Chemical Reaction Engineering 1 (Homogeneous Reactors)
Professor R. Krishnaiah
Department of Chemical Engineering
Indian Institute of Technology Madras
Lecture No 22
Kinetics of Homogenous reactions

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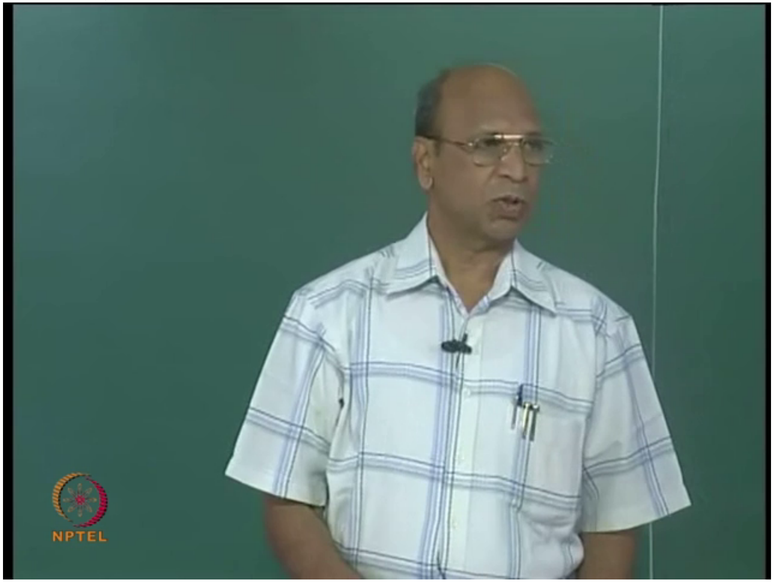

Shall we start now? So this slurry reactor I think till here, I have also written in between those steps,

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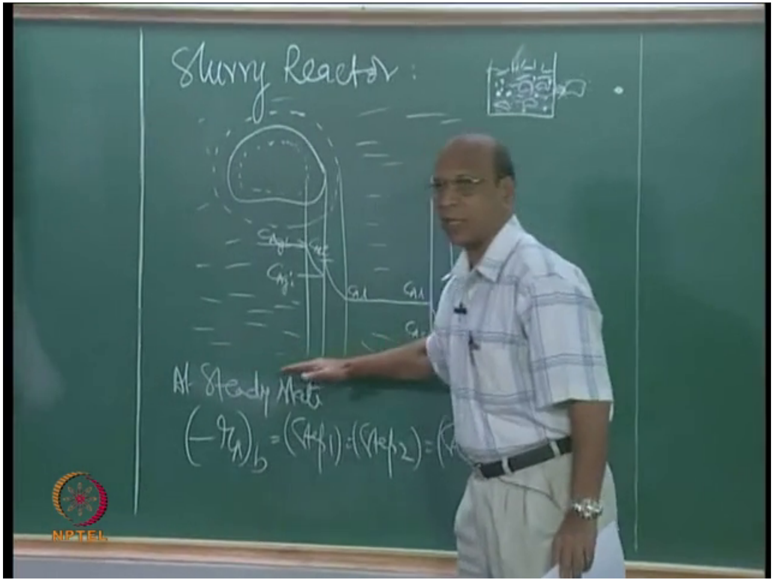

step 1, step 2, step 3, step 4, and what is left now is writing an equation for each and every step here. And step 1 and step 2, step 3 is mixing, no? Mixing of A in the bulk, so that will not contribute, so that is why we have not written. Step 4, Oh that is all, step 5.Oh yeah, step 4 and step 5, right?

So these are the 4 steps which we have to take into account and as I told you step 1,

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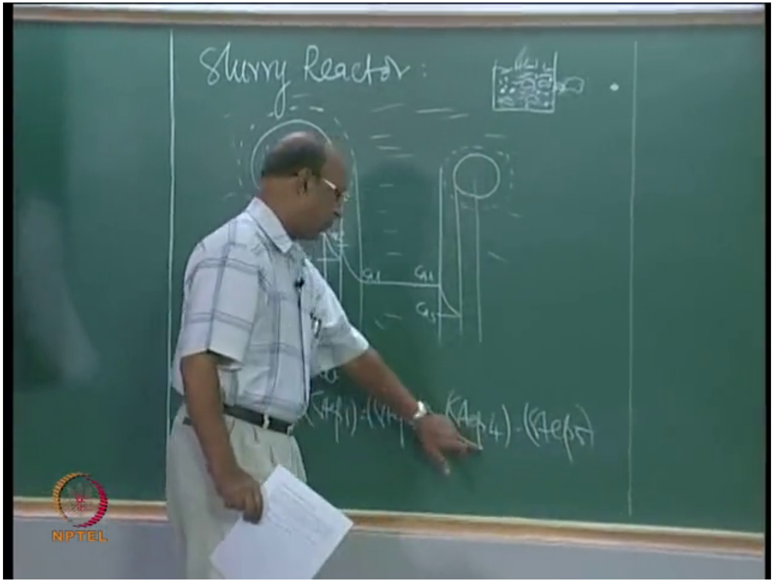

step 2, step 4, step 3 also are all mass transfer steps, right. And again you have to use only that simple convective mass transfer equation, right? Ok.

So that is why this, this I am writing now for step 1, step 2, step 3 all equal to, so minus r A b bulk will be, we have, yeah k g a g, I will let you know what is a g, C A, C A b, C A g b minus C A g i. That is why

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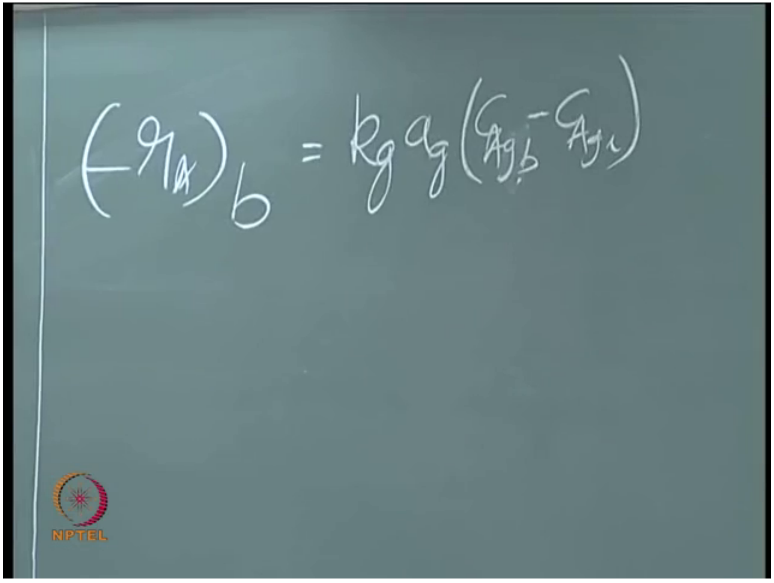

this diagram will,

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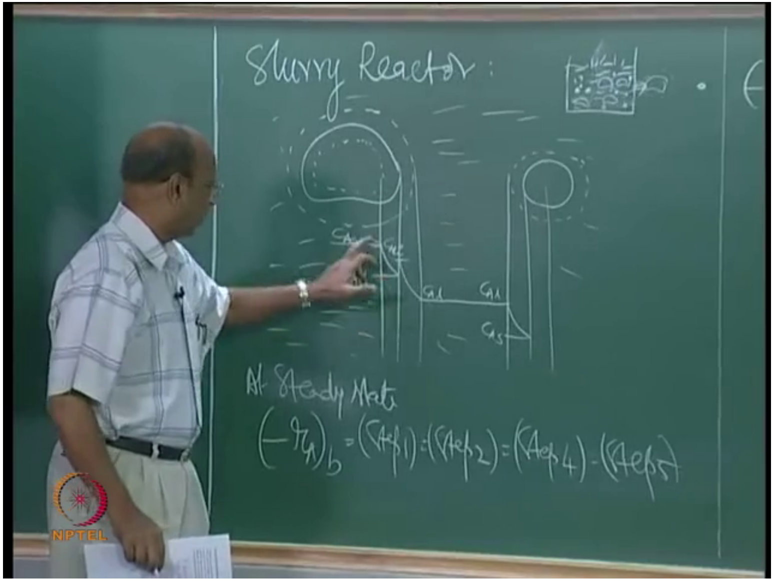

will be very, very good for you because you can identify what is the concentration gradients, right? So this is the first

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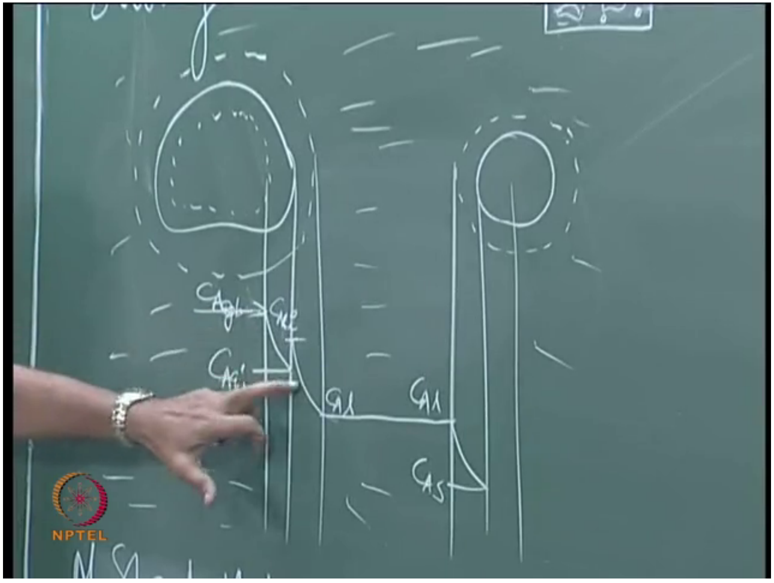

concentration gradient in the film.

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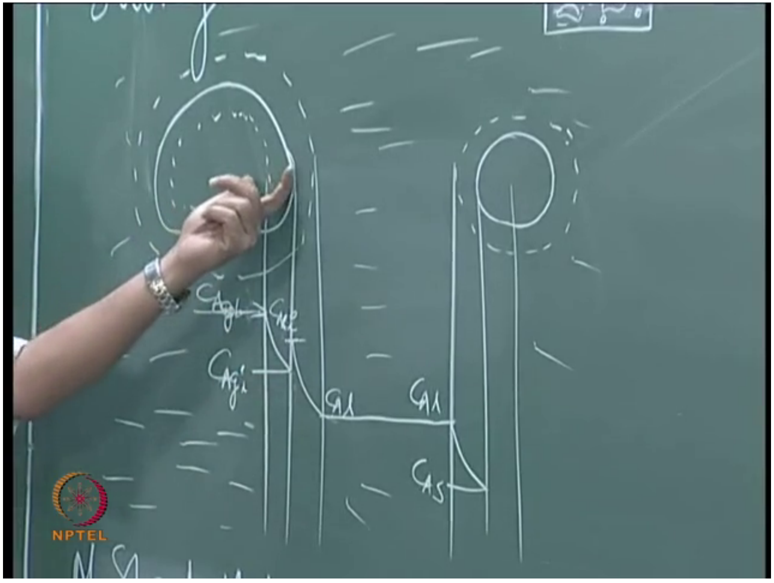

What film is this? Gas film. Then you have the liquid film. Through liquid film we will write here as k l, yeah ag, now what are the concentrations now? For this one?

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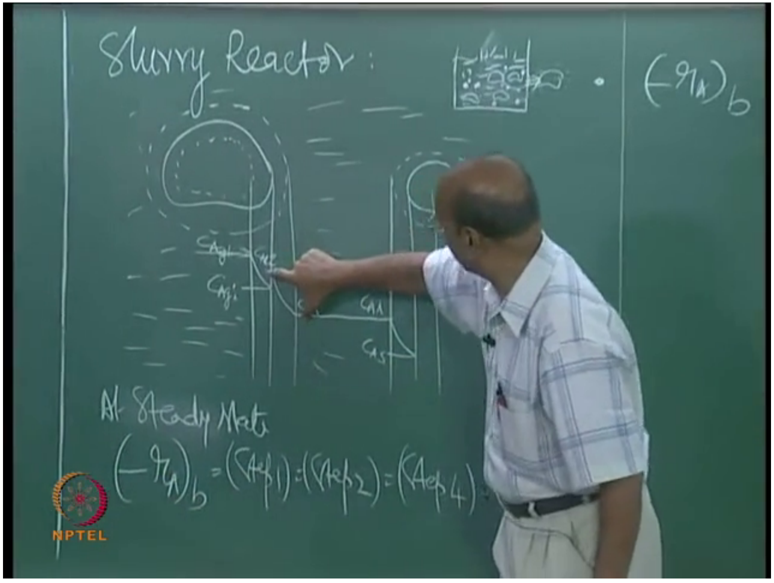

(Professor – student conversation starts)

Student: C A l minus

Professor: Yeah C A l i so that means concentration of A in liquid, right, but this earlier one is gas, you cannot write here liquid.

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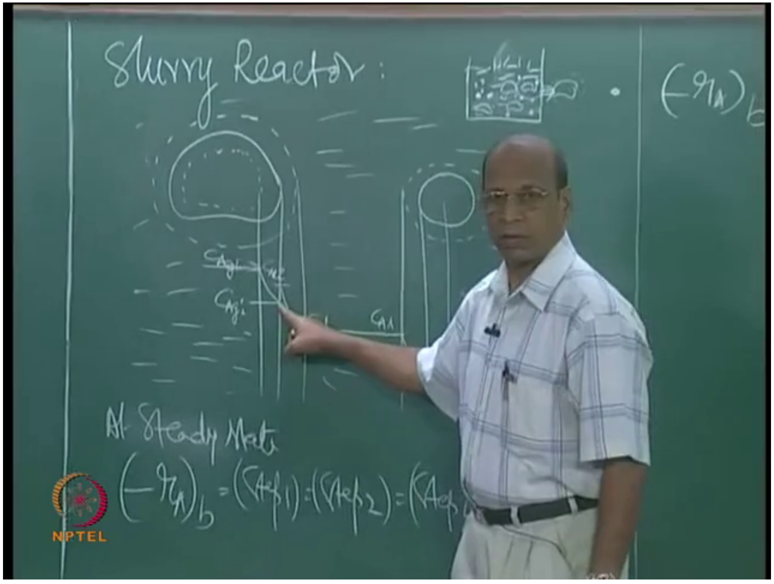

Because gas concentration is, the way you calculate is different. Liquid concentration is different. That is why you have to be careful there.

(Professor – student conversation ends)

So that is why here C A, C A l i, minus what is the C A l, that is the concentration gradient here. Now through the film

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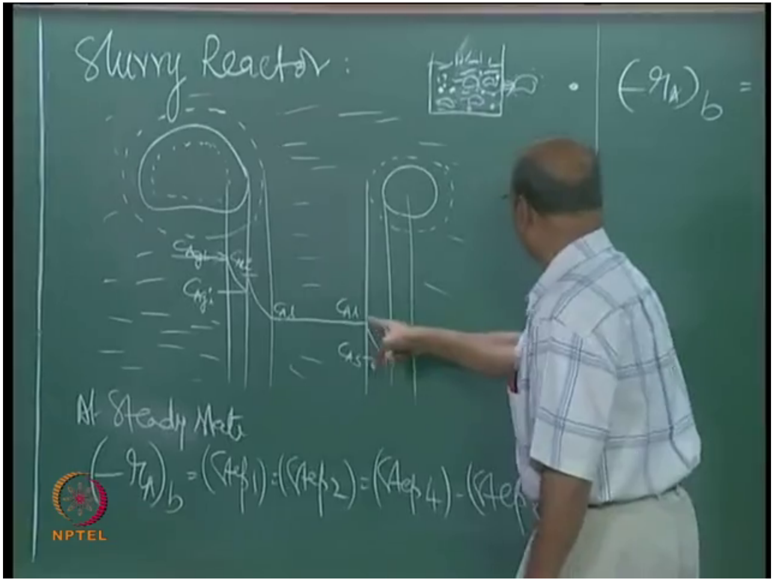

which is around the particle, around the catalyst particle, we have, yeah, this we call it as generally k c, this also we call a c, then we have C A l minus C A s, Ok. This is again this concentration gradient.

That is why this

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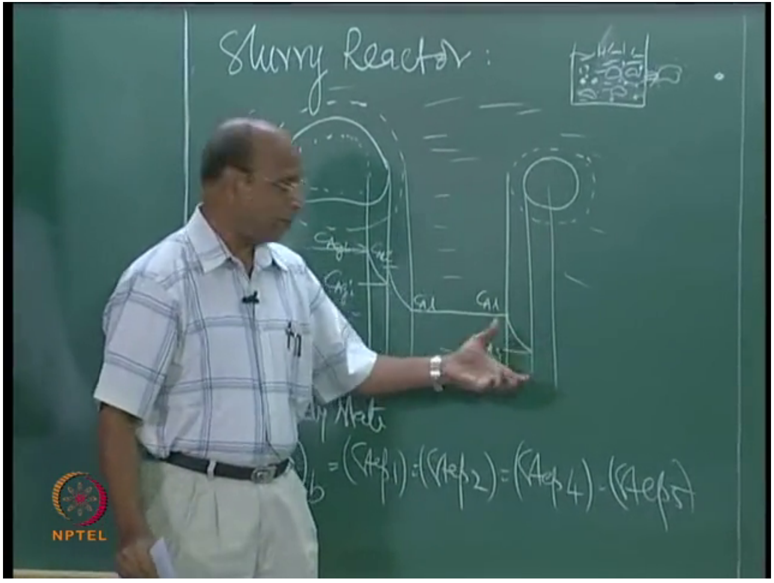

imagination is very, very important in all heterogeneous systems, Ok.

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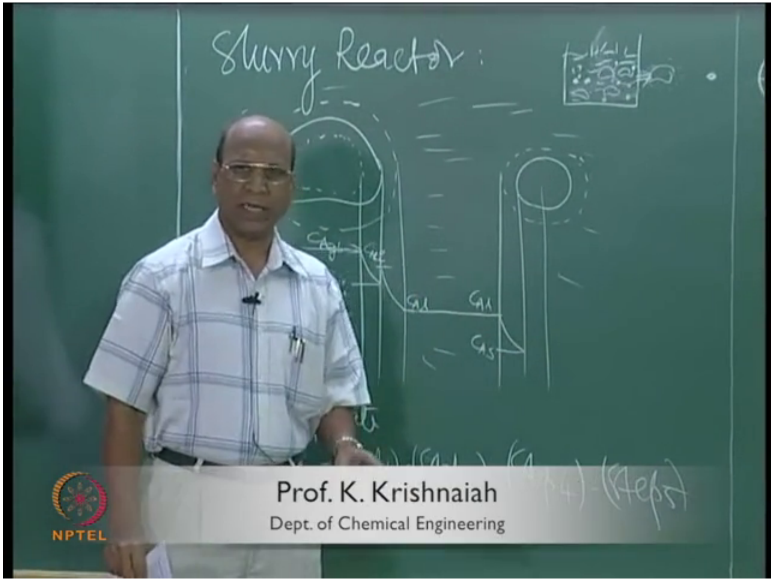

Why that imagination? That will give me clear picture of what are the equations I have to write. And to get to this level of imagining and then writing the diagrams, you know these pictures, you need lot of information in your mind for the process. All these things are only in the mind. And then that mind you translate, this one, this one and afterwards

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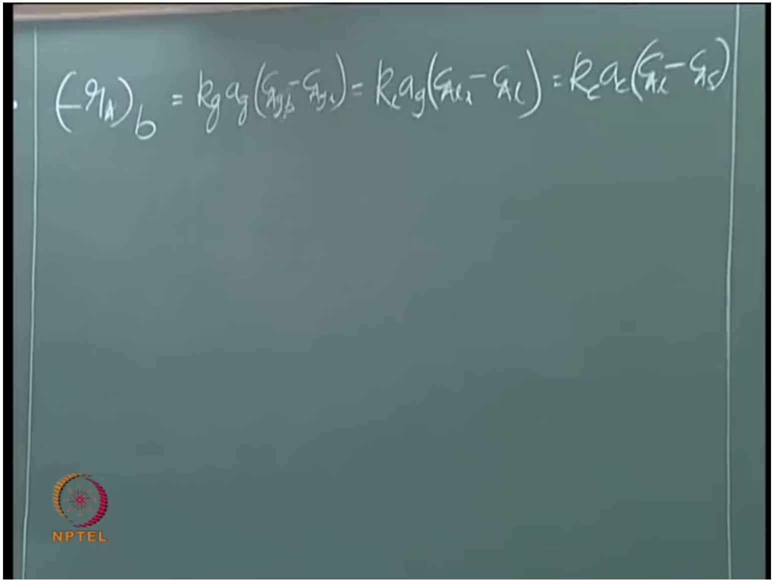

$$(-r_A)_b = k_g a_g (C_{Agb} - C_{Agi}) = k_L a_g (C_{ALi} - C_{AL}) = k_c a_c (C_{AL} - C_{As})$$

this one on the paper. Then it is very easy for you to write mathematics, right? So that is why we started that.

Now what is the next step? Next step is rate of reaction.

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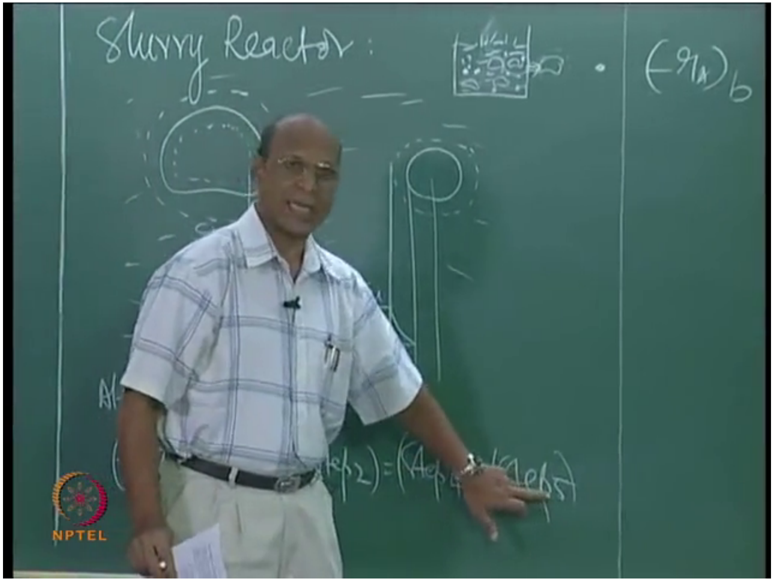

But this rate of reaction step, again imagination, you know it is not imagination. We have to find out separately without all these whether it is first order, second order or you know, some orders, right? Or it need not be first order, second order. It can be even any crazy type of equation, right?

But for simplicity, we will now take this one as simply k reaction, simply we will write k only. a c C A s that is where the reaction is taking place,

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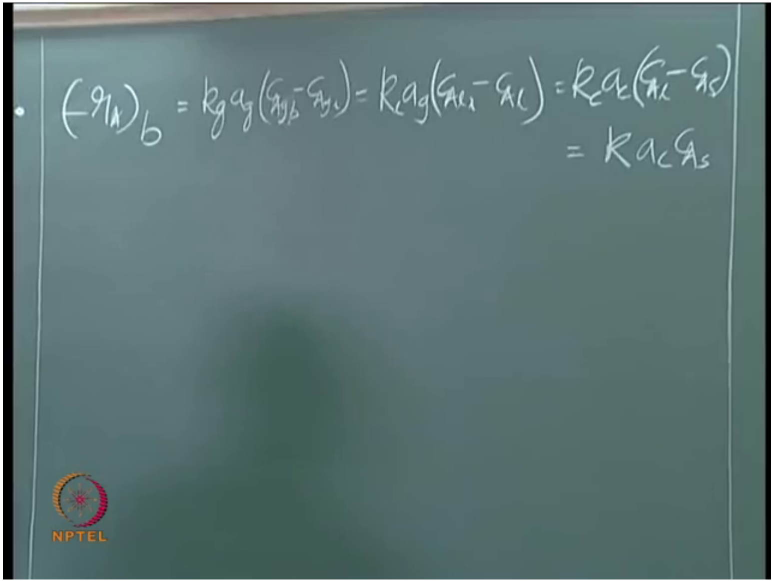

$$(-r_A)_b = k_g a_g (C_{Agb} - C_{Agi}) = k_L a_g (C_{ALi} - C_{AL}) = k_c a_c (C_{AL} - C_{As})$$
$$= k a_c C_{As}$$

Ok on the surface, good. So if it is porous particle, then you have another gradient here. It is inside. This gradient will be a function of r.

That means if I take the particle

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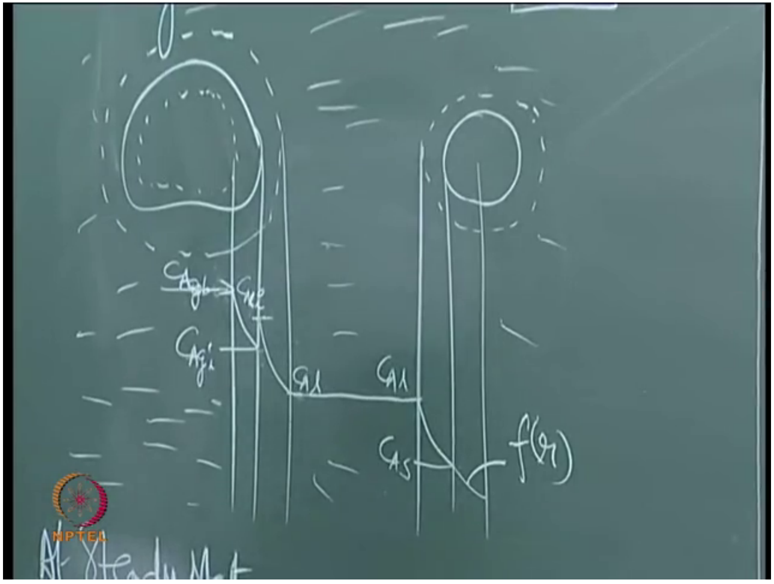

and then look at the concentration how it is changing, right so the air is diffusing through the pores and definitely it offers resistance and then you have the concentration gradient.

You know how you can beautifully you can take care of that by what is called effectiveness 0:04:36.5 factor. So this is the rate of reaction. This multiplied by eta; eta is the effectiveness factor which you would have heard of, right? Because most of you have taken two courses.

So catalytic reaction, there is what is called an effectiveness factor where the rate, the actual rate divided by the rate at bulk conditions, at bulk conditions, if it is isothermal reaction then always inside the particle you will have less concentration. And

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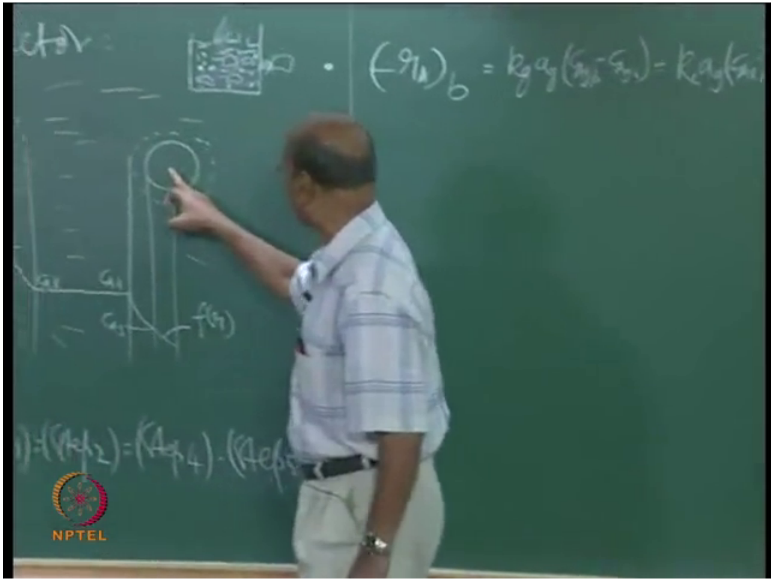

outside you have more concentration. Ok, isothermal, right?

So that is why the rate of reaction based on bulk will be more than rate of reaction based on the concentration profile that is inside the particle. So that is why you get effectiveness factor less than 1. This all these details again we have to discuss in the course Chemical and Catalytical Reaction Engineering, Ok. Good.

So that is why, that also can be taken by simply multiplying by eta; eta is a wonderful concept in the chemical reaction engineering. That also we can discuss in the next course but right now we are assuming non-porous particle.

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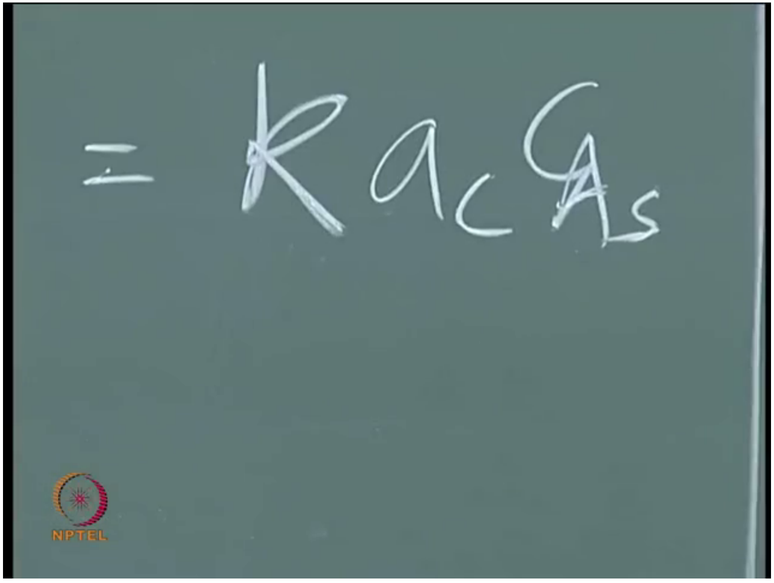

So that means there is no internal diffusion and all that coming. So simply it is, this constant multiplied by C A s, Ok. Now this is the equation.

So if I take this one as 1, this will be equation 2, yeah. So here, I need a

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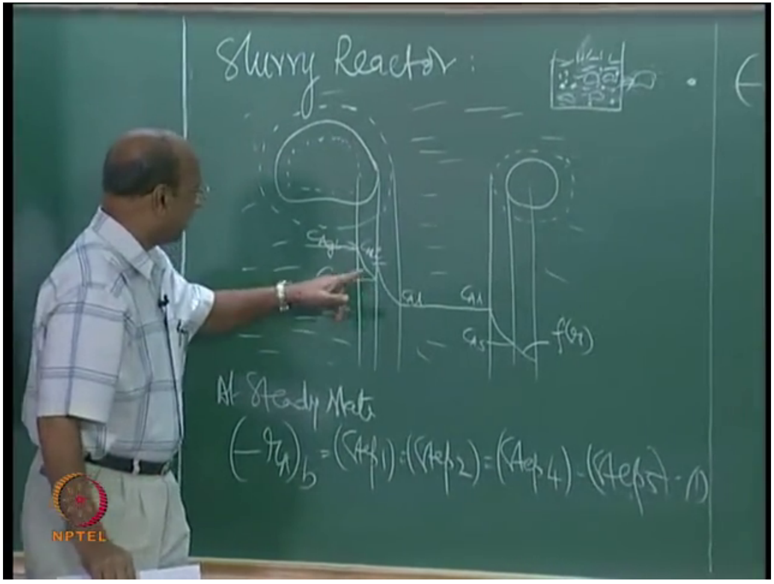

relationship at this point, at this point. That means C A g is coming to the interface. Now it is dissolving. After dissolving it shows C A l. C A l i, therefore at interface

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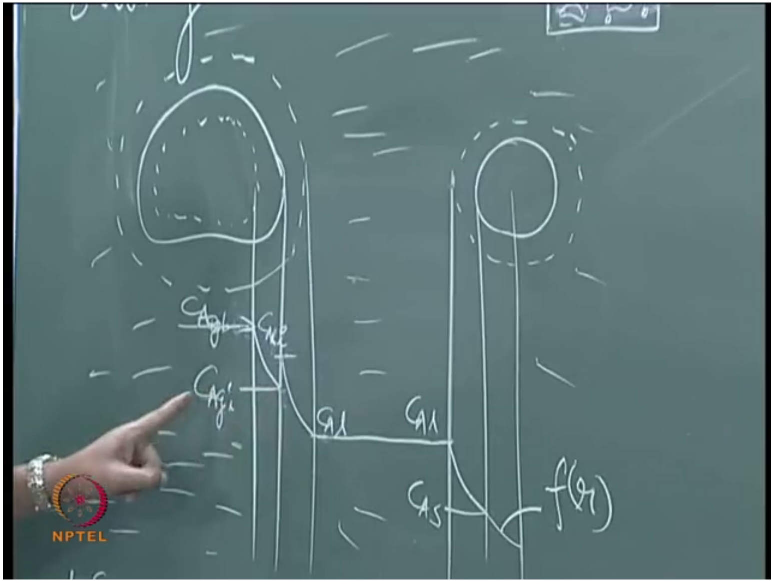

we have written C A g i and also C A l i. So how you connect this one? Henry's law.

So that is why we write here C A g i equal to H into C A l i,

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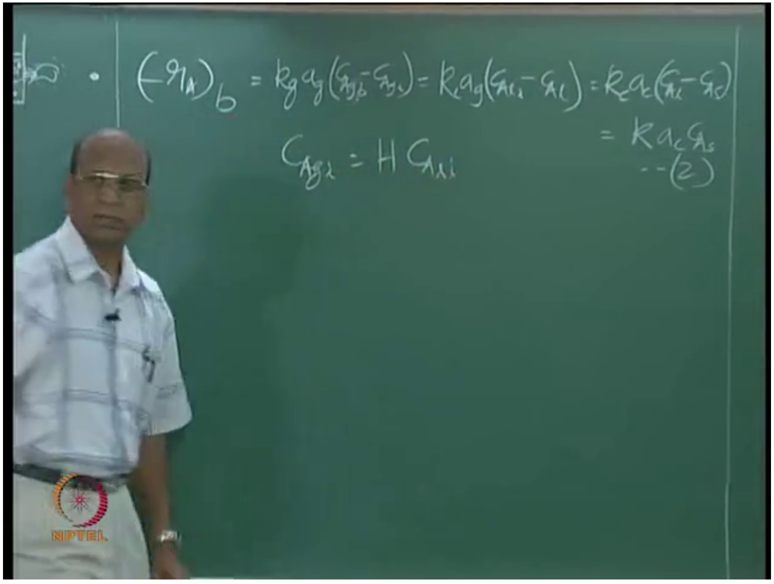

this also, that equation also you require. 3. So now using this equation, that means what is the procedure, approach? We have the universal approach in heterogeneous system. So that is why I am telling now, in all, in my course, in heterogeneous system is very simple for many people because the approach is very clear.

It is only mathematics which are more complicated depending on what kinds of reactions you take. Ok. What is the approach here? We started this one with catalytic reaction; we started with non-catalytic, we now starting writing that one for slurry reactor. What is the approach now?

(Professor – student conversation starts)
Student: 0:07:14.8
Professor: Yeah so now I have to express this rate in terms of measurable quantity that is called observed rate, global rate, yeah even bulk rate, measured rate. All these things, Ok.
(Professor – student conversation ends)

So this is also one of the questions I gave out of those 30 questions. Now if you remember. You would not remember now anything, Ok, but I know you are all excellent deleters. And I told you, no, most of you, all of you have P h D in forgetting, how to forget. Ok, not how to remember. Very quickly you forget. But anyway.

So now you first take these two, eliminate C A s, then these two, eliminate C A l, then these

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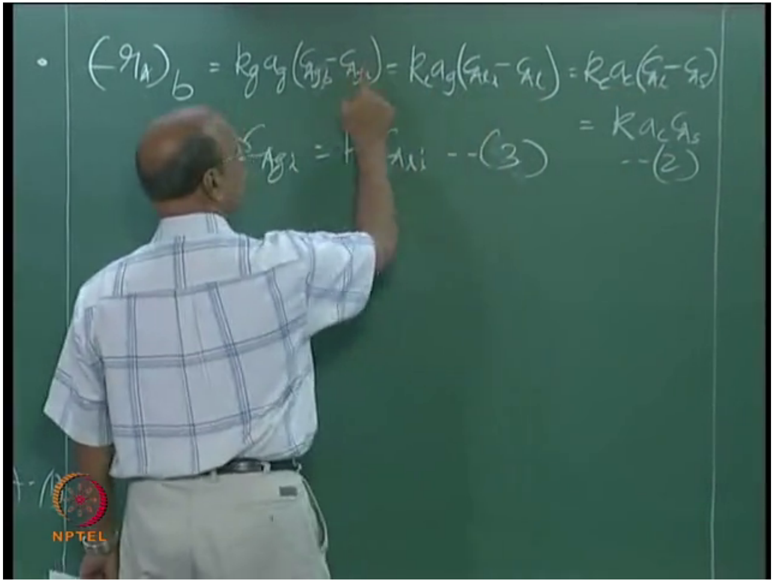

two, eliminate C A, you know, C A l and C A g using this equation, using this equation and finally you express in terms of C A g bulk. That is all. That I leave it to you. I may give in examination. Ok.

Unless you practice that at least in your room it is not that easy for you to solve this in the examination hall. Ok, you will take a lot of time, right? So that is why you try on your own and the final expression I will give you as minus r A b equal to yeah you see, this is the kind of equation what you get, C A g b bulk so then I have here a C by a g 1 by k g plus a C by a g, ag only right Ok a g, then H by k l plus I have H into 1 by k c plus 1 by k.

So this is the equation, where still I have not mentioned what is

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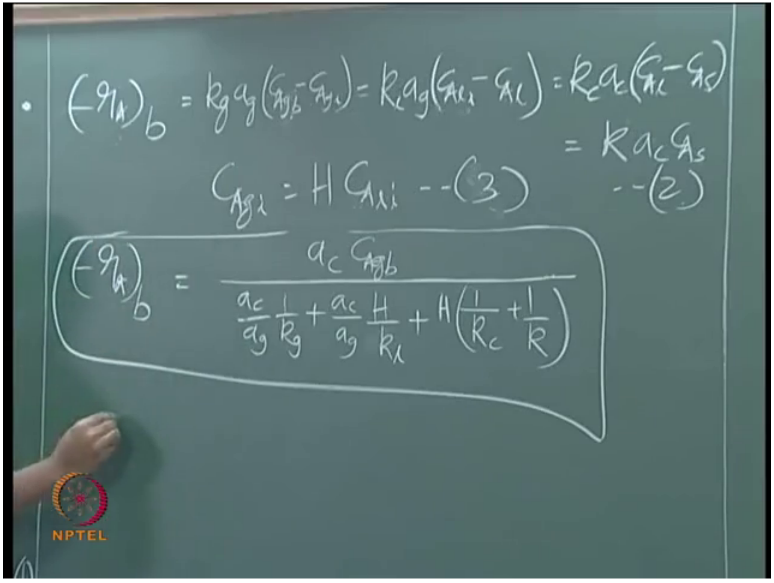

$$(-r_A)_b = k_g a_g (C_{Agb} - C_{Agi}) = k_l a_g (C_{Ali} - C_{Al}) = k_c a_c (C_{Al} - C_{As}) = k a_c C_{As} \quad \text{--(2)}$$

$$C_{Agi} = H C_{Ali} \quad \text{--(3)}$$

$$\boxed{(-r_A)_b = \frac{a_c C_{Agb}}{\frac{a_c}{a_g}\frac{1}{k_g} + \frac{a_c}{a_g}\frac{H}{k_l} + H\left(\frac{1}{k_c} + \frac{1}{k}\right)}}$$

a c and yeah, what is a g and a c.

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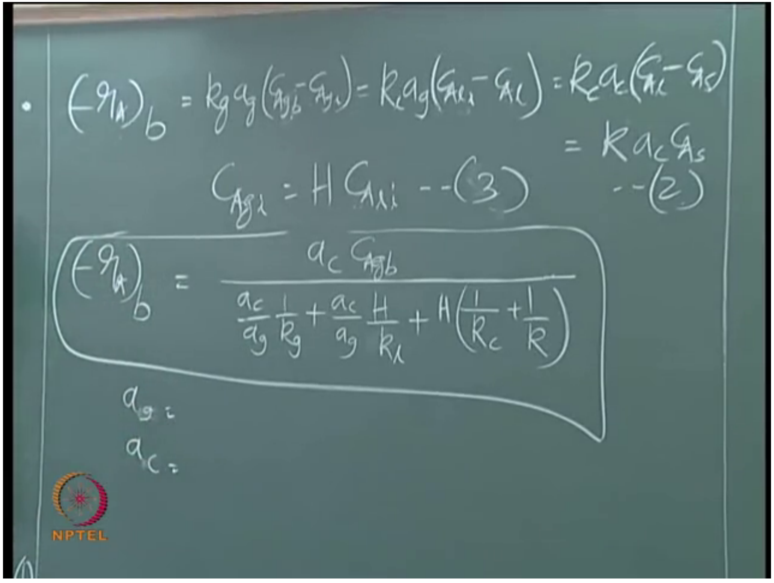

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$a_g =$

$a_c =$

Ok. a c and a g are the surface area, you know this is the, a g is interfacial area per unit volume of bubble slurry, bubble free slurry. a g is interfacial area, Ok; interfacial area means it is gas liquid, right, interfacial area of gas liquid per unit volume of bubble free slurry, yeah.

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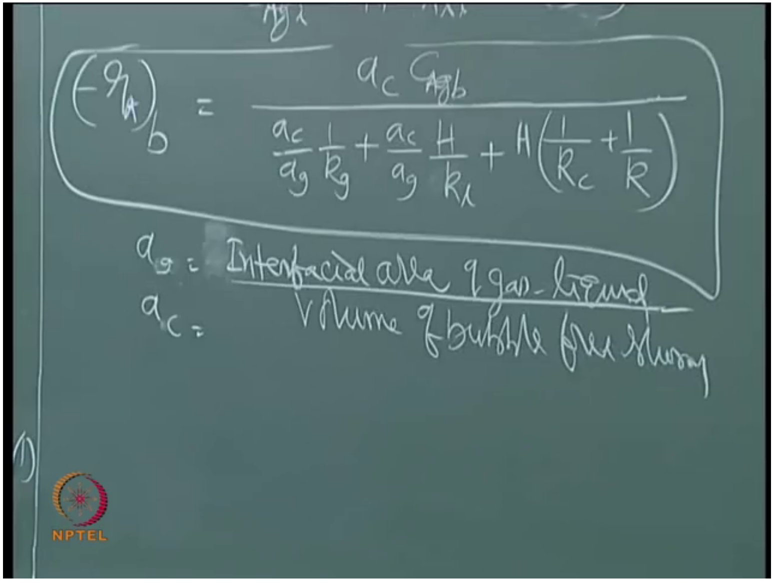

$$(-r_A)_b = \frac{a_c C_{Agb}}{\frac{a_c}{a_g}\frac{1}{k_g} + \frac{a_c}{a_g}\frac{H}{k_l} + H\left(\frac{1}{k_c} + \frac{1}{k}\right)}$$

a_g = $\frac{\text{Interfacial area of gas-liquid}}{\text{Volume of bubble free slurry}}$

a_c =

Ok, bubble free slurry.

And a c is surface area of catalyst, yeah, per unit bubble free, per unit volume of bubble free slurry, yeah, bubble free slurry. Why we have to do that is, I will give you a clue. This is

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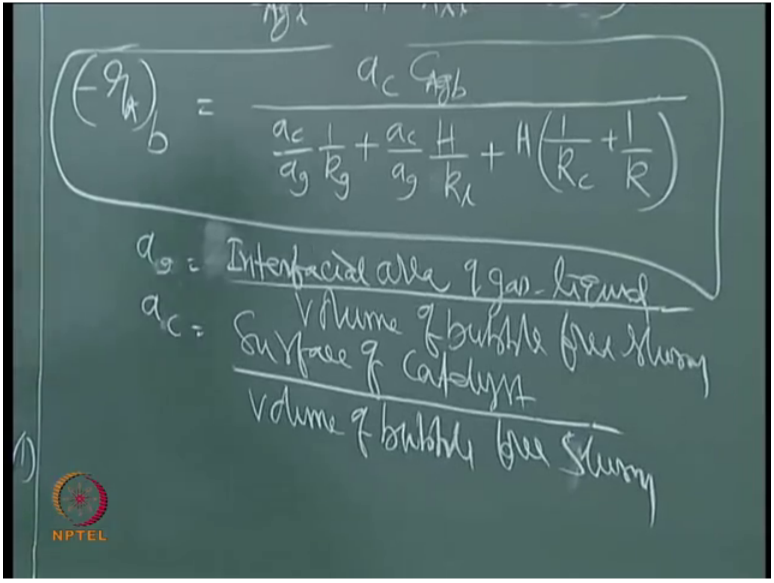

$$(-r_A)_b = \frac{a_c C_{Agb}}{\frac{a_c}{a_g}\frac{1}{k_g} + \frac{a_c}{a_g}\frac{H}{k_l} + H\left(\frac{1}{k_c} + \frac{1}{k}\right)}$$

a_g = $\frac{\text{Interfacial area of gas-liquid}}{\text{Volume of bubble free slurry}}$

a_c = $\frac{\text{Surface of catalyst}}{\text{volume of bubble free slurry}}$

equation number 4. Now can you tell me what should be the units of minus r A b? If you

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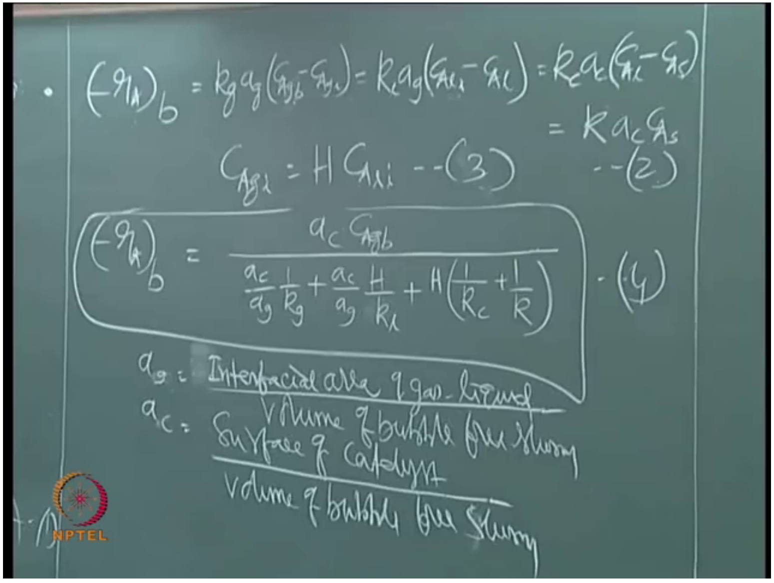

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a_g = $\frac{\text{Interfacial area of gas-liquid}}{\text{volume of bubble free slurry}}$

a_c = $\frac{\text{Surface of catalyst}}{\text{volume of bubble free slurry}}$

take simply k g into C A b minus C A s, general expression I am telling, Ok, k g into C A b into C A c, I think that is concentration, what are the units, just tell me.

That means I am talking about minus r A, yeah simply k g into C A b minus C A s, mass transfer equations. What are the units?

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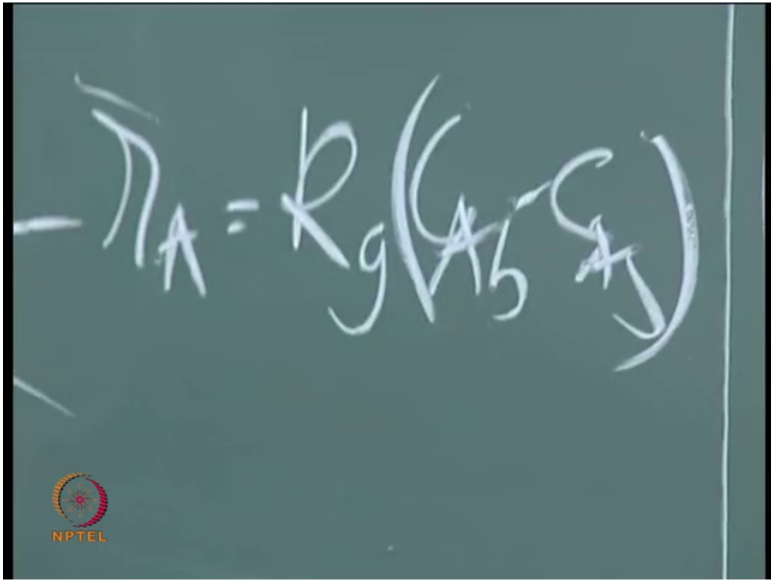

$$-r_A = k_g (C_{Ab} - C_{As})$$

Quickly. Moles per, see you know what are the units of C A

(Professor – student conversation starts)

Student: Moles per liter.

Professor: Moles per liter. What is k?

Student: Per unit time.

Student: Time inverse

Student: Second inverse.

Professor: I am talking about mass transfer equation.

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See. Mass transfer, convective equation, convective mass transfer equation. How much, Sushmita?

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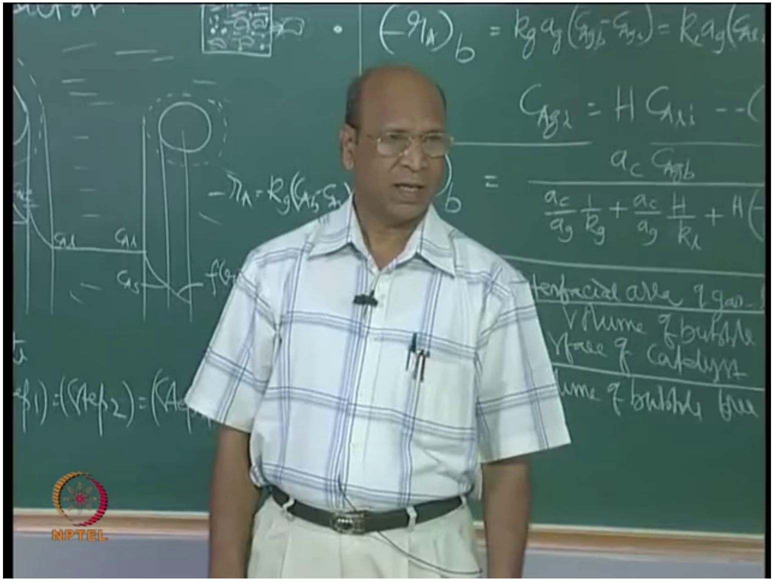

Student: Time inverse

Professor: Time inverse you get in mass transfer equation? Your N A, J A and N A. Mass transfer

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equation, convection?

Student: moles per meter square second

Professor: moles per meter square second, right?

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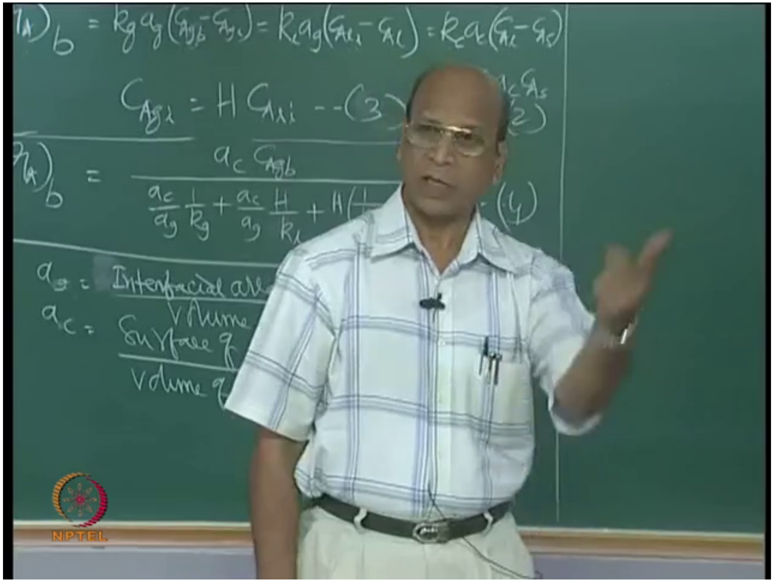

For surface area only you express there. Usually. Then if you write concentrations in terms of partial pressures then you have many, many you know dimensions for the k value. Ok. But usually we express as a flux. Either convective flux or diffusion flux. What are the units of diffusion flux?

Student: Meter square per second

Professor: Yeah, what are the units of flux?

Student: per unit area.

Student: Rate per unit area.

Professor: Yeah, rate per unit area. Rate is so many moles per, or need not be, so many mass flux also. So many k g per time per meter square. Ok, mass flux. Like that you know, mole flux and all that, you know, rate, so that is what. So now, now

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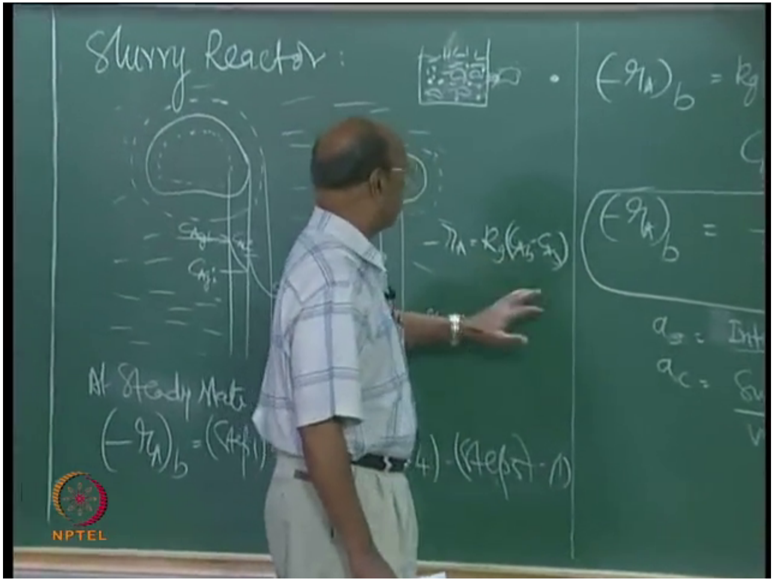

tell me with this clue, what are the units of minus r A?

Student: Moles per liter per second.

Professor: Moles per liter

Student: Per second.

Professor: What liter? Liter of what?

Student: Liquid.

Student: Meter cube.

Professor: Meter cubed of what? Meter cubed of Krishnaih. (laugh) What is meter cubed? What meter cubed? Because in heterogeneous system, there are many metered cubes

Student: Slurry

Professor: Yeah that is what. Usually that is the way in slurry reactor the rate is expressed. Ok moles converted per unit time per unit volume of bubble free slurry. Bubble free slurry. That means what?

Student: We have considered initial amount of slurry...

Professor: Yeah, slurry contains what? Yeah, liquid and solid.

Student: Solid

Professor: Why we have not taken bubble? Because in the presence of bubbles, volume measurement is very difficult. So something solid which I can tell. Ok and also the original rate was that it is moles per meter square, no, I mean surface area wise if you take which surface area you can take?
(Professor – student conversation ends)

You can take surface area of solid, surface area of gas and both are difficult to measure. Surface area of solid is slightly better but surface area of bubbles is very, very I mean difficult to measure because you do not have, first of all uniform bubbles, right? You have various kinds of bubbles, small bubbles, large bubble and all that.

So how do you find out what is the total interfacial area? So that is why, safest bet is, for hetero/heterogeneous, that is why for heterogeneous systems defining rate itself is a difficult problem, Ok. Defining rate itself is a difficult problem. So that is why these things are given there, Ok. So these

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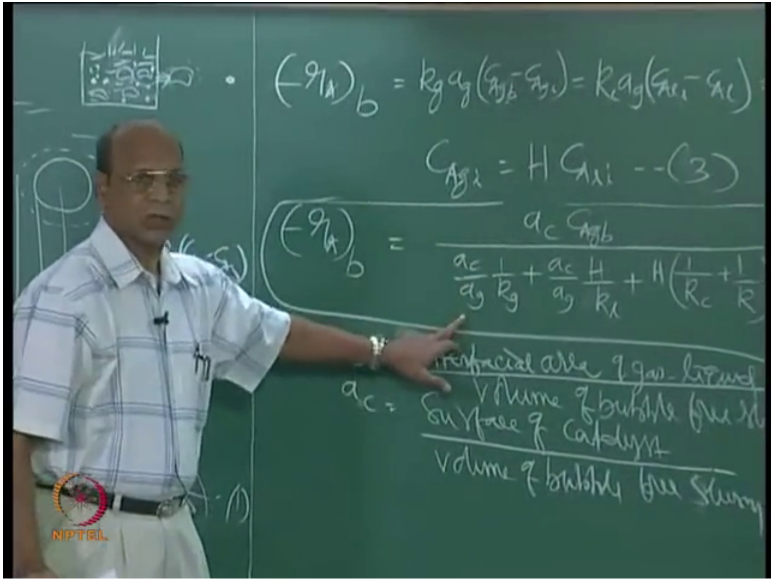

are the constants, will not change for a given system.

So now you can simplify this, k g and you know when I have very, very fast

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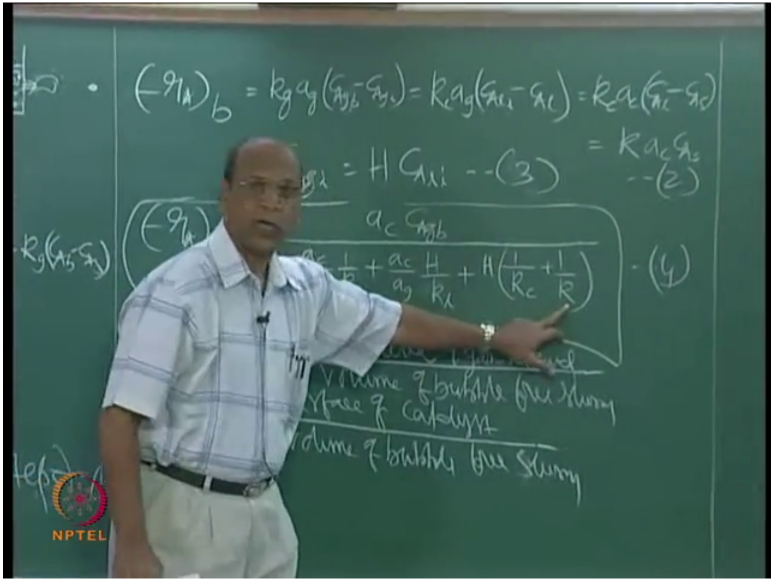

reaction again, so that means mathematically speaking, k will be very, very large. So 1 by k will be zero. So similarly here, this k g, this film, this film no one asked me, Sir why there is a film inside the bubble? So that is why

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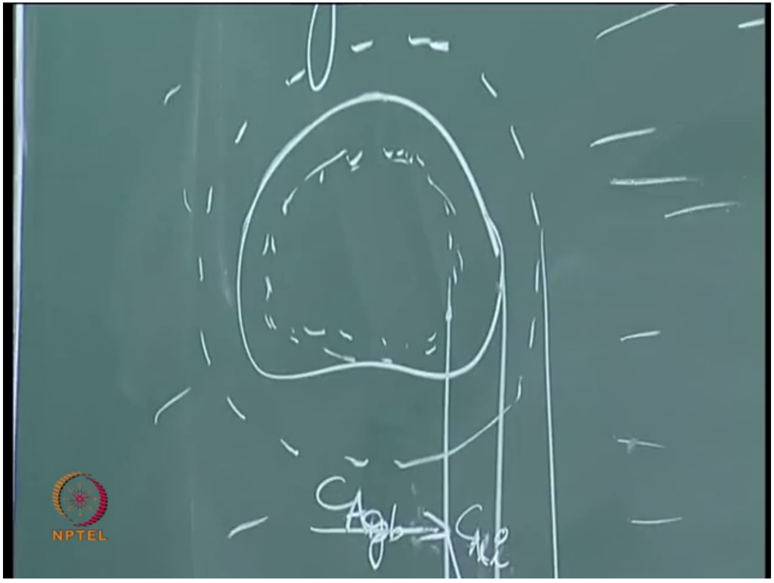

I am asking you now. You are asking no? What Sushmita? Why there is a film inside the bubble? What is there inside the bubble?

(Professor – student conversation starts)

Student: Gas

Professor: Gas. Ok, can I have a film there?

Student: 0:14:57.5

Professor: Yes. 0:15:00.8 why yes? I will also tell then, why no.

Student: At the bubble the concentration of reactant is less. So...

Professor: Why it is less?

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Student: Because the diffusion 0:15:10.4 will be from center to interface.

Professor: Yeah, if I have, suppose I have fuel gas. 0:15:19.4 Yeah, so whenever you have that gas inside

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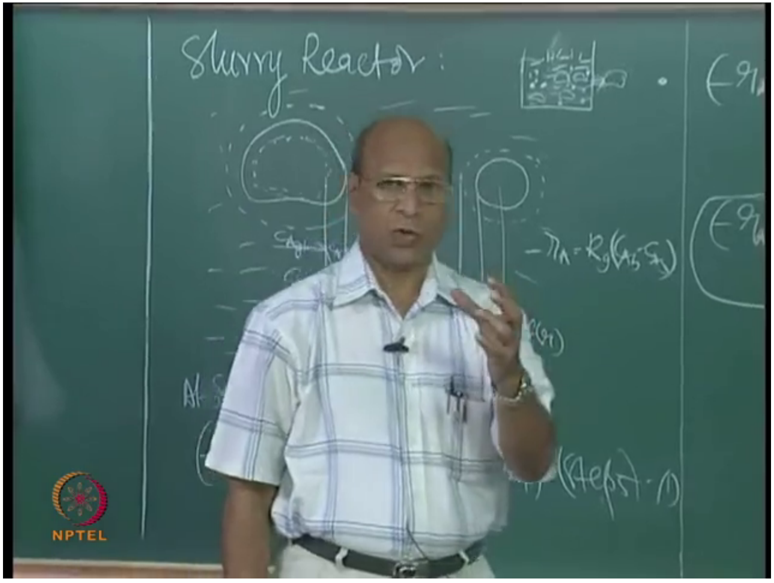

and you have more than one gas, then what he said is right.

(Professor – student conversation ends)

The molecules, what we are interested in the reactant molecule. That fellow has to diffuse from the center to interfacial area, interface. So what is our imagination? All that diffusion, even though it is moving from center to the interface, but film theory tells me all that is Ok but all the resistance inside the bubble I can now imagine as a, yeah resistance only through the small film.

That is why we can never measure those films, Ok. Liquid films and all that you can find out from outside. Gas film also, if I have a solid particle, I can. I have the solid particle and gas is moving around that, I think people can measure and they can also predict with equations, all that is there. So inside the bubble when I have 2 gases, one gas has to definitely diffuse through the other gas so that it can reach the surface.

Why it should reach the surface? Once the reaction starts, some of the gas that is here

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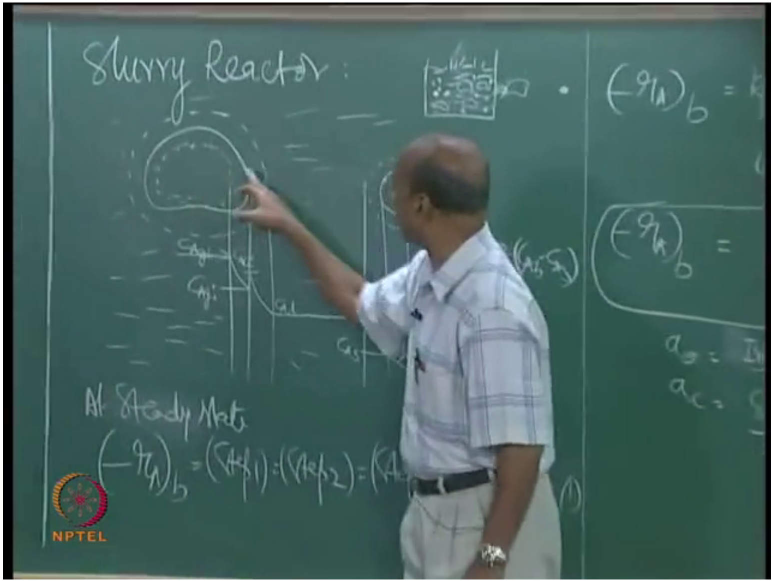

is already leaving and then reacting. Reacting means it is in the bulk it is dissolving. So there is a concentration gradient. That is why that fellow moves. The other fellow, like for oxygen and nitrogen both you send, air you bubble, oxygen will dissolve. Nitrogen solubility is almost negligible, no?

So that is why now oxygen has to dissolve because of the concentration, has to move because of the concentration gradient. So from our film theory we say that, yeah so it is encountering many molecules when it is going through, but all that, I will imagine that the entire resistance film is only through a small film. That is a wonderful concept given by who?

(Professor – student conversation starts)

Student: Lightfoot

Professor: Lightfoot was a kid at that time. Ok, when the theories have come, Lightfoot may not be there. Boundary layer theory you learnt in Fluid Mechanics, by who? Yeah

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Prandtl later used it before him.

Student: Reynolds

Professor: Reynolds not talked about boundary and all, yeah what is that?

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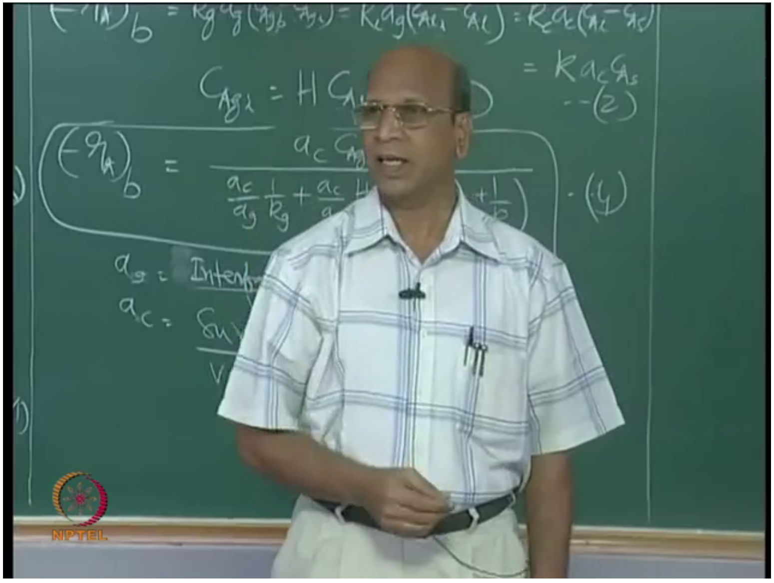

Who?

Student: 0:17:28.9

Professor: No, not heard this name, Schlichting. Boundary layer Theory by Schlichting, there is a big book in the library. Schlichting. Name is S c h l i c h t i ...Schlichting, Ok.

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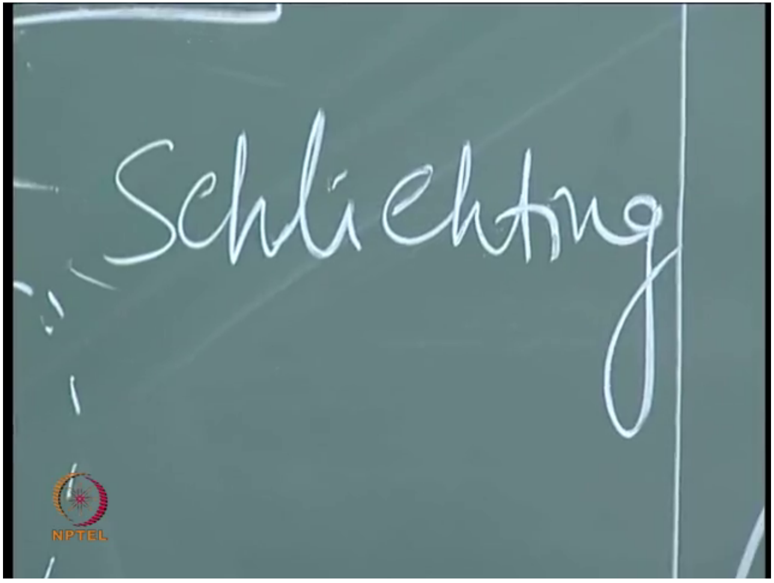

Sushmita, not able to...

Student: 0:17:54.7

Professor: Schlichting, that is German words are very difficult to pronounce. You have to say Schlich ting. Schlich, so that is what, Schlichting, so he is the person originally boundary layer theory, then Prandtl beautifully used it. Then of course for application of absorption and all that Lewis and Whitman proposed that Two Film Theory.

Ok so that means one side we have gas film, another side you have liquid film. In absorption same thing happened, Ok. Good. So that is why most of the time, gas-gas diffusion is easy. So that is why again you will have k g values normally

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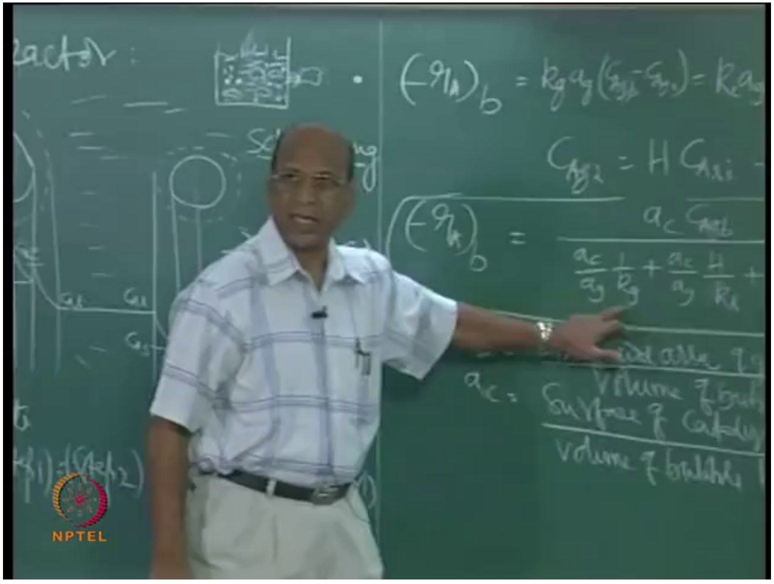

large or small, when diffusion is easy, k g will be large or small?

Student: Large

Professor: Large, so this also can be neglected. Then you will have only these 2 terms,

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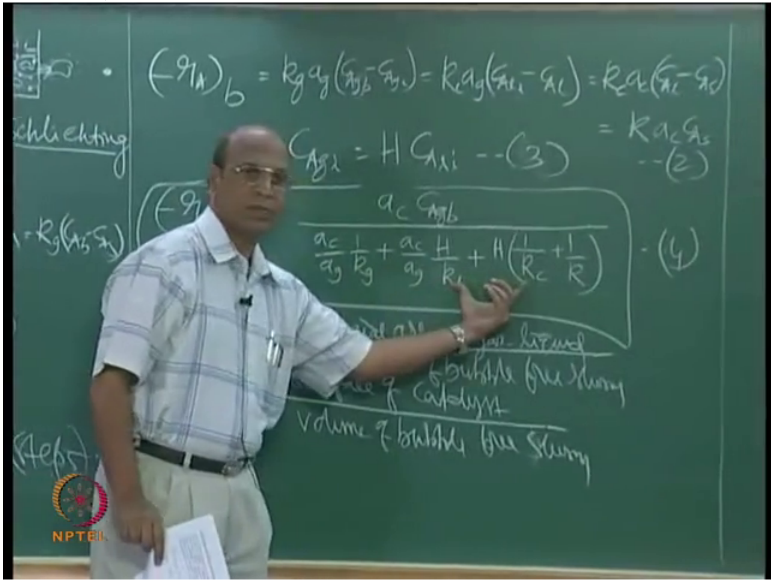

correct no. k, normally we use in slurry reactor, what are the catalysts used? At least one example? Which every day you eat in your hostel? Dalda?

Student: Hydrogenation

Professor: Hydrogenation of vegetable oil; that is one of the examples of slurry reactor. What is the catalyst they use?
Student: Nickel
Professor: Nickel. So most of these catalysts are very, very active.
(Professor – student conversation ends)

When the catalyst is very active what will happen to rate of reaction? Very high. So what will happen to k? Very large. So 1 by k is, can be neglected. And the other side we have the gas diffusing within the gas which is much faster than gas diffusing in the liquid, Ok. And gas diffusing through the particle where these pores are very, very small.

You see diffusion, I am teaching the entire chemical engineering I say. That is why; you know I am not able to complete quickly C R E, Ok, yeah. So that is why we should know that which are the terms here important, which are the terms unimportant, right.

So when I have

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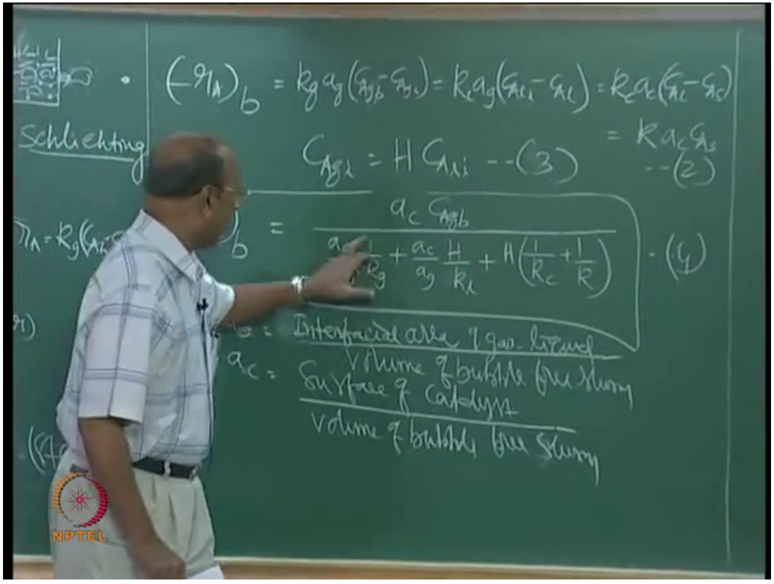

k g value very large, 1 by k g zero, this fellow will go out.

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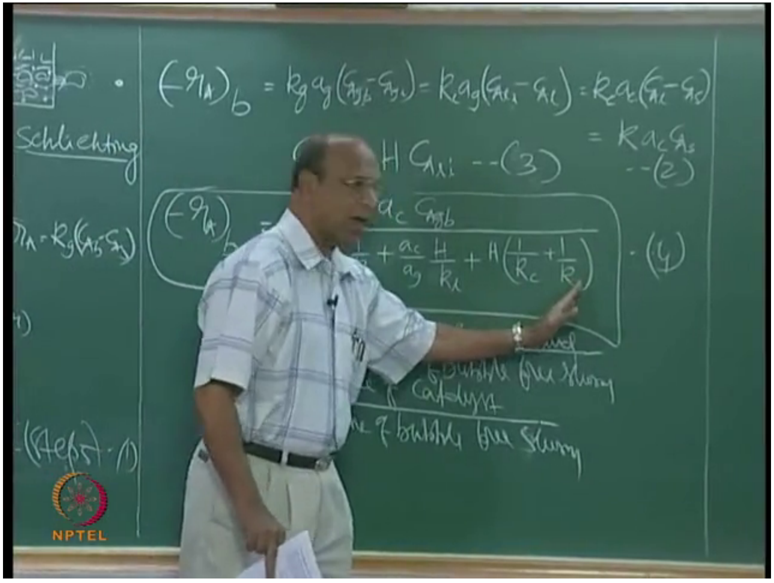

When I have very large catalyst, I mean very active catalyst, then this fellow will go out. Then you have again these two equations, no, no, these two terms. Then again what is that we are left with? 2 mass transfer coefficients. Reaction disappears.

Now that is the equation which we have to use, minus r A, sorry, V by F A naught equal to zero to X A, d X A by minus r A b,

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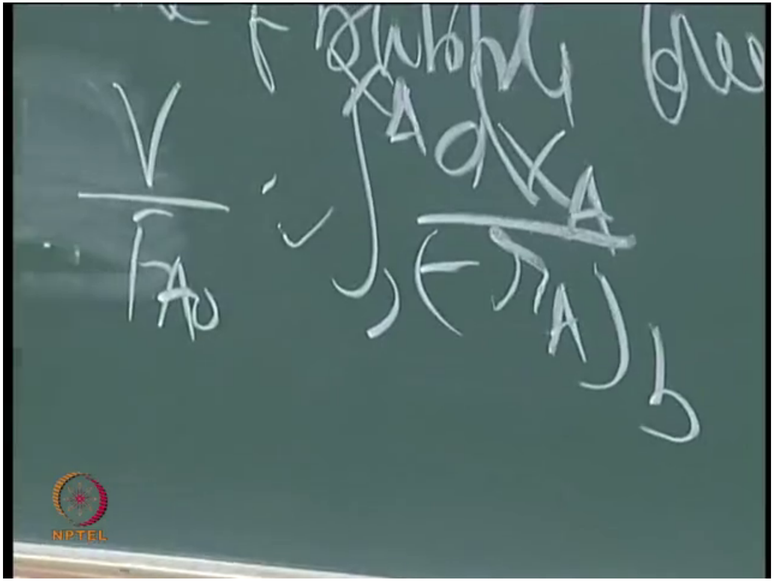

Ok, so this b, 4 is here. That is the equation you have to use. Now I think definitely you can never forget about that diagram, contacting, kinetics, physical, chemical, now you know all the terms in that equation, in that diagram. Now I do not draw, you have to only draw in your mind. Just closed, like this, like this. Yeah, what are the terms? Input

(Professor – student conversation starts)

Professor: input

Student: Output

Professor: Output

Student: Kinetics

Student: Contact

Professor: Two arrows, yeah kinetics and contacting

Student: Physical and chemical

Professor: Physical and chemical. Now you have the meaning of what is physical and what is chemical?

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Student: Yes, Sir

Professor: Yes, Ok. That is why in heterogeneous systems only, that comes because mass transfer plays a role in heterogeneous system.

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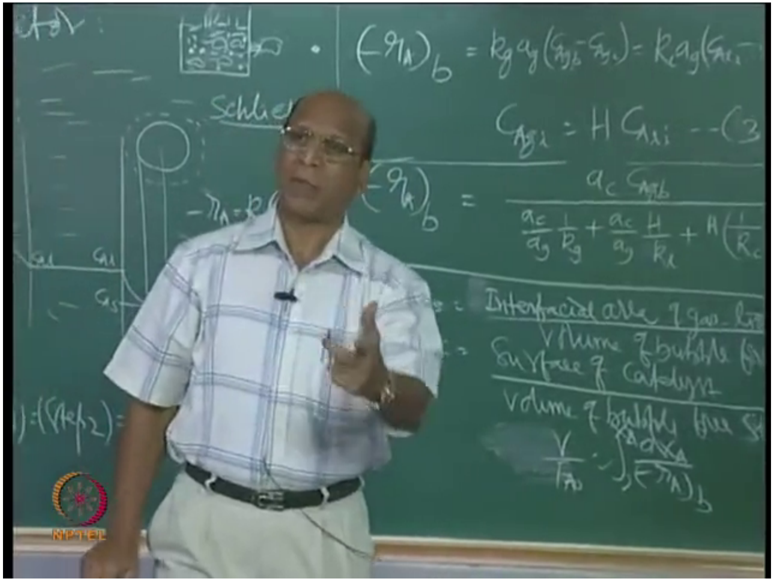

Next time when someone asks what is the difference between heterogeneous and homogeneous, do not tell single phase, multiphase. Yeah, in homogeneous all the molecules are available, so mass transfer will not be a problem there. Whereas in heterogeneous, mass transfer step comes in between. Including heat transfer step also will come in between. So that is the meaning there.

So that is why you need physical and chemical. The other side you have contacting. Ok, so what are the things we have there? Batch and kinetics, you know when you have to use batch.
Student: When you have 0:21:41.4
Professor: Yeah, yeah, so all this C R T, do not save in temporary files. It should be in permanent hard disk. Ok, no one should delete that. Abdul, no one should be able to delete. Ok So that is why, yeah that is right. So batch you know when to choose and continuous, you know when to choose, and do you still remember when do you choose mixed flow, when do you choose plug flow?
Student: 0:22:06.2
Professor: Very good, at least that part you remember. At least that part you remember I think you know first 5 questions which I have given with that then you know that what is going to happen, or what is happening in C R E. And C R E is the basis for the entire chemical engineering; because if there is not reactor, there is no chemical engineering because there is no chemical engineering plant.
(Professor – student conversation ends)

Because our idea of chemical engineering is converting some product, some reactants into products. That is what is the main thing. In between all these things you have.

You have to heat it, so heat exchanger will come. You have to pump it, pumping will come. You have to store it, storage tank will come. You have to separate unconverted and converted, you know that mixture from the reactor, so you use distillation. Or you use absorption tank, you know something like that only all the time. Ok, all those things are only outside things.

That is why we say real heart is theory; reactor is the real heart of any process. Now I think you know what is the meaning. Earlier you know only heart and process. But now you know, you have the feel, Ok. That feeling is very important in subject. If you do not have feel, you will forget very quickly. Ok, yeah.

That is why you know when we are walking on the road, you see so many people. You do not have any feel. That you will forget. But by looking if you start having some feeling, then you do not forget that figure so easily.

So this is the equation what we have to use.

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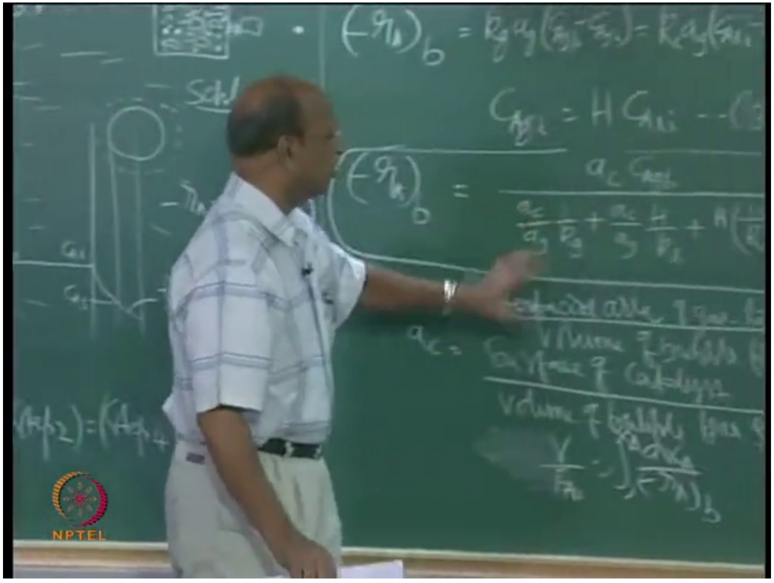

And now with this, I think you know by solving an equation for slurry reactor, you got I think fairly good overview of what is heterogeneous system, Ok. So now this fellow will not change. What is this fellow,

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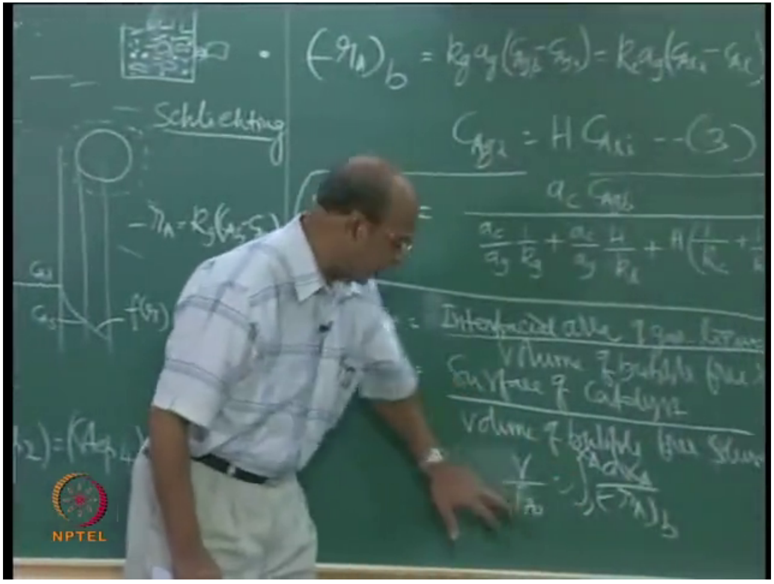

this equation corresponding to which contacting pattern?

(Professor – student conversation starts)

Student: Plug flow

Professor: Plug flow. If it is mixed flow I will write V by F A naught equal to d of X A by

Student: minus r A

Professor: minus r A. If it is batch, corresponding equation. So that is why, actually it is very easy to remember contacting. Only 3, ideal. Non-ideal we rarely go. Non ideal we very, very rarely go. Right.

(Professor – student conversation ends)

So that is why contacting is much easier to remember and the other part, the heterogeneous part is the, kinetic part is the terrible headache. So now, yeah, after seeing this now we will go

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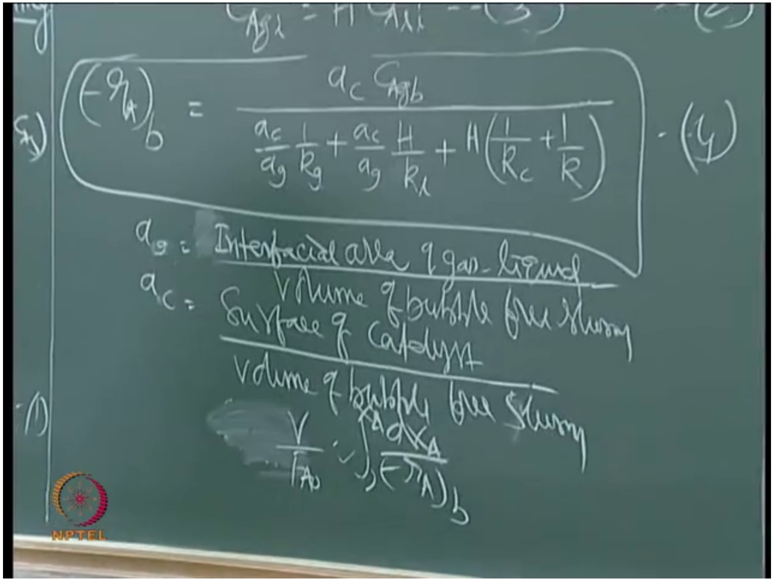

$$(-r_A)_b = \frac{a_c C_{Agb}}{\frac{a_c}{a_g}\frac{1}{k_g} + \frac{a_c}{a_g}\frac{H}{k_l} + H\left(\frac{1}{k_c} + \frac{1}{k}\right)} \quad (4)$$

a_g = Interfacial area of gas-liquid / volume of bubble free slurry

a_c = Surface of catalyst / volume of bubble free slurry

$$\frac{V}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{(-r_A)_b}$$

for homogeneous kinetics, how do we actually find out, right? So now we will start homogeneous kinetics.

Homogeneous kinetic equations. Ok, so what do you get from that? Homogeneous kinetic equations means, yeah I think I can also write here, kinetic rate equations.

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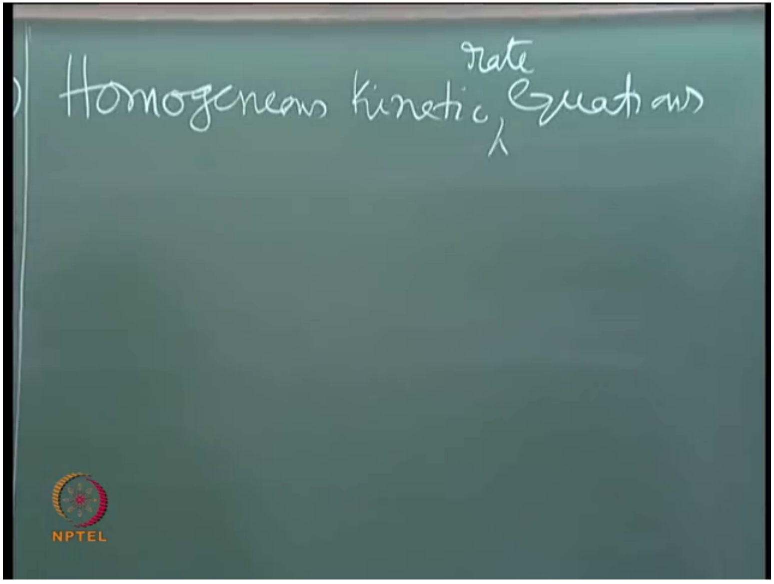

Homogeneous kinetic rate equations

So that you will remember what is that word, meaning of rate equations.

Yeah, what we have discussed earlier was, that you may have either heterogeneous or homogeneous, the stoichiometry can be anything. Simply A going to R. Simply otherwise A going to R plus S, A going to R plus S plus T. Similarly you can also add here. A plus B going to R plus S. Or A plus B going to only R.

So how many combinations you have? And particularly you have hell if I simply change; you know I may give there A plus, A going to R. But the moment I ask you A plus B going to R, then entire kinetic equation will change. So that is why most headache part is this kinetic rate equation.

And also we have unfortunately so many kinds of stoichiometric equations, that A plus B and all that, and in heterogeneous system also, you have the same equations. Now what you have to write there is Ok, A solid, or Ok A gas plus B solid giving me some other product. I think fortunately most of the time there, heterogeneous system I am talking, if I am talking gas-solid system, I have A gas plus B solid, example coal. Ok.

So coal is solid and oxygen, so this A is oxygen, B is solid giving me C O 2 gas. And same thing again. I have A solid, sorry A gas and B solid, iron ore is the solid, B. And hydrogen is gas. I am talking of reduction of iron ore to iron. So then the other side what we get? Solid plus gas also. H 2 O you get and also you get solid. So like that you have real headache with this kinetic equation.

For homogeneous systems how do you really solve it? Right? But fortunately before starting any process, we know what is a kinetic equation. Right. That is the assumption in the beginning itself. Right? Otherwise you cannot even calculate what is minus r A, sorry what is F A naught, right?

So you go to market and then find out so much product you have to produce, now you go to stoichiometric equation and come back to reactants, so so much reactants you have to feed. But again you have to assume, this is 90 percent or 50 percent, 30 percent, you have already burnt your fingers in that problem, right?

When you are back-calculating, in batch reactor, all of you took 100 percent that. Actually that is only 30 percent. That is why you get, you know you can see. You choose between point 7 meter cubed or 7 meter cubed. So if it is actually 7 meter cubed and you tell your boss in the company, that Sir it is only 700 liters, you will be happy in the beginning.

You start construction. And then you know you produce. What do you produce?

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You will not have sufficient production rate. So then he will,

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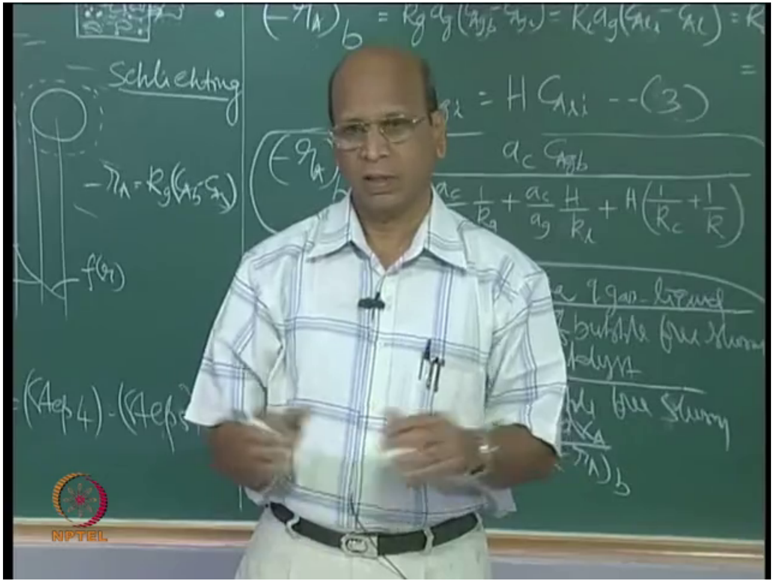

what he will do? Fire. Ok (laugh). You will not get job, right? You will be thrown out of that company. So that is what happens. So that is why we have to be careful with the stoichiometric equation, good.

So now what is the, what is the, how do you find out rate equation? How do you find rate equation? What is the first step? So that means I know stoichiometric equation. May be I have, simple thing is A going to R. Let us start with simple thing.

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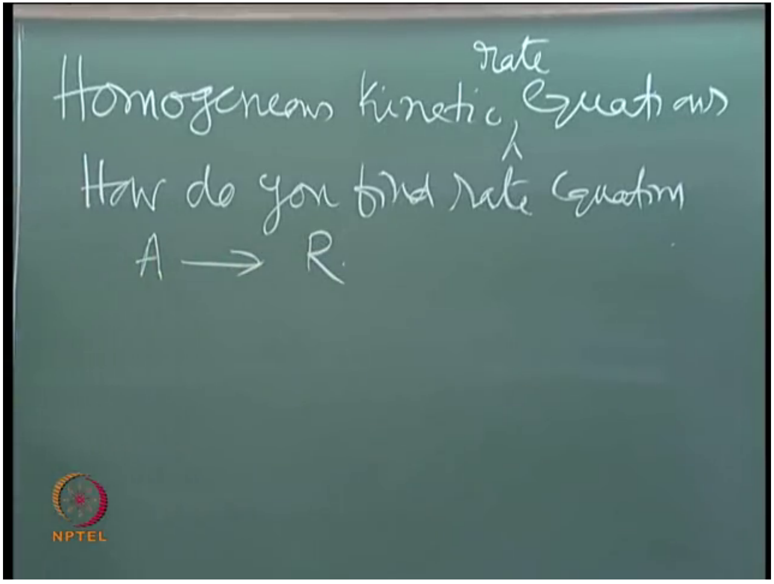

Homogeneous kinetic rate Equations

How do you find rate Equation

$A \rightarrow R$

How do I find out rate equation? What is the starting point?

(Professor – student conversation starts)

Student: Find 0:28:21.5

Professor: Yeah, so what is that you are trying to do? You are trying to do the experiment first. Correct no? Yeah.

(Professor – student conversation ends)

So now when I have this A going to R, now I have to choose, maybe A is liquid, too easy imagination, gas is slightly difficult imagination, so this is now, that is why always, nowadays, now onwards, if you write always,

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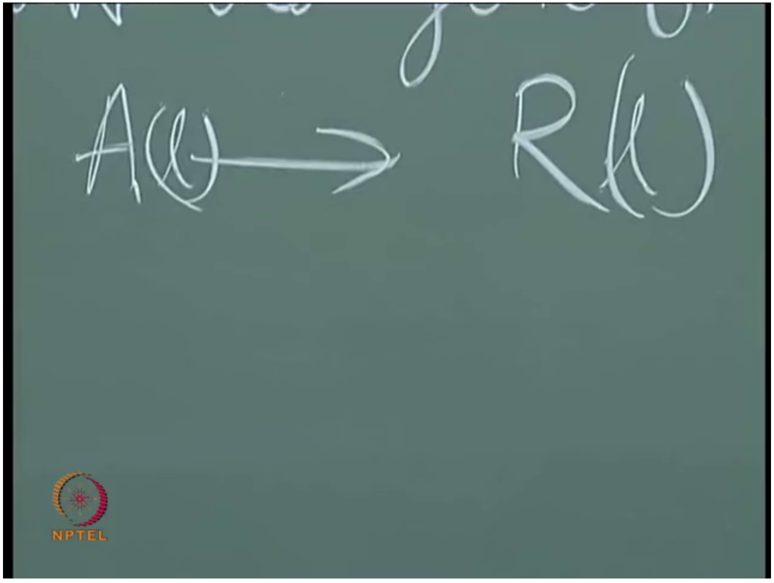

$A(l) \rightarrow R(l)$

the phase that is very good for you. Now onwards. Earlier you had never thought of that.

So if you are able to write that always, then that will clearly tell you whether you have homogeneous reaction or heterogeneous reaction. Here I have homogeneous reaction. A l going to R l. Now I want to find out kinetics. What is the starting point? Experiment, right? How do you do the experiment?

Because,

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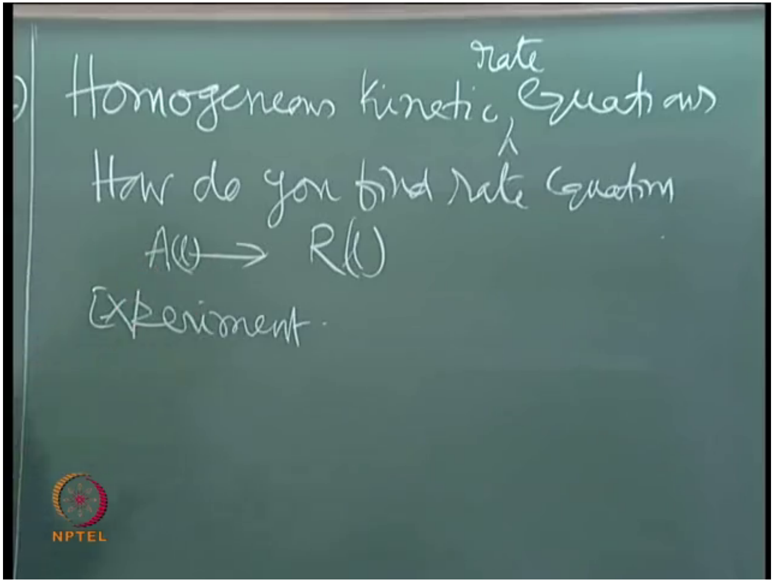

Homogeneous kinetic rate Equations

How do you find rate Equation

$A(l) \rightarrow R(l)$

Experiment.

even now we do not have theory to predict what kind of rate you will get when you have this kind of equation. Otherwise theory is the best. Because you do not have to do experiment.

Experiment

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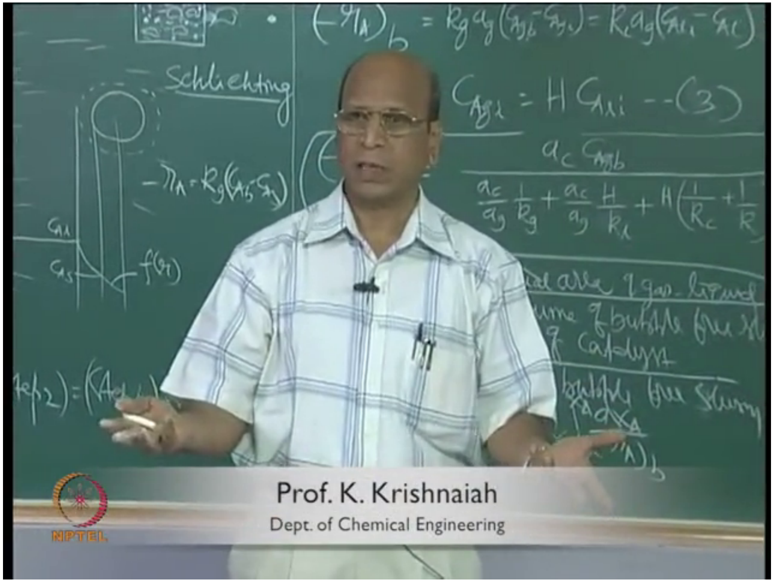

may be time waste. If you know the theory, you can always calculate, Ok, for this stoichiometry this is the order or this kind of rate equation you get. Order you remove.

What we are trying to find out here is how do you find out, Ok, question mark. How do you find rate equation means what is this minus r A? Minus r A is a function of C A and t, that is what only what we know. But what

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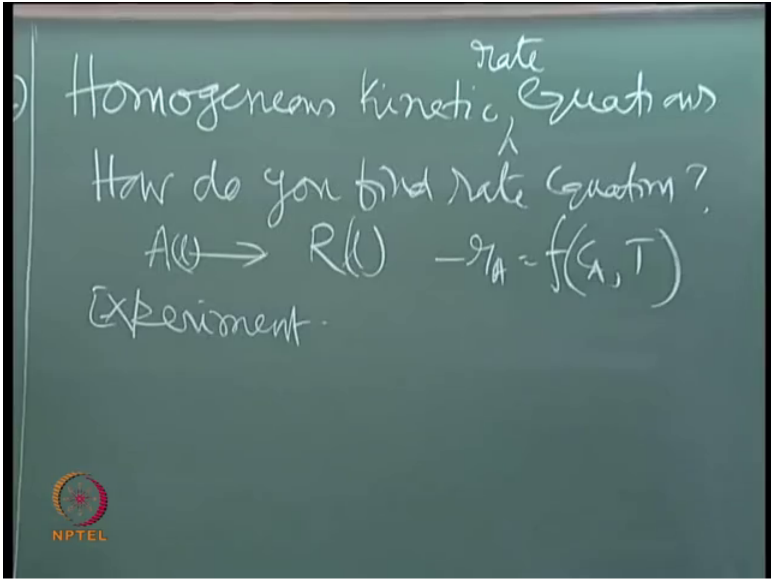

Homogeneous kinetic rate equations

How do you find rate equation?

$A(l) \rightarrow R(l) \quad -r_A = f(C_A, T)$

Experiment.

is the format only we are trying to find out, good. Ok. So experiment is a must.

So how do you do experiment depends on individuals, I think what kind of tactics you have, your intuition and also your hands, how they work. Because for some people, I think hands are very bad. Whatever they touch, it will break. So I think...no, no, no there are many people like that. Like that, some of you also are really allergic to the experiments. But I think, as engineers you cannot survive like that. You have to do the experiment, right.

How do you do the experiment? If it is liquid, most of you would have done kinetics no, kinetic experiments in B Tech, reaction engineering lab? What did you do? Abdul, what did you do?

(Professor – student conversation starts)
Student: Reaction

(Refer Slide Time: 30:24)

Professor: Take reaction. You cannot take reactions
Student: (laugh)
Student: 0:30:27.5 reactions, sorry.
Professor: Yes. That was a joke. Ok. (laugh) First of all, you cannot take reaction, now? Take reactor?
Student: We run the reaction process. We proceed and we collect the concentration of the products
Professor: Is it so simple? I mean how do you do the thing means, Ok, let us allow

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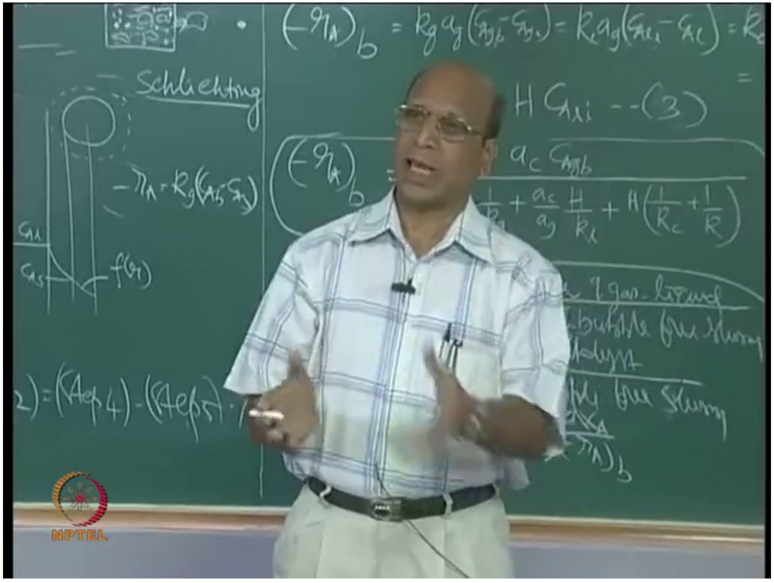

the reaction to proceed. What reaction, where you have to proceed? I am asking you to describe step by step. I ask you, Ok, I will give same thing, you know what you have done in the, in your B Tech, what is the thing you have done, sodium hydroxide and?

Student: Ethyl acetate

Professor: Ethyl acetate. That is very famous reaction. I give you now and then ask you to proceed. You know, you get me the kinetics of that. What is the starting point?

(Refer Slide Time: 31:14)

Then you have to tell me, Sir I cannot proceed unless you give me the procedure. You know that...

Student: (laugh)

Professor: You know that is what we gave, no? What do you call that?

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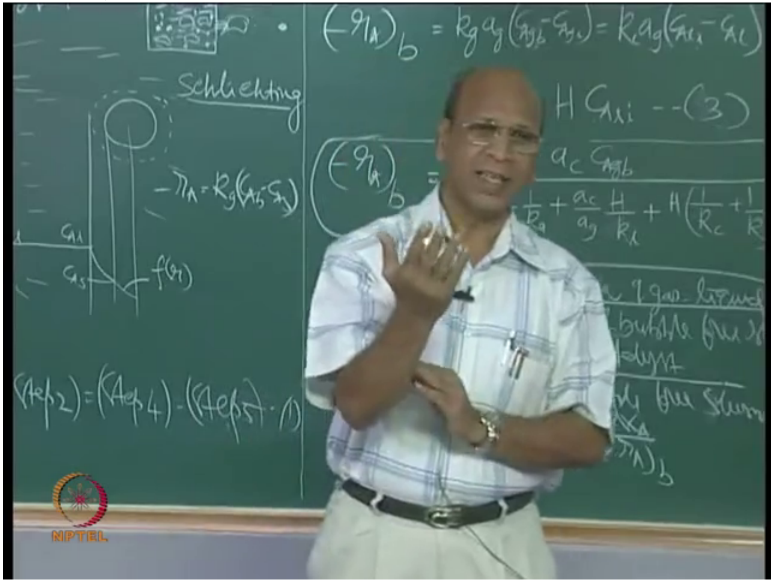

Student: Lab manual

Professor: Lab manual, yeah. Lab manual. Now you do not have lab manual. You have to imagine. Because this is new reaction. I told ethyl acetate and sodium hydroxide because you know those things. But you do not have a manual now. How do you start?

(Refer Slide Time: 31:39)

Student: Solutions

Professor: Prepare solutions.

Student: Reactants

Professor: Reactants only, yeah, right, correct. Prepare solutions. You know now, that is the first step.

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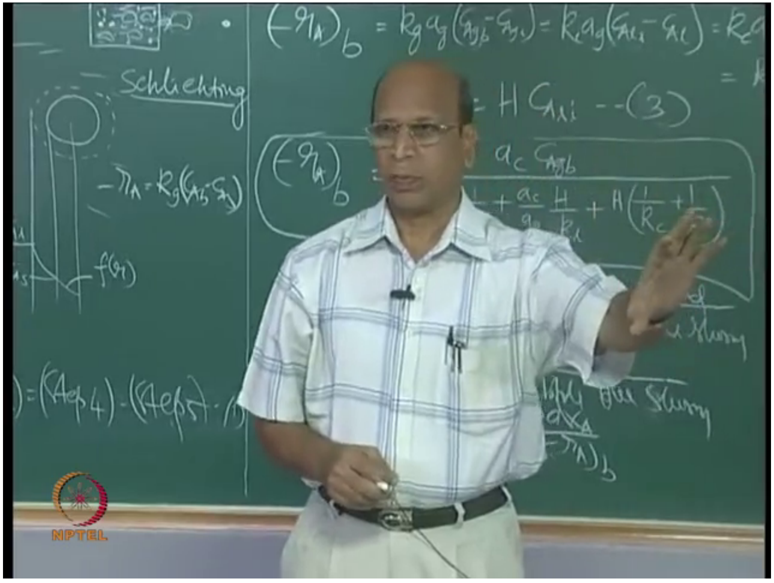

And yeah, and what concentration? Yeah it is not that easy, no the way we are discussing that, it is not that easy when you are actually starting.
(Professor – student conversation ends)

That is why doing experiment is much, much, much difficult than solving an equation on the computer. Because there all the things are available. If you go to Matlab, solutions are available for most of the things. If you go to Excel, many things you do not have to do. Draw the line, drag, you will get the answer.

But here I think if you drag, nothing will come. Only reactor may break (laugh). Ok, so that is why it is not that easy. Please appreciate experimentalists who are doing that. Process control needs theory and experiment, both. So that is why many people would be happy in doing theory but I know I think Shankar will be very happy to do experiment. Even though he started with theory.

That is why doing experiment. You know, the first question what kind of concentrations you take. Before making that, how much you make? 1 liter, 10 liters, 100 liters. So all these are the questions which you have to answer. Then once you have that information, Ok, now I make the solution.

Let us say 1 normal, point 1 normal, right so then you bring these reactants together, that means you take the reactor, put these reactants if there are 2, or only 1, and now you have to heat to that temperature, and what temperature? This is also question mark. What pressure question mark? What kind of reactor, is it open or closed? Because in laboratory we only take open cylinder. Why open cylinder?

Because sometimes if it is dangerous, you know liquid where slowly it is vaporizing also, that vapor pressure. So then you have, you know poisonous gases coming and that may affect your health. Then what do you, you have to close. So that is why, if I give, that is what I told you know no, we are only filling up the bucket but we are not opening the tap.

Ok, so what I am trying to tell there is, experiment is not so easy. So you have to think a lot before doing the experiment. Why are you doing experiment, 0:33:52.8? Yes, kinetics Ok but what do you get from the experiment?

(Professor – student conversation starts)
Student: So that we 0:33:56.3
Professor: yeah, to get the data.
Student: Data
Professor: Ok, yeah. So in kinetics what do you get? Concentration versus
Student: Time
Professor: Ok, so again there is a big assumption that is why, the L K G assumption already so that is why, all of you told that concentration versus time.
Why concentration versus time? If I take a C S T R, will I get concentration versus time? C S T R also I can take. The same reactant I can send through, so here I will put, yeah, so reactant is continuously added. Reactant is removed, that is A, C A naught, coming C A.

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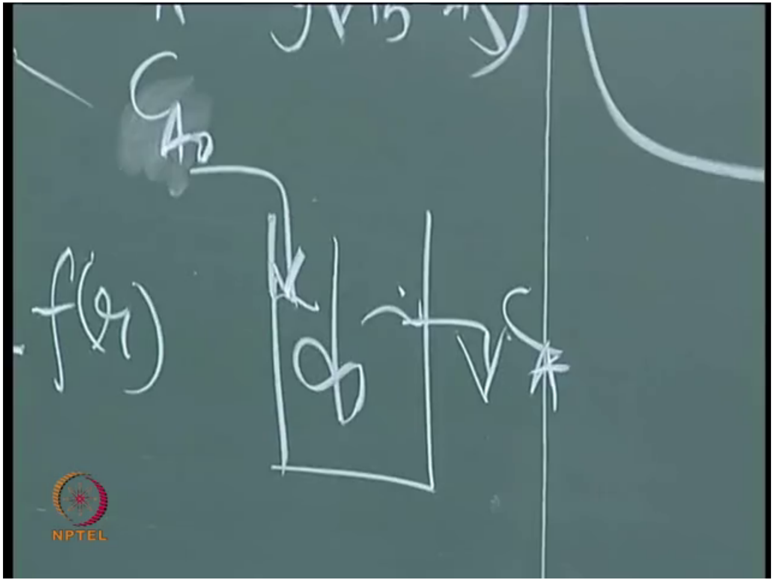

C S T R also I can use as a reactor. Why should we use only batch reactor? We do not have to use. Ok, but...

Student: Species will be fixed and they won't change,

Professor: yeah so that is why that is much easier for me.

(Refer Slide Time: 34:57)

Student: Only contact, volume, if we do not need the concentrations.

Student: Sir, actually mixture product will do, Sir the concentration of product any time. In batch reactor you have to wait till

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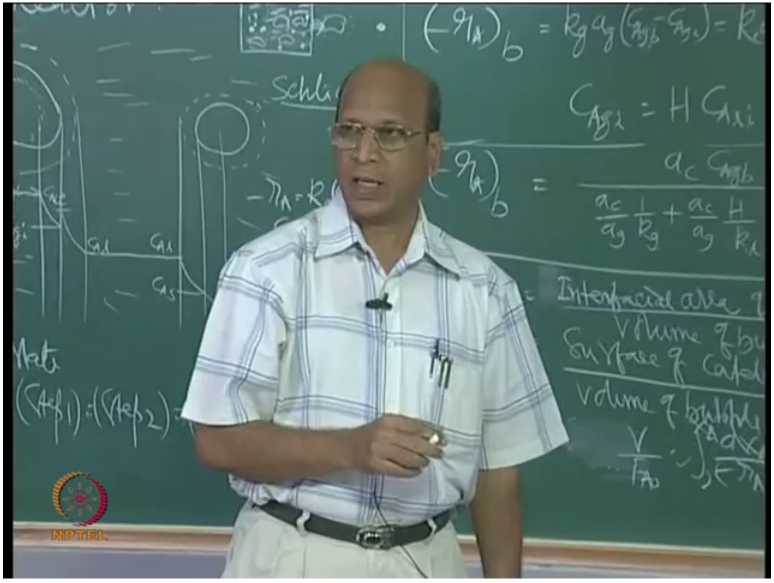

get this concentration

Professor: Yeah, product or concentration I mean, reactant that is not the problem.

Student: If it will overflow, then we can just draw that sample and

(Refer Slide Time: 35:17)

measure what is the concentration now?

Professor: Where, you are talking of a batch reactor or?

Student: C S T R

Professor: C S T R, here I can simply collect sample and then find out

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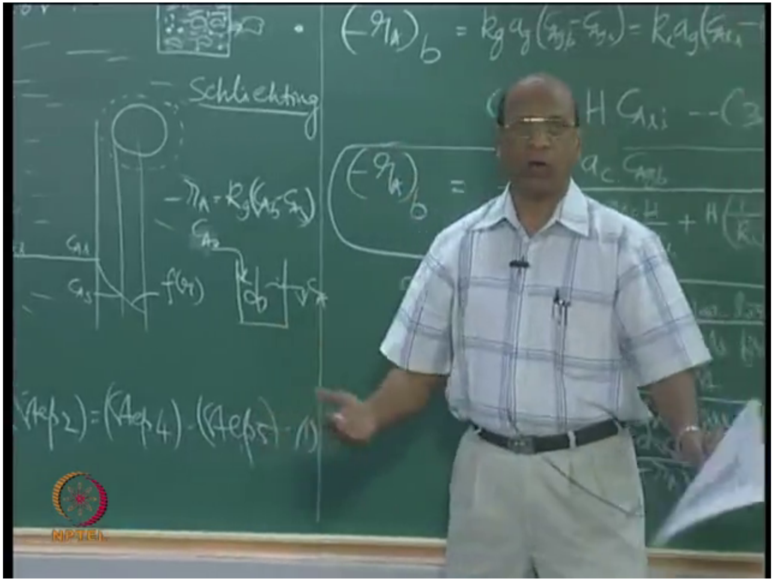

what is the

Student: Concentration

Professor: Concentration also you can find out, Ok. So you can also use this.

(Professor – student conversation ends)

But it is not that easy to conduct this rate for plug flow reactor because along the height also you have the change in concentration. Or along the length or height, yeah. But the C S T R is one of the excellent reactors, why I will tell you later. Right. I will tell you that one later but Ok, we will go to batch reactor as you said, what do you get in batch reactor, concentration versus time, Ok.

So I will give an example here, concentration versus time which I have taken from Levenspiel, the data which we get is, I will write this horizontally, t seconds and then I have C A in moles per liter, C A moles per liter, moles per liter.

So then I have here, zero, then I have 10, 8, no sorry, 20 seconds I have 8, 40 seconds I have 6, and 60 seconds I have 5, 120 seconds I have 3, and 180 seconds I have 2, then 300, ah, 300 seconds I have 1, this is the data what I got.

Ok there are lot of things here which you can see even from the data.

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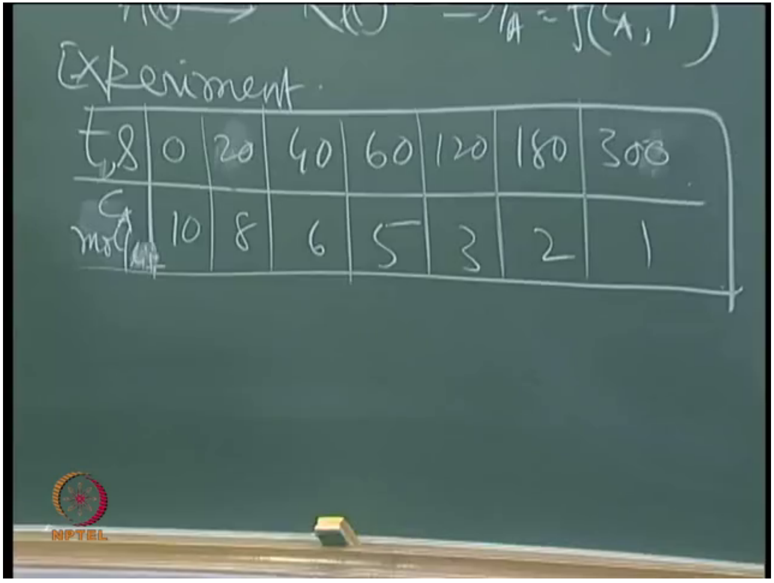

Experiment.

t, s	0	20	40	60	120	180	300
C_A mol/lit	10	8	6	5	3	2	1

C A naught, at time equal to zero, that is equal to C A naught, there is no problem. You see now, first I collected zeroth time is C A naught, the moment I started the reaction. Then what is the time? 20 seconds. Afterwards 40, afterwards 60. Then what did I do? 120 then 180, then 300.

Even choosing this interval is a big problem for you, when you are doing first time, you know even choosing that, you know timings. Otherwise what you do is you know you will miss actually some concentrations where you will not get correct rate.

So initially you have to take as many samples as possible within short interval. And at the end, you do not have to take so many samples so time can be large. Why? Our imagination. What is our imagination? Our imagination is concentration versus time, if I have batch reactor, it will be,

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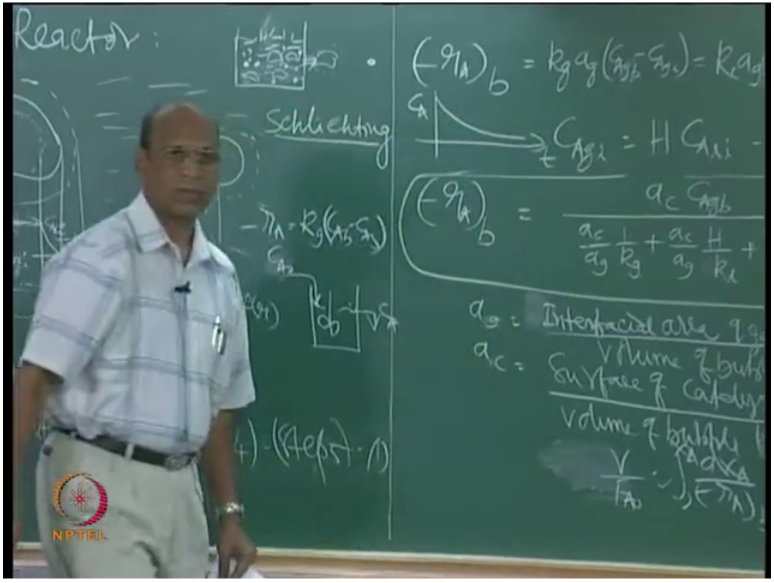

so here you see, slow change, not much change. Whereas here, quick change and sometimes this also may go like this.

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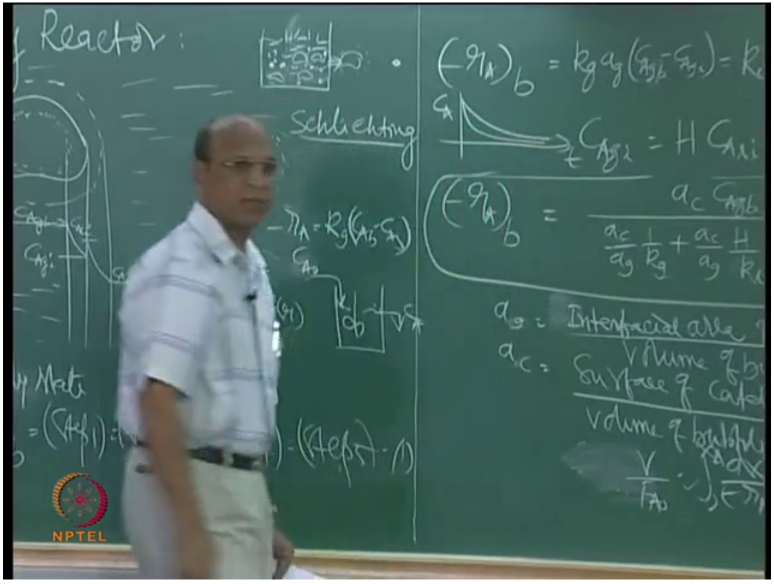

So that is why when you are taking samples also on your own, it is trial and error. First few runs you will spoil it. Definitely you will spoil it, Ok. Good. So then once I have this data, what do you do? I have given this data. Now I ask you to plot the rate equation. Plot the graph, what graph you plot?

(Professor – student conversation starts)

Student: k versus time

Professor: But first of all, why are you plotting that graph?

Student: 0:38:43.6

(Refer Slide Time: 38:43)

Professor: There must be some aim, no, some objective to plot the graph?

Student: To get the slope.

Professor: Why should I get the slope?

Student: That is 0:38:52.8

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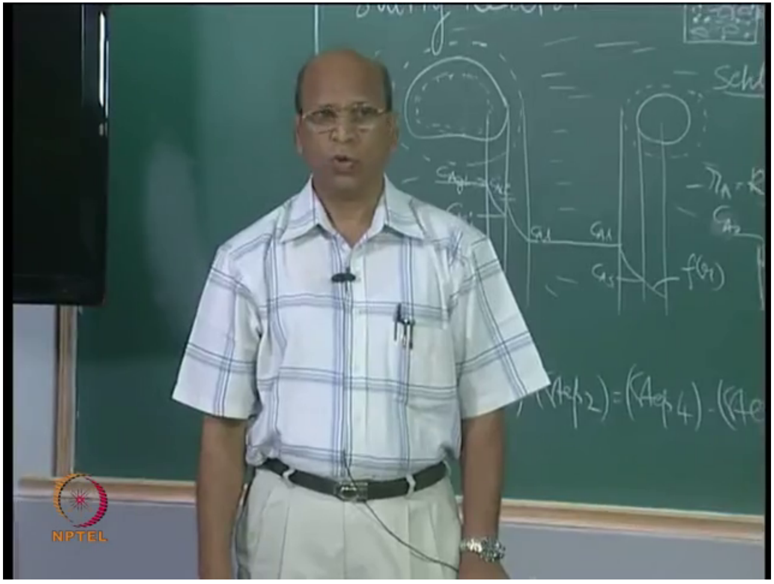

Professor: To get the rate.

Student: d k by d t.

Professor: Ok so what method are you following now for this?

Student: Differential

Student: Graphical

Professor: He says integral

Student: Differential

Professor: Why do you say it is integral, where is integration coming there?

Student: Concentration decreases

Professor: Concentration decrease, it does not mean integration. So that is why again my question is you have to choose whether you are following a differential method or integral method.

(Professor – student conversation ends)

We told you in the C R E lab that Ok, plot the graph first and then you take the slope. So you are repeating the same thing. You know, like parrots. Ok but why we are plotting, I mean drawing the slopes, that means what method you are following? All that we are not telling you.

Right we have now, you know the differential method and also integral method. Which method you have to follow? Which method is best? Which method is bad? Differential is bad or good? Why?

(Professor – student conversation starts)

Student: Because it gives slope at a particular time.

(Refer Slide Time: 39:54)

That is what we need.

Professor: So what, if it gives slope, you like it?

Student: No, we need the rate at a particular time.

Professor: Yes

Student: That is why it is more accurate. Sir, at a particular time we know the rate.

Professor: Yes, Ok good. What do you do in integral?

Student: There we assume an order

Professor: Yeah, assuming an order of reaction

Student: 0:40:14.6 integrated

Professor: Ok,

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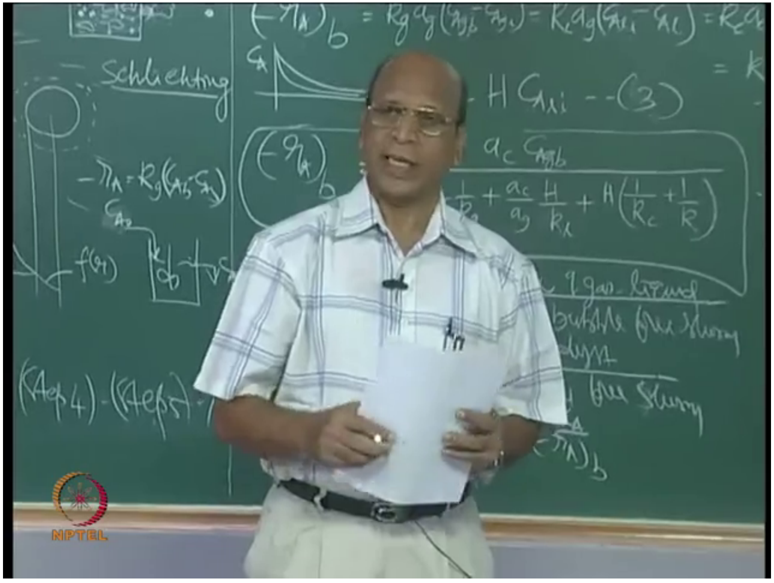

so in integral, you assume a particular order. The simplest thing which we can assume is the first order reaction for example. So that means that equation I have to develop, right, that equation.

(Professor – student conversation ends)

Now we have integral method as well as differential method. In fact if integral method works that is the best method. For normal first order reaction, second order, if you are lucky, if your order is second order or first order, you are really lucky. Then you know you will get a beautiful fit, beautiful values, correct values for the constants also to determine, Ok.

Why? Because I do not have to again plot graph. And then plot you know the slope, draw the slope. That means I do not have to evaluate even minus r A. Why? I am imagining my minus r A already. And then integrating.

Now that integral expression where it is only in terms of concentration and time if it is a batch reactor, concentration and time, so that is what now I will try to fit. If it is exactly fitting, then excellent. So that is why, so now we have to talk about, choose one method either differential, or integral method, integral method of analysis. Ok.

And before choosing this also, by looking

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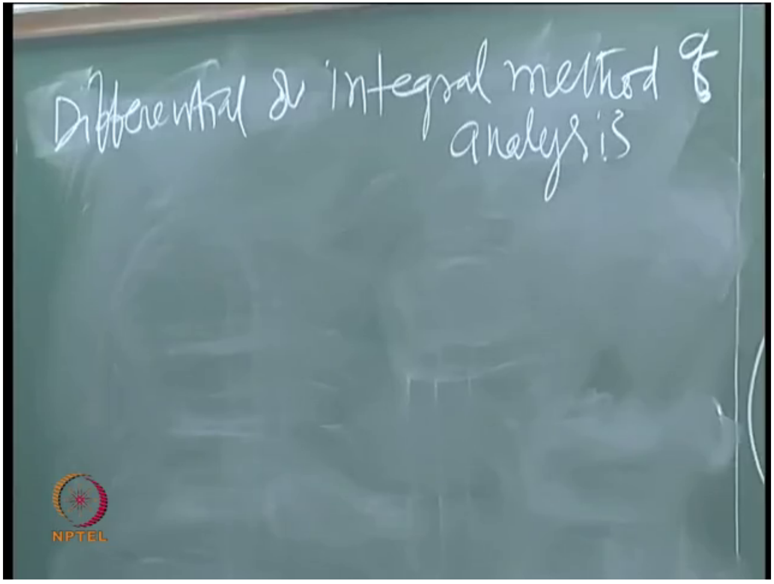

Differential & integral method of analysis

at the data you can understand a lot, you can really understand a lot. By looking

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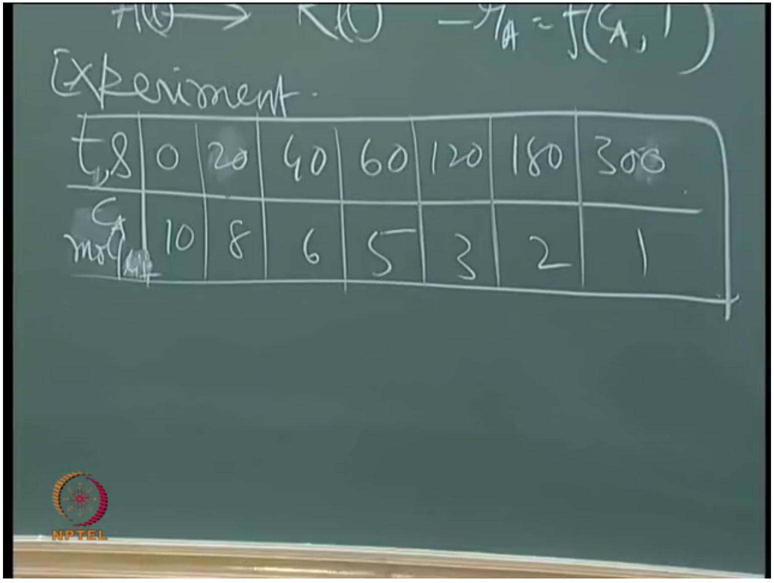

A(l) → R(l) $-r_A = f(C_A, T)$

Experiment.

t, s	0	20	40	60	120	180	300
C_A mol/lit	10	8	6	5	3	2	1

at that can we say it is reversible reaction or irreversible reaction?

(Professor – student conversation starts)

Student: irreversible 0:42:00.5

Professor: Why?

Student: Because the quantity

Professor: Yeah, in the irreversible reaction it increases?

Student: No

Professor: Sorry, reversible reaction what happens?

Student: Reversible reaction some 0:42:14.4

(Refer Slide Time: 42:14)

Professor: How do I find out whether the reaction is reversible or irreversible?

Student: Because 0:42:21.4

Student: Sir optimum 0:42:18.6

Professor: Optimum?

Student: Sometimes...

Professor: You are talking about concentration of A?

Student: Yeah

Professor: Ok, yeah, continuously

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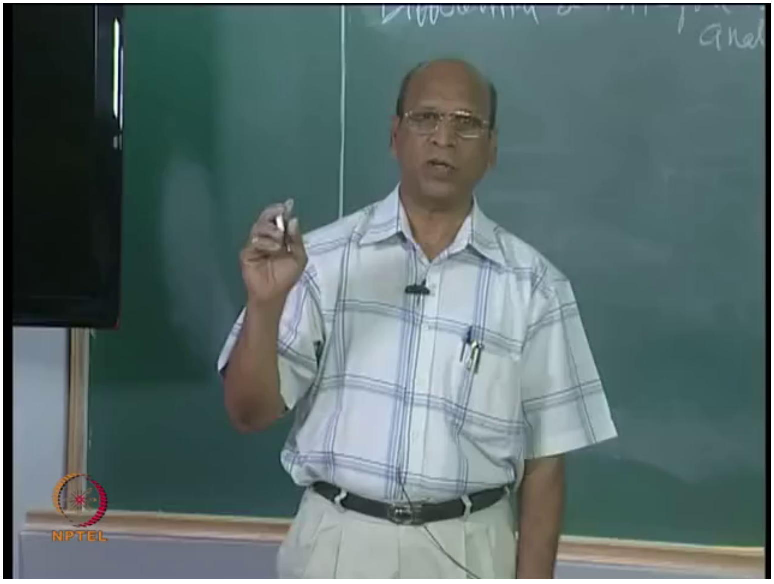

decrease, here also continuously decrease.

Student: Decreasing below particular point

Professor: Again it increases?

Student: No, it will stop there. It will be constant.

Professor: Cannot increase because you are plotting only C A.

Student: Reversible reaction 0:42:43.5

Professor: Yeah, so every point what you are measuring there is the combination of this reversible only with time. Ok.

(Professor – student conversation ends)

So then how do you really find out from experiment whether you have reversible equation or irreversible equation? Irreversible is easy because you conduct for 1 day; you will get zero concentration of A at the end, right? So this one day if you repeat the same thing for reversible reaction, end of the day still you have some concentration of A.

So that is why Levenspiel also beautifully puts in some problems that he will write there, infinite time, still some concentration. That means he has taken for long time, infinity means, Ok. So then that is a reversible reaction.

(Professor – student conversation starts)
Student: 0:43:34.6 infinity is given in
Professor: (laugh), yeah infinity is given in Levenspiel book or not. That infinity means very, very long time you go, still you have some concentration there.
(Professor – student conversation ends)

So that is how you have to determine whether you have reversible or irreversible. Because that determines which rate you are trying, right. If I am trying integral method, and if I am assuming A going to R, that is

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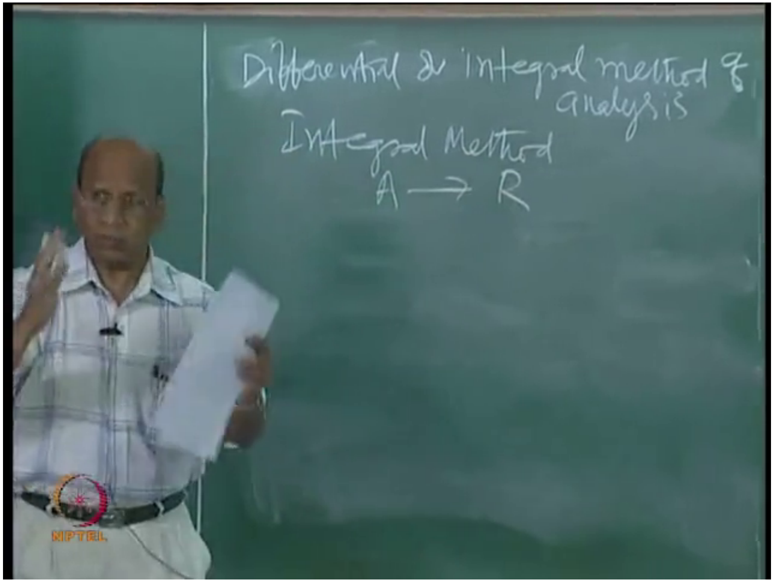

easy best, easy bet. So to start with the simplest reaction that is possible. If you are lucky you are hitting the jackpot, right?

So if you are not lucky then you know then complications will increase. So best thing is once the data given and ask, if someone asks you to find out what is the rate equation if you are following integral method, the best thing is imagine first order reaction, Ok. Now if I put infinity there and still I have some concentrations, then I should put reversible, this I have to try.

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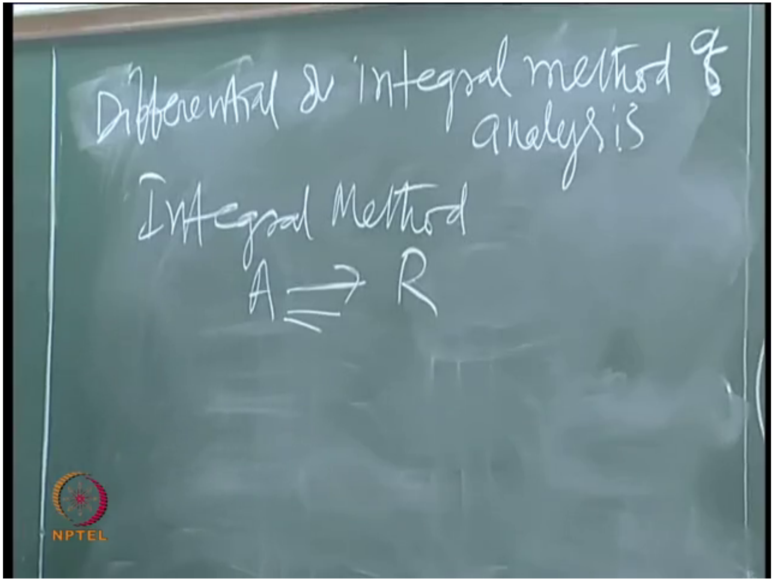

That means it is definitely reversible reaction. And also when you give infinity, it is not only, you know, just telling you reversibility, that is why I told you, you know not only I am talking about reaction engineering to find out rate, even tomorrow when you are doing project, this thinking is required. From data itself you can get lot of physics that is going on if you are able to collect data carefully.

So from the data, even without using an equation, you can tell many things. Why this data is coming. And now using one or two points also you can again check what is happening, the process. Here for example when I told you I have infinite, and then still there is concentration, what is that concentration is equivalent to? Infinite I have put there, and then I have still 5, for example there.

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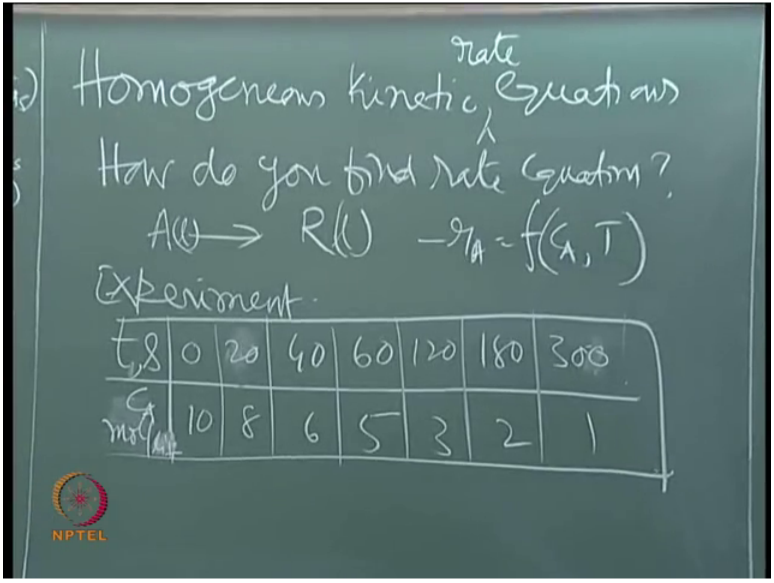

Homogeneous Kinetic rate Equations

How do you find rate Equation?

$A(l) \rightarrow R(l) \quad -r_A = f(C_A, T)$

Experiment.

t, s	0	20	40	60	120	180	300
C_A mol/lit	10	8	6	5	3	2	1

(Professor – student conversation starts)

Student: Equilibrium concentration

Professor: Yeah, that is equilibrium concentration. If it is first order reaction, it is, you know, the stoichiometric equation you know.

(Professor – student conversation ends)

If you know how much reactant has reacted, can you also, 0:45:43.5 is expert. Always he says products. Because he came from industry, no, he is interested only in products. 0:45:48.7, can you calculate how many moles of products has come? You measured reactants.

(Professor – student conversation starts)

Student: Back calculation

Professor: Yeah back calculation, that calculation (laugh) I think. You can calculate. So that means I know concentration of reactants and also concentration of product at equilibrium.

(Professor – student conversation ends)

Once I know these two, can I calculate what is equilibrium constant? Now imagining I have simple first order, now we have to imagine it is irreversible first order reaction, what is the rate expression; that we should know. What is k C A? Minus r A equal to ... k C A, right?

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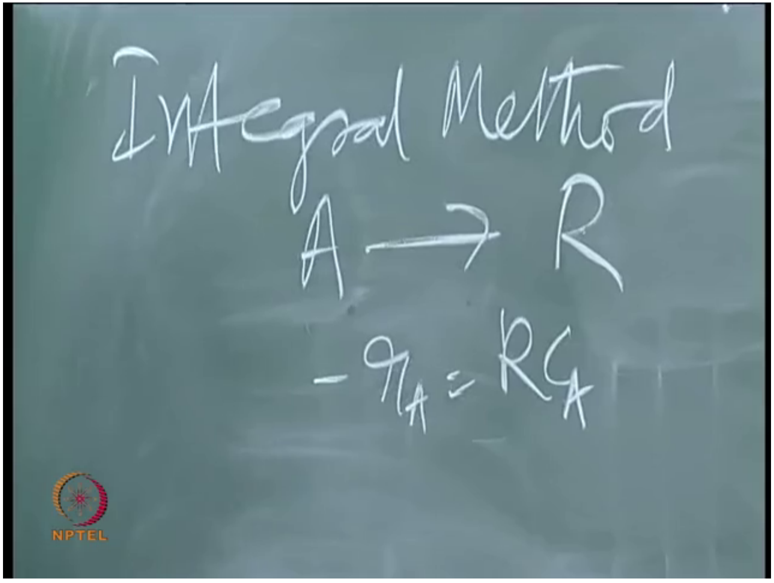

Integral Method

$A \rightarrow R$

$-r_A = kC_A$

Now it is a batch reactor what we have used. So what is batch reactor equation? C A naught equal to zero to X A, d X A by minus r A, right? Now minus r A equal to d X A by k into C A,

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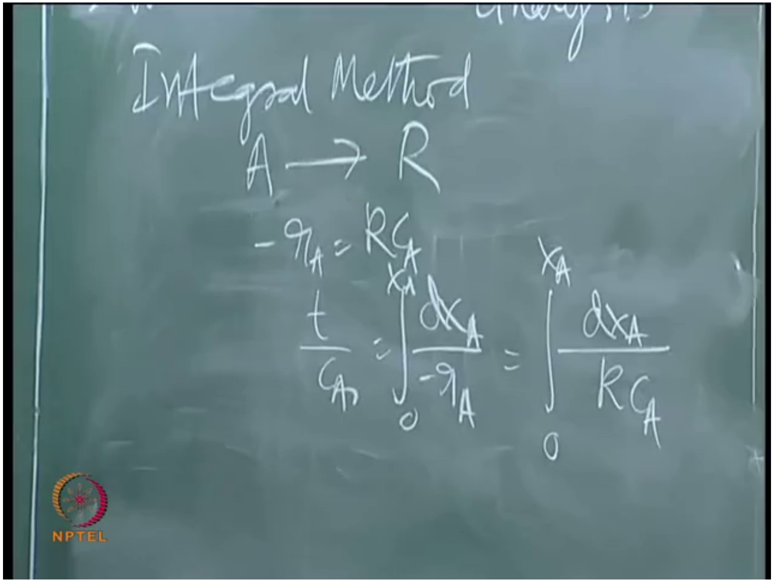

Integral Method

$A \rightarrow R$

$-r_A = kC_A$

$$\frac{t}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} = \int_0^{X_A} \frac{dX_A}{kC_A}$$

right but this I cannot integrate. Why? Yeah, because this is in concentration, this is in conversions.

So now I have to have an equation for, yeah the relationship between conversion and concentration and that we know already, most of you will be knowing that. So C A equal to C A naught into ... That I have to substitute here, Ok. Now substitute and tell me what is the equation, integral equation. Minus l n 1 minus X A equal to... Excellent, very good.

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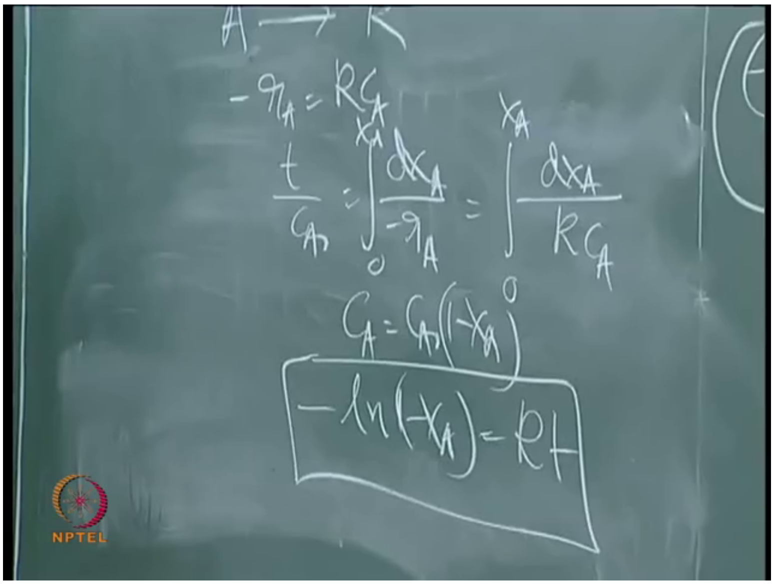

$$A \rightarrow R$$

$$-r_A = kC_A$$

$$\frac{t}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} = \int_0^{X_A} \frac{dX_A}{kC_A}$$

$$C_A = C_{A0}(1-X_A)$$

$$\boxed{-\ln(1-X_A) = kt}$$

Yeah now I have to test that data. I have now concentration and time. There also I have concentration and time. So how I imagine this one is this is all I plot as y. And this as, because

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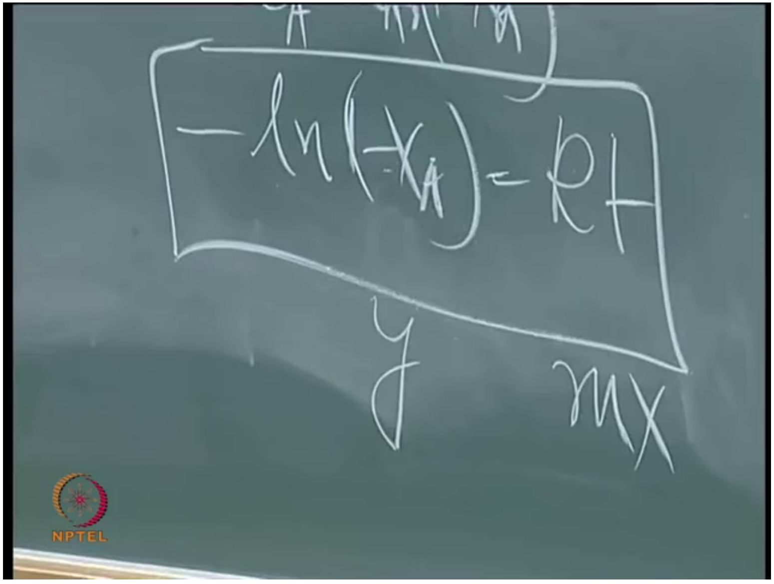

$$\boxed{-\ln(1-X_A) = kt}$$

I think everything you have to convert into our y equal to m x plus c. Straight lines, Ok. But where is c here? For this equation there is no c, no constant. So that means if I plot this, how it should go?

(Professor – student conversation starts)

Student: Straight

Professor: Yeah, it should go through the origin and straight line. And with a slope of m.

(Professor – student conversation ends)

So now what is m here for me? k. So that is why Ok, because now I am checking that data, now I have to calculate that data in terms of this concentration. You have to convert into, conversion, yeah 1 minus X A, and also yeah, correspondingly, then what you have to do, you have to also take logarithm of that, so more systematic people will also do this minus 1 minus X A, again all that, right. Now

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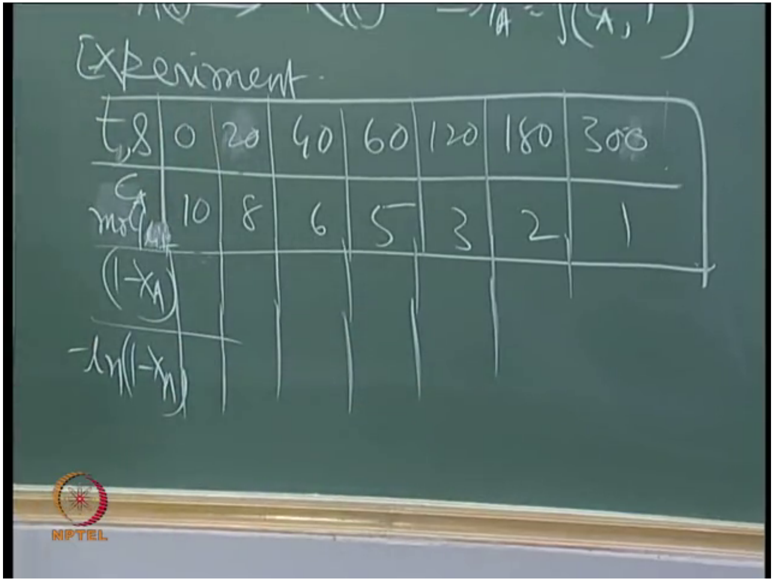

Experiment.

t, s	0	20	40	60	120	180	300
C_A mol/lit	10	8	6	5	3	2	1
$(1-X_A)$							
$-\ln(1-X_A)$							

that is y for you. You plot here those things. So ... beautiful straight line.

(Professor – student conversation starts)

Student: (laugh)

Professor: Ok. But do not expect life to

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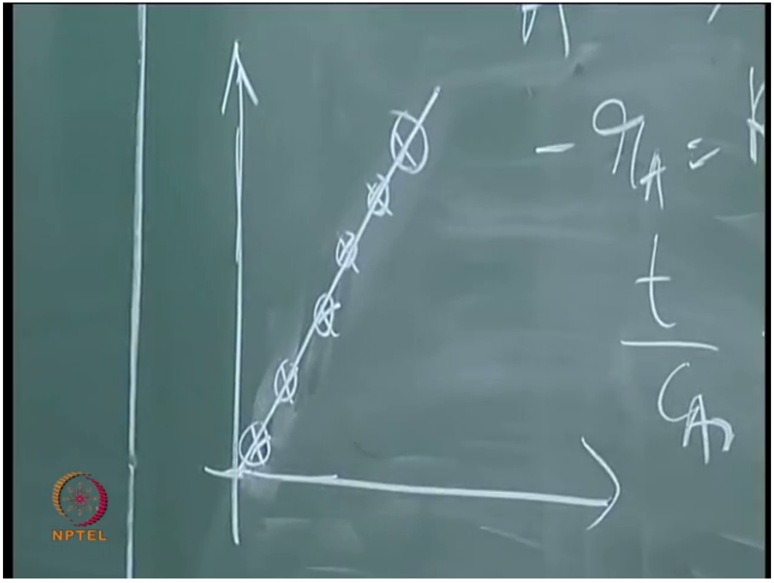

be so happy, you cannot.

(Professor – student conversation ends)

Actually if you plot that you will not get a straight line. Actual data if you plot that, Ok. So if this is the one, then you have this slope measurement where many people, Ok, this is t where many people do not know how to measure this slope also, you know I can tell you. Many people do not know, right, how to calculate or how to measure. So this slope will give you k.

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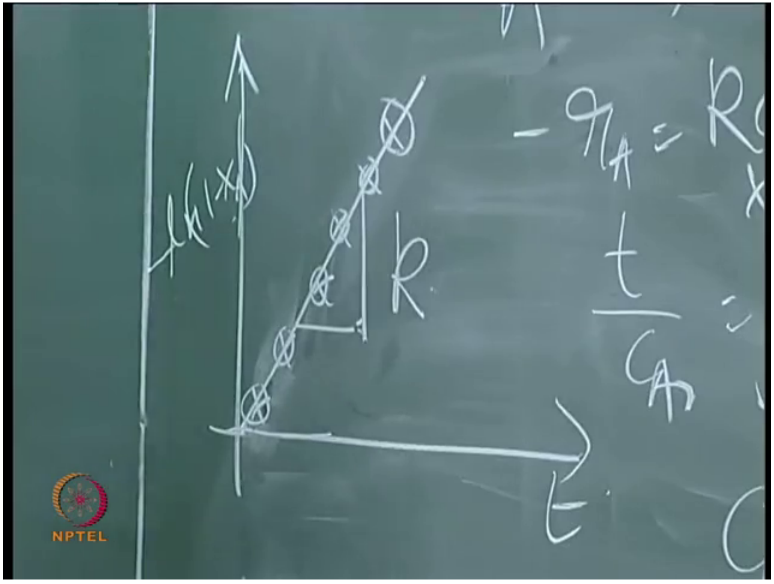

So then what is the order of reaction for you? It is first order if it is straight line, confirmed.

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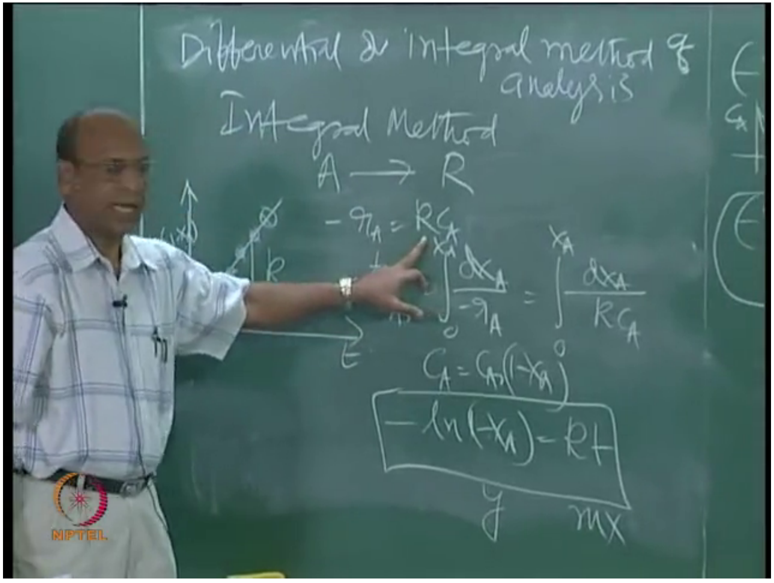

And k value you know. So as an example, in this case this may be minus point naught 5 C A. That is all,

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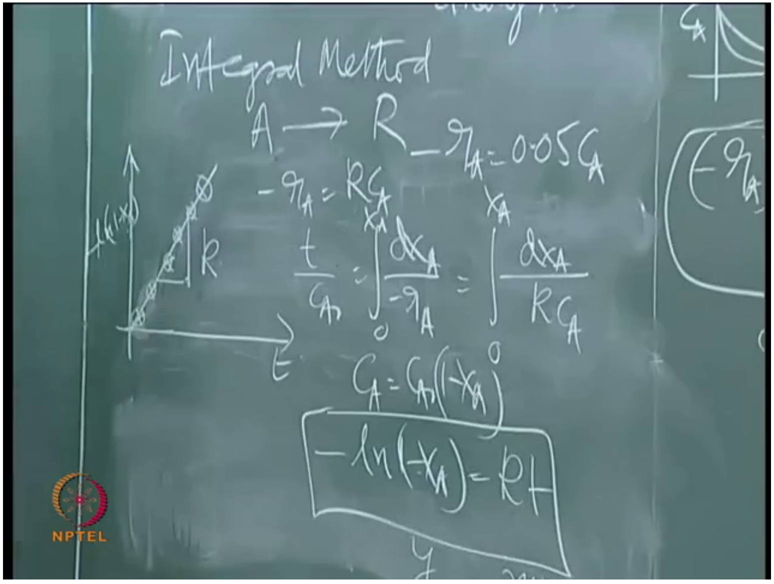

Ok. So this is what. That means with respect to concentration, it is, order is first order

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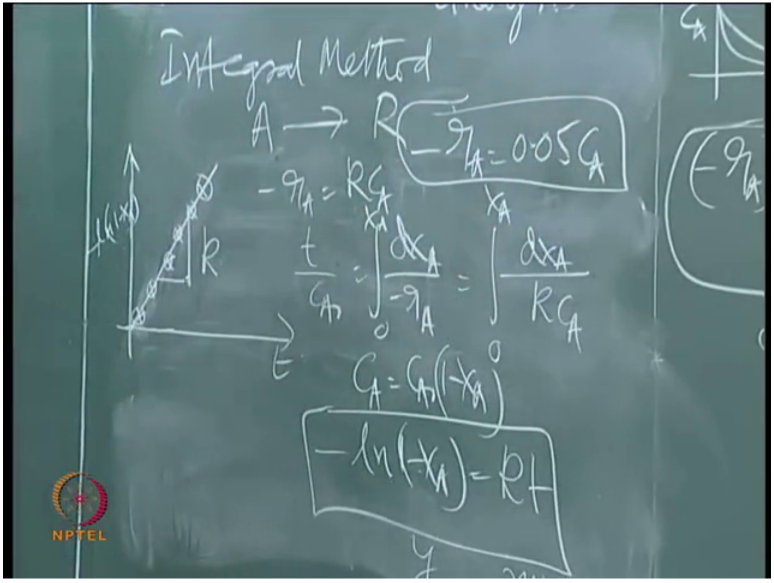

and I have this k value but what I have done all the time without mentioning is that, at one particular temperature.

Now I have to also get in rate that Arrhenius equation that means few different temperatures also I can try. So then if I try to different temperatures, I may get like this, like this, Ok, like this another curve. So this slope is for high temperature or low temperature?

(Professor – student conversation starts)
Student: Low
Professor: Yeah, slope is low. So k is, so this will increase, temperature will increase in this direction. This is T,

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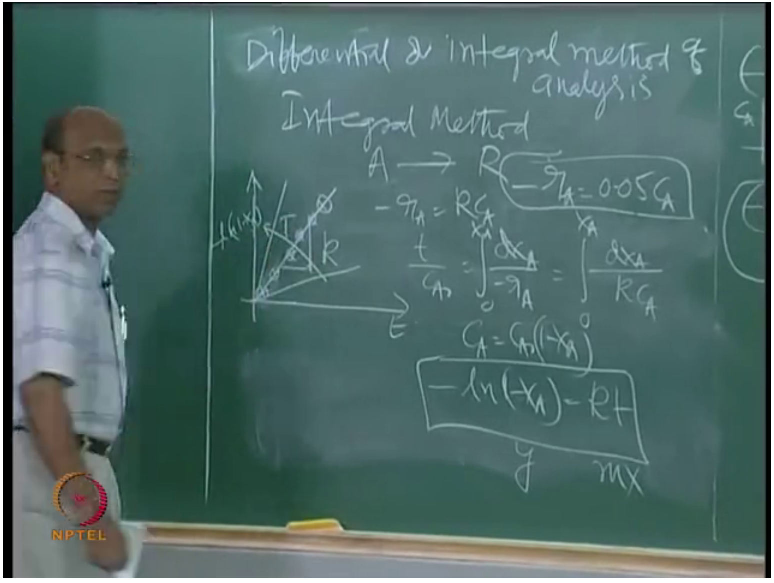

right so now once you have this, again you have Arrhenius equation to calculate. So Arrhenius equation is minus k equal to k zero e power minus E by R T, right?

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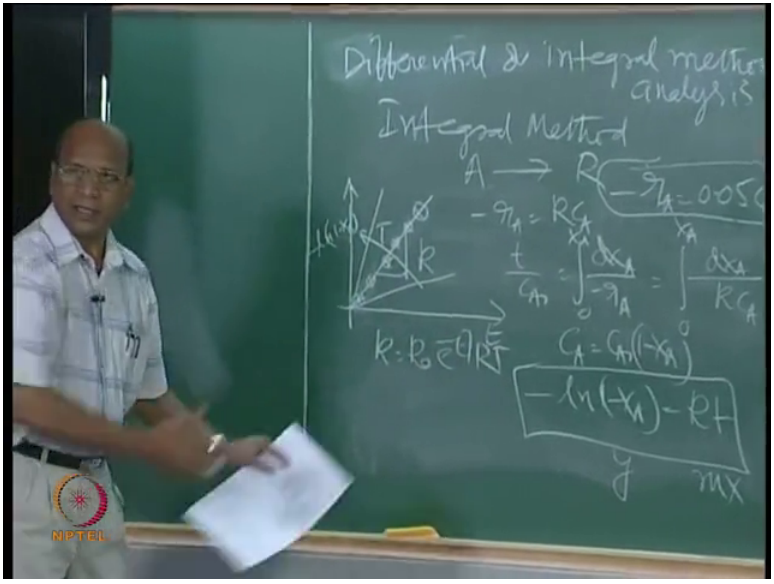

Take logarithms and then you will plot, this plot you know, minus l n k versus 1 by, 1 by T. R is a constant.

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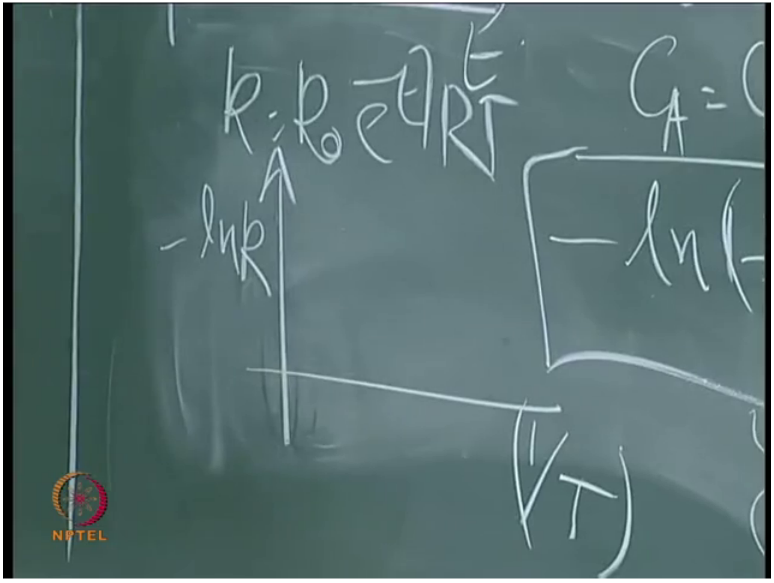

Ok, yeah. How the, if it is correct, how the straight line should come?

Student: Like this

Professor: Yeah, because it is negative slope, it should come like this. So this slope will give me, yeah it is already negative, so it is E by R, decreasing.

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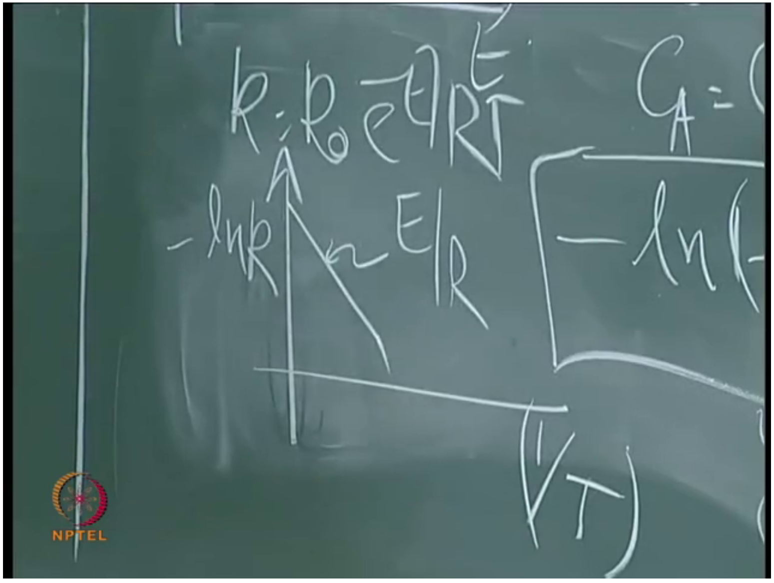

E by R.

(Professor – student conversation ends)

So then you have the complete equation as minus r A equal to, yeah using this E by R you can now go to this equation and then calculate

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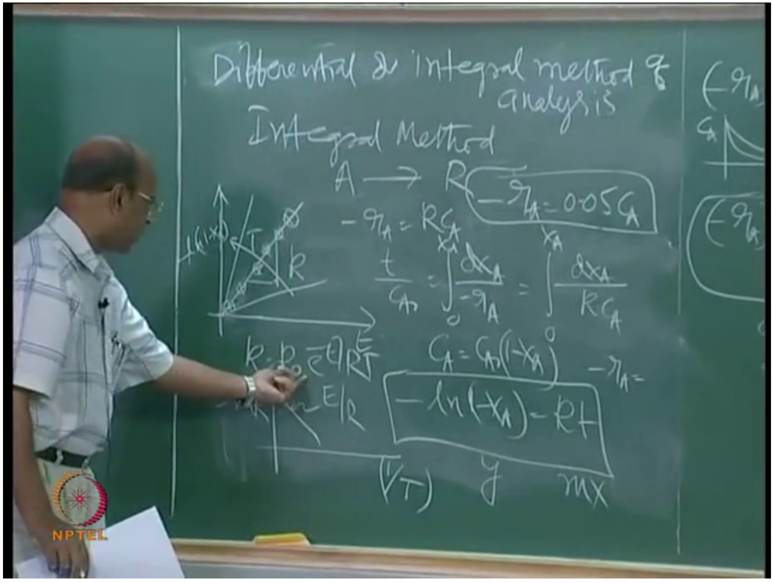

k zero. E to R ratio 0:51:23.4 we already know from the slope. Otherwise intercept you go and then find out what is k naught, right?

So then I have all the information, may be k naught may be 10 to power of 5, as an example. Ok and this is e power minus; this may be 20000 by R T, Ok, into C A. So that is the expression.

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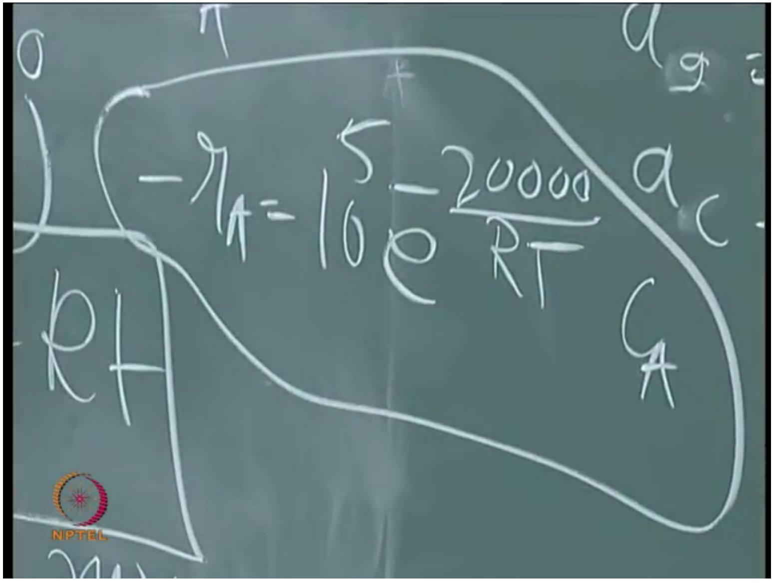

That is the expression what you have. That is the rate expression in terms of temperatures. This is how you have to do. We have taken the simplest example. But life is not that easy. Every time it is very, very difficult. That is why, now you see if you go for integral method you need all

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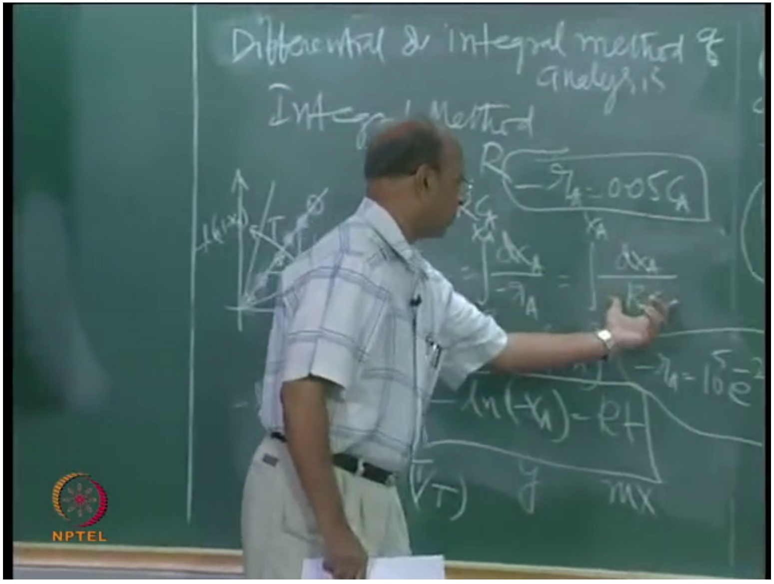

integral expressions. Entire third chapter of Levenspiel is only integral expressions.

That is why those who have not solved those integrals, you know it is first order, second order, reversible, irreversible, and you know third order also, and you have also auto-catalytic reactions and parallel reactions, the procedure is same. Ok series reactions. All these things are there. So those people, particularly I think chemistry background and also, you have Levenspiel book? Yeah.

So that third chapter, you know please solve all those equations which he has already given, right? He even gives each and every step. But you have to solve on your own. Otherwise in this course most of the time it is, you know, even though I talk all words here, in the examination I will only give problems.

Ok. I mean you cannot tell all the time I will give only problems, I can give anything. But most of the time, in engineering, we will try to give you know this kind of, if it is not numerical problem, derivation. Ok, so these things. Otherwise simple concepts. So that is why you have to practice. Others are supposed to have practiced earlier. Correct no?

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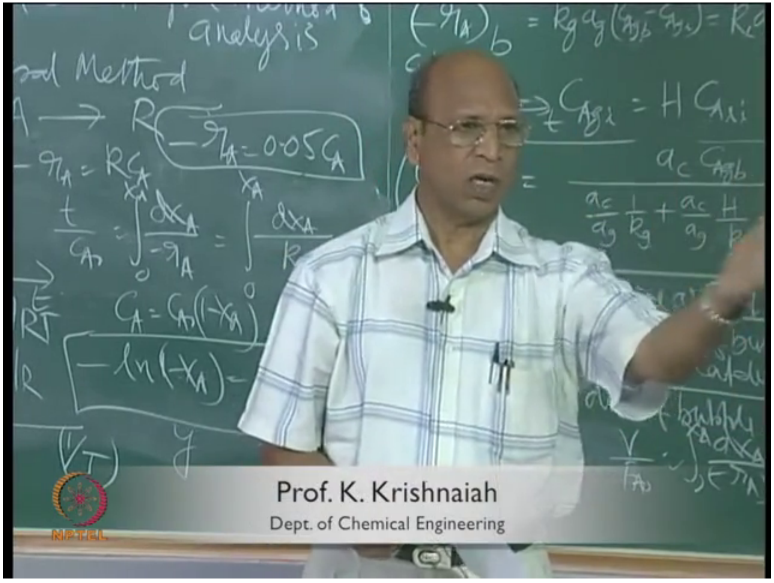

All third chapter derivations you are supposed to do it. Otherwise if you have not done that, do it now. Otherwise it is very difficult for you in the examination because in this reactor theory course I am not allowing any formula sheets whereas in the next course, you are matured enough. Then I will give formula sheets there for C R E 2, that is Chemical and Catalytic Reaction only. Good.

So that is why when I give you a problem, you have to now derive that equation and then substitute the given values and then you have to find out what is asked. We will stop here.