So then what will happen to that equation, ah number, this is 7, 8. Ok. So now, yeah minus r A equal to, minus r A B equal to

(Professor – student conversation starts)

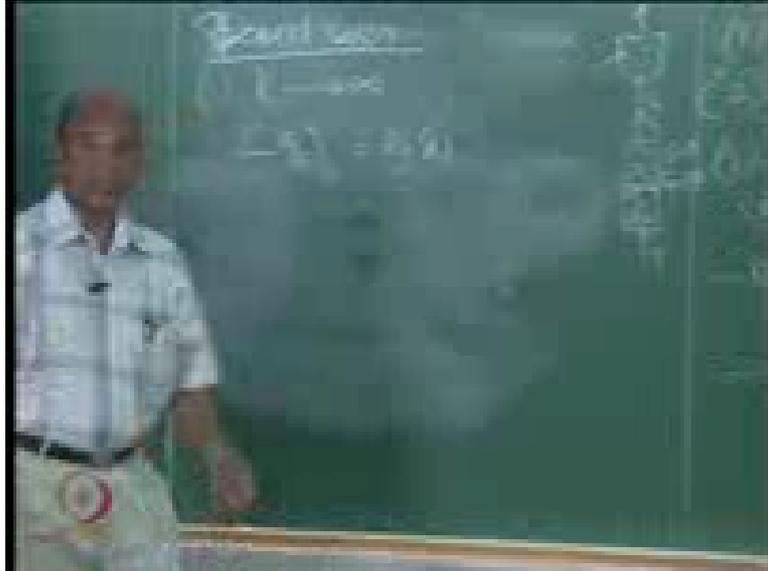
Student: 1 by C A b

Professor: k g into

Student: C A

Professor: This is

(Refer Slide Time: 43:30)



what is very, very important thing in heterogeneous systems, Ok.

(Professor – student conversation ends)

Now do we have anywhere rate constant there? Now it is controlled by which phenomena? Mass transfer. Why? Because that is the slowest step, Ok. I told you no, sometimes back you have one example. I may have, I told you also which is the costliest car, which can go to 500, 600 kilometers per hour but in Mount Road if I go, if there are 10 buffaloes walking very slowly, what is the use of my 500 kilometers per hour? No use. It is controlled by only buffaloes. And what is the buffalo walking speed? Abdul?

(Professor – student conversation starts)

Student: 5 kilometers per hour

Professor: That is all, logical. 5 kilometers per hour. You see 500 to

(Refer Slide Time: 44:17)



Student: 5

Professor: 5 kilometers, so who is controlling now?

Student: Buffaloes

Professor: Ok so that is what is rate controlling step,

(Refer Slide Time: 44:25)



right? And also I think when time comes I will tell.

(Professor – student conversation ends)

Another example also I have. You are hungry. When you are very, very hungry, mess, all of you are very hungry after the class and then go to the mess. Imagine that they are only serving idlis. Idlis are coming over the conveyor belt, Ok. So you all of you stand this side

and that side, idlis are coming. When you are very hungry, practically can you see any idlis on the conveyor belt? Because the moment idli comes, 0:44:54.1.

(Professor – student conversation starts)

Student: (laugh)

Professor: Over. So on surface it is almost clean. But may be how much time you can eat? It may be half an hour you ate idlis. Ok, continuously. After eating half an hour what will happen to your hunger? Saturated.

(Professor – student conversation ends)

So once you have that saturation what will be now concentration of idlis on the conveyor belt? Full, nothing will happen. Everything will be going on. So that is what is the profiles now we are going to draw with these two examples. Because now your hunger was so fast and you will scold the cooks if they are not quickly supplying the idlis. So what is rate controlling step at that time?

(Professor – student conversation starts)

Student: Hunger

Professor: Not hunger, hunger you have. Mass transfer. Cook, because he is not able to produce.

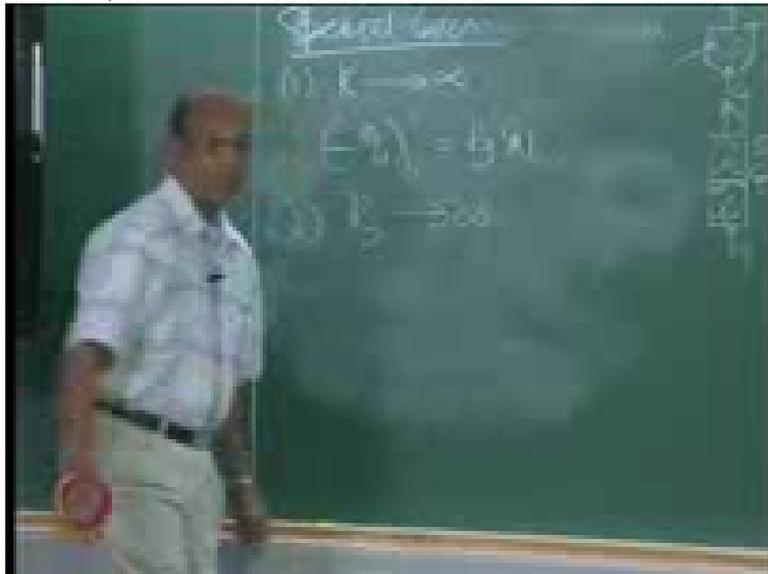
(Professor – student conversation ends)

There is no sufficient mass of idlis on the conveyor. You have the reaction, you know hunger. Tremendous reaction is going on inside, Ok, capable of, you know, eating anything. But you are not able to eat because there is no mass transfer. Ok no idlis. That is the same thing that is happening.

Particle may be at very high temperature capable of converting any molecule coming on to the surface. But where are the molecules? Cook is not supplying. So mass transfer is controlling. So that is what it means. Mass transfer controlling.

And when you have the other thing that is $k \rightarrow \infty$

(Refer Slide Time: 46:14)



that means, when do you get this case? This is M T controlled. This is M T controlled. Yeah. In the second case $k g$ is infinity. Yeah, no resistance with the film. When can I get that? When do you get infinity?

(Professor – student conversation starts)

Student: High flow rate

Professor: Very high flow rate. You see

(Refer Slide Time: 46:44)



there is a relationship, as Reynolds number around the particle is

(Refer Slide Time: 46:46)



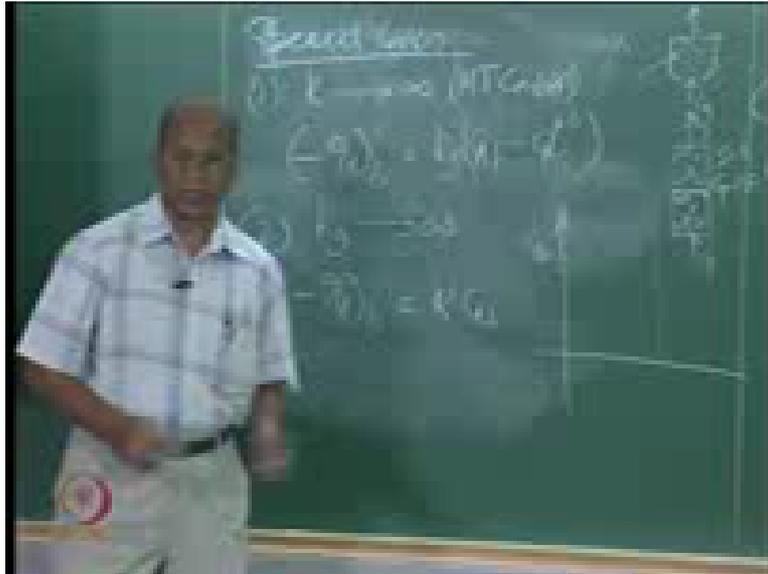
increasing your film thickness also go on reducing, reducing, reducing.

(Professor – student conversation ends)

But you know you do not have much use of that. Because by sending infinity velocity, residence time will not be sufficient, correct no? So that is why. That is the case, k g. So you can also reduce the mass transfer, increase mass transfer, increase mass transfer by increasing the velocity around the particle, velocity around the particle, Ok.

So then you have minus r A b bulk or observed is now K A s, no K into A b. This is mass transfer equation where, we can also write this is C A s which is zero on the surface. Ok, when I plot these, the profiles again, that is the film thickness and this is C b, C A b right for this one, when k equal to infinity how do I draw the

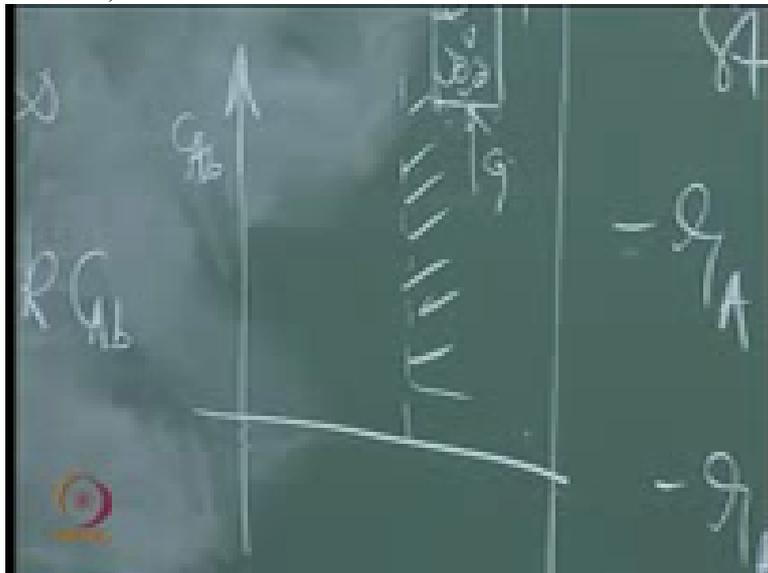
(Refer Slide Time: 47:47)



profile? Extremes.

k equal to infinity that means reaction is very, very fast, right. So this is surface, this is surface.

(Refer Slide Time: 48:01)



What is the concentration on the surface?

(Professor – student conversation starts)

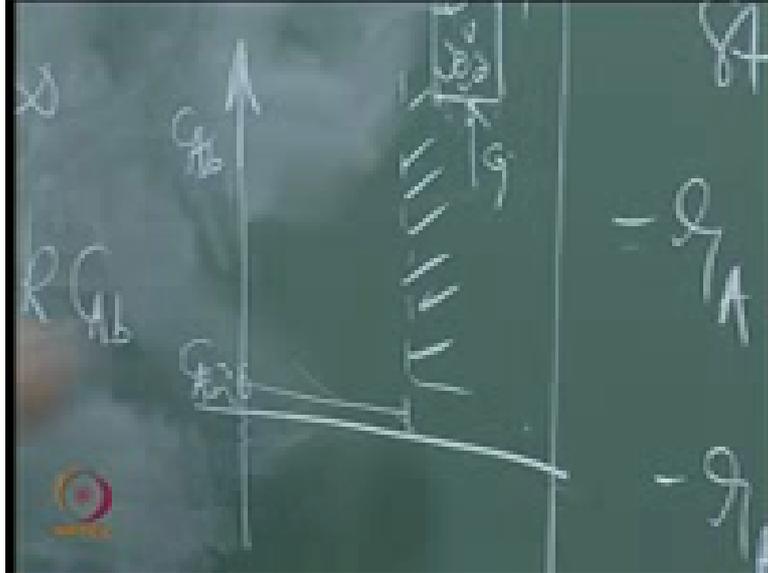
Student: Zero

Professor: Zero. Idlis, remember idlis.

(Professor – student conversation ends)

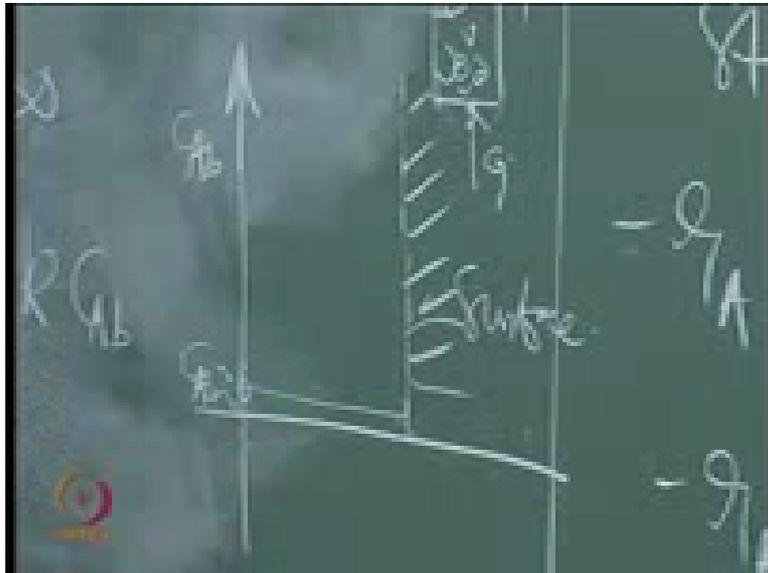
Reaction very fast means you are very hungry, so you can eat any number of idlis and on the conveyor belt you will not have any idlis left at all. That is zero. So that is why it may go to almost zero, like this. This is here, approximately C_A equal to zero on the surface,

(Refer Slide Time: 48:29)



this is the surface. Ok, this is surface, Ok,

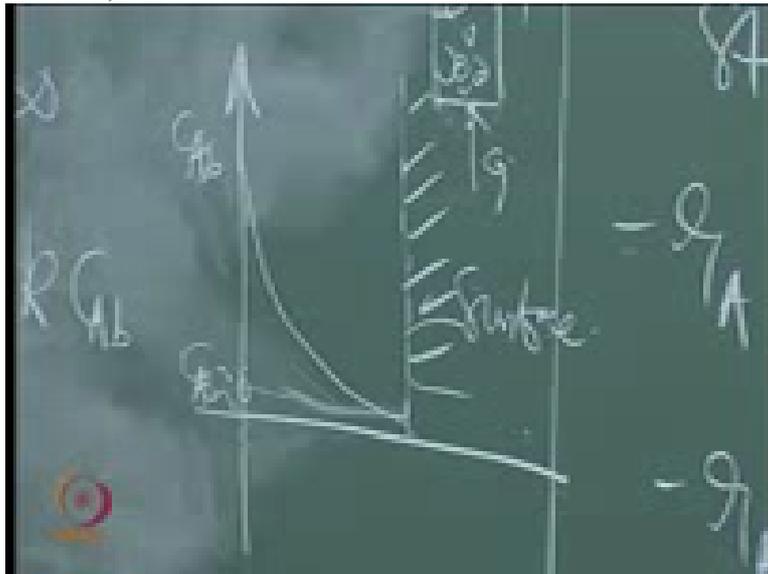
(Refer Slide Time: 48:36)



good.

Now that means I may write this one as something, shape also may be like this.

(Refer Slide Time: 48:42)



Ok, it is not sudden. Through the film you will have some concentration. But on the surface it is, on the surface, I know you have not understood.

(Professor – student conversation starts)

Student: Yes Sir

Professor: Yeah, why? What....

Student: After reaction, will 0:48:59.3?

Professor: Very good question. The concentration is zero, there is no reaction. Correct, what he said? On the surface. What is the meaning of that? What is the meaning of k equal to infinity?

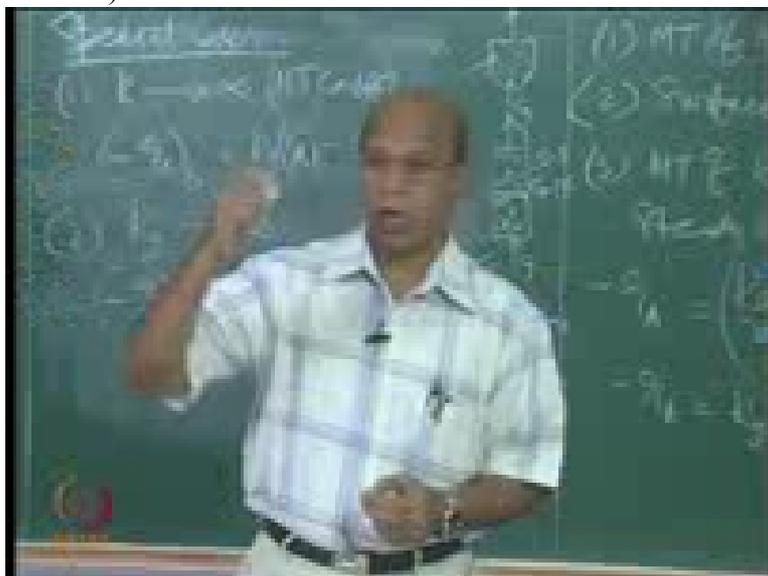
(Refer Slide Time: 49:14)



Student: No resistance

Professor: Surface is capable of

(Refer Slide Time: 49:20)



converting any molecule when it just comes there.

(Professor – student conversation ends)

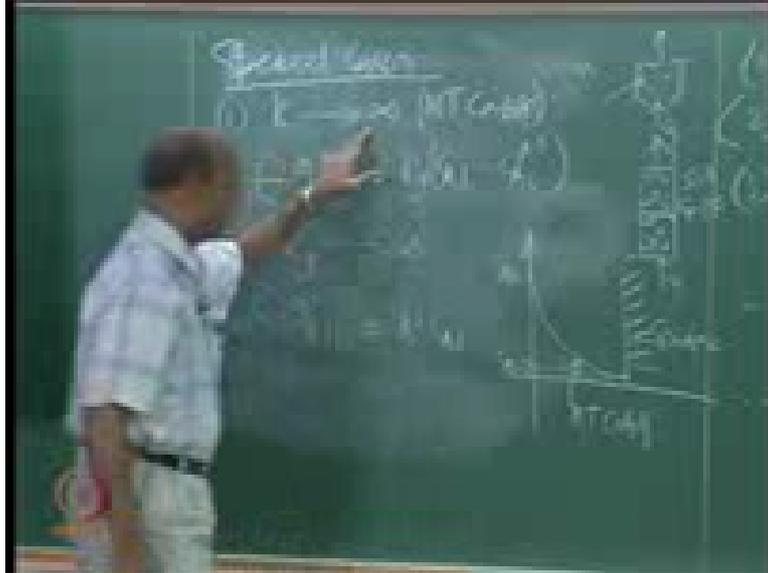
Does not mean that reaction is not there. Whatever molecule comes there, and also what you are drawing for? You are drawing for C A b, reactant, reactant. So the moment it touches the surface then it is converted to product.

Then what is the concentration of A? That is the meaning of zero. It is not L K G zero means no reaction, Ok. Extend, delta x mind, right? Yeah. So that is what is the meaning. Ok good, now this is the one.

Now my example is very easy to remember. When you are very hungry, Ok, idlis are coming. Ok, it is not that he is not supplying. But he is continuously sending may be 100 idlis for may be, per second or so. But now immediately all of you are so hungry, the moment idli comes you are eating. That means there is no rate of reaction? There is. You are eating idlis. Right. That is rate of reaction.

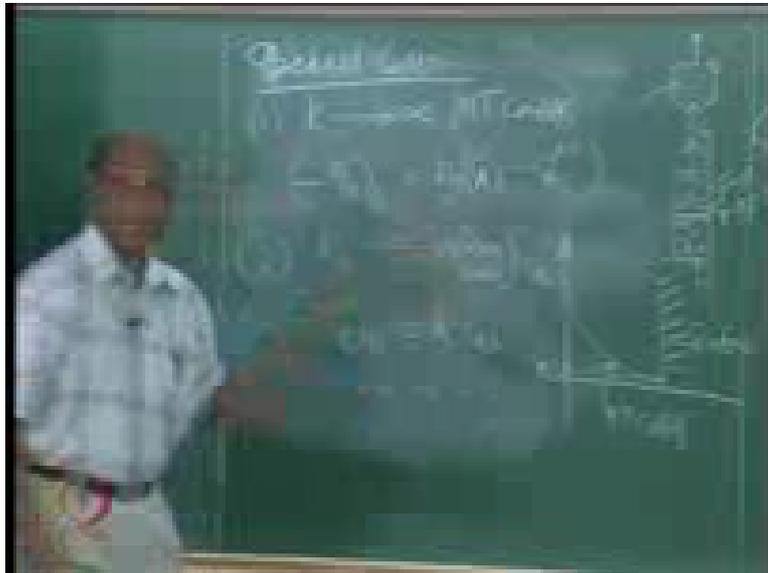
But on the surface what is idli concentration? Zero, that means you do not find any idlis. That is what is the meaning of it, right. Ok. This is mass transfer control, Ok This is M T controlled. Yeah, yeah the other one. What is the other one?

(Refer Slide Time: 50:41)



Reaction controlled. Yeah, we have to also write here, reaction controlled.

(Refer Slide Time: 50:52)



Yeah, in reaction controlled how do I draw? When you are satisfied, you are not able to eat anymore, what is the concentration now? All the idlis what you have are also simply coming. So what is the concentration now?

(Professor – student conversation starts)

Student: Almost same.

Professor: Almost same, that means how do I draw that line? Straight, excellent. This is CA b, everywhere. This is which control?

Student: Reaction controlled

Professor: The reaction is

(Refer Slide Time: 51:21)



very, very slow. The fellow is not able to convert, right?

(Professor – student conversation ends)

On the surface, reaction is very, very slow. So that is why that entire surface is flooded with molecules. Because the surface is not able to convert those molecules into products. So that is why everywhere you will have C A b.

Whereas in the other place it is able to convert so fast, practically you will never see, practically you will never see the A molecules reactant molecules on the surface. But in reality you will have this kind of profile.

(Refer Slide Time: 51:57)



So this equation, this is the equation, this equation 8 is this, this is equation 8. This one is equation, mass transfer control? Yeah here I have to put no, this is 9, this is 10. Mass transfer control, yeah Ok 9, so this is equation 9, and this is equation 10,

(Refer Slide Time: 52:35)



you see.

And now when you want to design a reactor. for example you know the equation now. I think I will just take this example and then I leave it to you. Now let us say that I have a packed bed where I am now, I am trying to design to find out what is the volume of the reactor Ok, and we can also convert it to weight of the catalyst later, volume and you know that packed bed is a plug flow reactor.

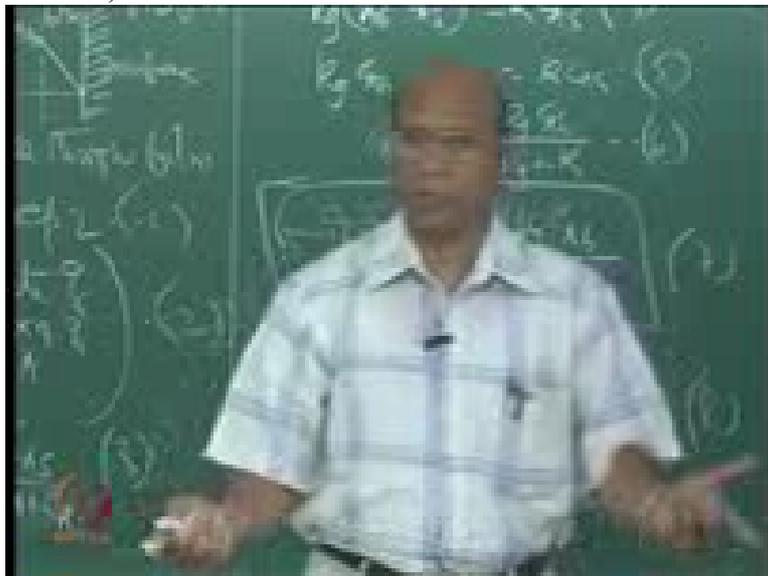
So which design expression you take?

(Refer Slide Time: 53:05)



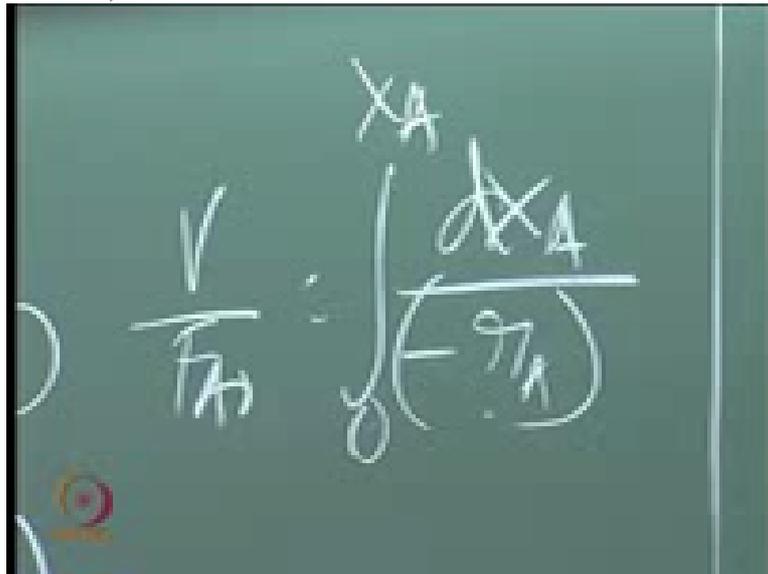
This is a rate no, which we got from heterogeneous kinetics. Minus r_A I have, F_A naught I have, $M_B A$, already people have given me, right and then minus r_A I have, now if I know conversion, I can calculate volume. Or if I know volume I can calculate conversion. If it is a new reactor, I do not have volume.

(Refer Slide Time: 53:24)



So that is why I will say that Ok, 90 percent conversion. How much is the volume. So what is the equation I have to use? Very good. V by F_A naught equal to, so V by F_A naught equal to zero to X_A d X_A minus r_A . So this minus r_A is, if it is mass transfer controlled,

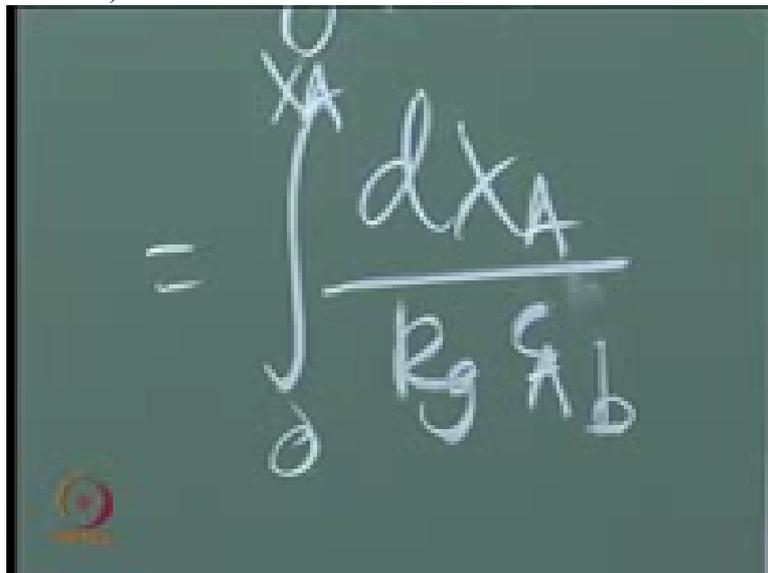
(Refer Slide Time: 53:48)


$$\frac{V}{F_A} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

what is equation you are using here? Yeah that is the beauty there.

This is dX_A integral $k_g C_A b$, zero to X_A . You see now? It is actually a

(Refer Slide Time: 54:02)


$$= \int_0^{X_A} \frac{dX_A}{k_g C_A b}$$

reactor where nothing connected with reactor is there. That means reaction rate constant is not there. It is only the mass transfer coefficient what you require, mass transfer coefficient. So this is what is the meaning of heterogeneous reaction system.

So under some conditions, it is only the physical steps that are controlling but it is not the chemical step which is controlling. Chemical step is pure chemical reaction. Now that

chemical reaction is influenced by mass transfer step. If there is not sufficient amount of mass transfer to the surface, reaction also is poor.

That is the difference between heterogeneous and homogeneous whereas, yes, whereas there is no this kind of mass transfer availability is not at all there in homogeneous. It is there all the time you have sufficient mass, yeah Pooja?

(Professor – student conversation starts)

Student: Calculate volume by taking it as a batch reactor also?

Professor: Batch reactor again

(Refer Slide Time: 54:58)



Student: You told us no, how to

Professor: C_A by C_A naught

Student: How to convert, means relationship between C and V in batch

Professor: Same thing what you have done in that problem. You have already done that problem. So if you have contacting pattern as batch

(Refer Slide Time: 55:14)



then what you get is C by $C A$ naught equal to, you know that integral, that integral is same as this integral. That will not change.

Student: 0:55:23.1 Batch

Professor: No, no, you are talking about again volume change and all that. Did I say any volume change and all that here?

Student: But Sir, still it is heterogeneous reaction

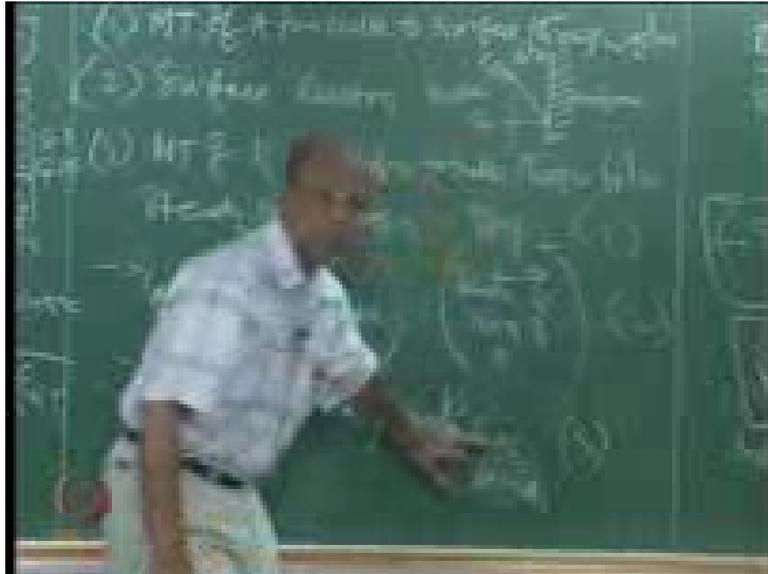
Professor: Heterogeneous reaction does not mean you have volume change. If I have only A, 1 mole, 1 mole going to 1 mole, where is the volume change?

(Professor – student conversation ends)

See again please do not get confused. I think Pooja that question is good because you know; all Indians are brothers and sisters. Ok, so we do not know. Definitely same confusion also you may have. Heterogeneous does not mean that volume changes. Volume change will come in the reaction only when you have mole change.

Here I have taken simple first order, A going to B, or A going to R. So that is why that problem you should not imagine at all. Ok. So if there is real change in the moles, automatically this rate equation will change.

(Refer Slide Time: 56:14)



This is not the same rate equation what you get, you know if you want to write in terms of conversion and all that.

Whenever the concentration is converted that equation is different for, if you have volume change that volume change will come when I come to again the homogeneous reaction. So idea is now this, where we can clearly say what is the difference between heterogeneous and homogeneous. And under certain conditions you do not have to worry about reaction rate constants. You do not have to worry about what is the order of reaction, but you have to worry about only mass transfer coefficient.

Mass transfer coefficient. You know, can you give me one example where this can happen in heterogeneous system? It is very, all the time it happens. Every day you see.

(Refer Slide Time: 56:55)



Every day, when you go to kitchen and all that also, you see.

(Professor – student conversation starts)

Student: Tea

Professor: Not tea. In kitchen you can make tea, but what is making tea?

Student: Flame

Professor: Flame. What is that? Combustion. Yeah. In all combustion reactions it is

(Refer Slide Time: 57:12)



mass transfer equation. It is the oxygen supplied to, you know, to the flame. Why?

Student: Oxidation reaction

Professor: So?

Student: Oxygen is required for it.

(Refer Slide Time: 57:24)



Professor: Oxygen is required. I am saying that all the time it is that oxygen supply to the flame that is controlling rather than reaction.

(Refer Slide Time: 57:35)



Student: The product is also formed

Student: From air or

Professor: Pure oxygen also you can supply but even then it controls.

Student: Combustion

Professor: That is the point. Ok, Savita that is the point. You heard of him?

(Refer Slide Time: 57:47)

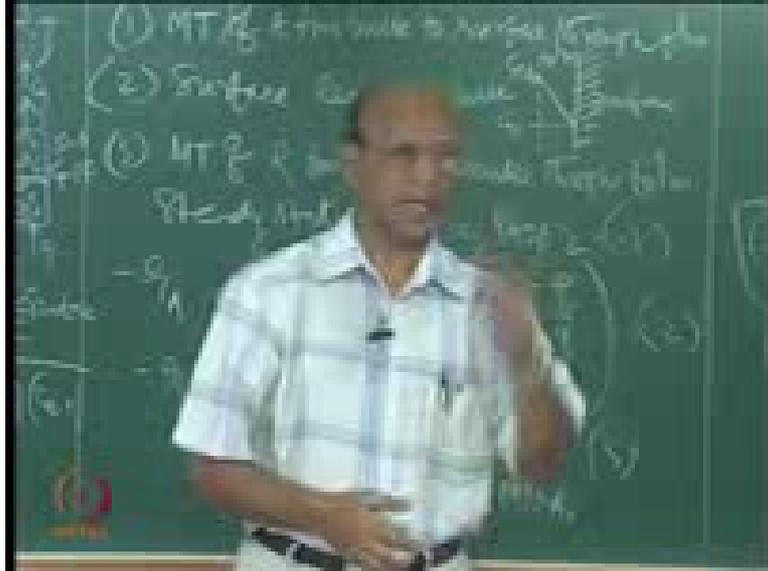


You have not heard of him no? He said something, temperature.

(Professor – student conversation ends)

In all combustion reactions, temperature is very, very high.

(Refer Slide Time: 57:54)



You want to find out with your finger? Ok, so if it is not burning, not much combustion. All combustion reactions, you know the moment you see that red flame you know what is the temperature? That is approximate estimate? How much it will be?

At least, cigarette smokers, do not smoke cigarette it is very bad for health. But unfortunately if you are smoking, you should know the temperature. Ok, what is the temperature when you are, that means that tip will be glowing? You know what is the temperature at that time?

(Professor – student conversation starts)

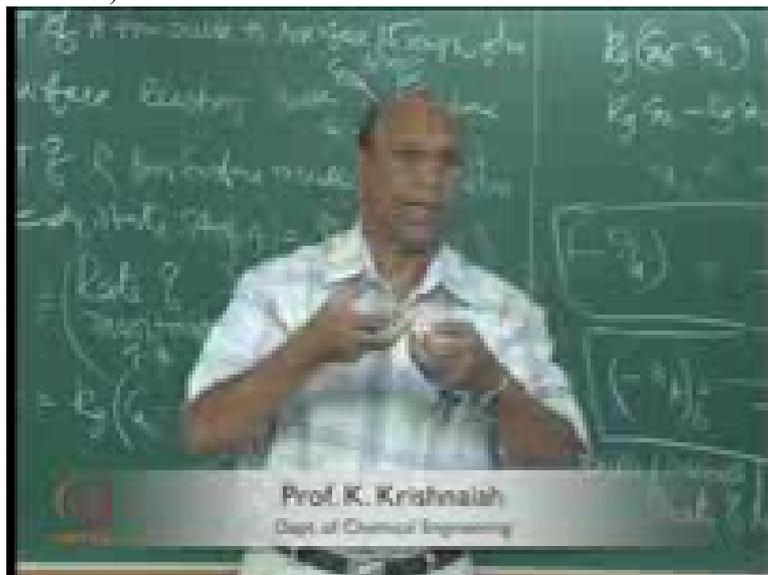
Student: 85

Professor: 85. 600 degrees Centigrade. 600.

(Professor – student conversation ends)

Ok and you know what is that buy doing 0:58:37.2, like that what are you doing, you know? You are only supplying mass, oxygen. When you are doing 0:58:46.0 like this, it is a porous, so it sucks oxygen from the, not only oxygen, air and all from the surrounding air.

(Refer Slide Time: 58:52)



Ok. Because it is porous, you are able to, 0:58:54.6 like that you are able to do.

That means it is now taking more oxygen, the glow will be more and more red. I do not know whether you know smokers, now you start smoking as a smoker. And if they do not, 0:59:05.8 like that if they do not do, what will happen? You do not see the, glow will not be there. So mass is supplied there, mass transfer, you see how beautiful! Even cigarette smoking there is lot of chemical engineering.

It is heterogeneous reaction, oxygen has to be supplied. Ok. It is a porous one. That is why if you do not take porous one and then you cannot smoke cigarette at all if it is not porous. Correct no? How do you supply oxygen? Because it is porous 0:59:34.6 like that you do. Then oxygen is coming inside. Not only oxygen, air and all that is coming inside. So that is why you are able to smoke cigarette.

Tell your friends. Because you are doing 0:59:45.3 like that, more stress on the lungs. Not only more stress, high temperature because now air is getting heated through that flame going into your lungs. So that is why 100 percent guarantee damaged lungs after 10 years. That is why you should not smoke cigarettes, Ok.

You see, from we started with heterogeneous, heterogeneous reactions and stopped with cigarette smoking.