Chemical Reaction Engineering 2 (Heterogeneous Reactors)
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Lecture 17
Catalytic Reactions (LHHW Kinetic Model)

I think we have done the non catalytic reactions and we started with that performance equation diagram. Now again I am going to draw the same diagram. This is a reactor. I think this diagram will come in your dreams I think. Output, kinetics, contacting, then we have here chemical, physical, batch, continuous. And here we have in continuous P F, M F. And the performance equation is given as output as a function of input, kinetics, contacting. So this is the equation.

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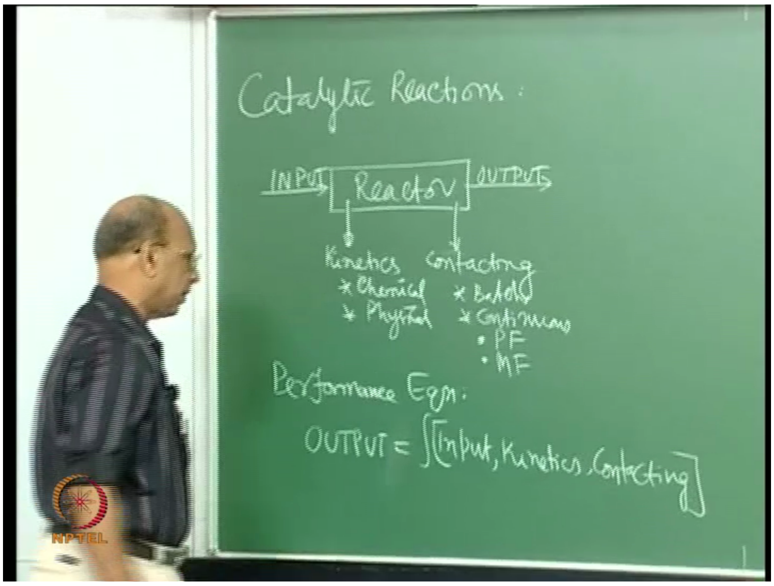

And when you are discussing about non catalytic reactions this equation has been beautifully used. I do not know whether you appreciate it or not. I appreciate it myself because there is information that is required from kinetics. That one we have seen for single particles and contacting. Contacting mainly comes through R T D in fact, okay, yes E t, either ideal or non ideal so that means we have a broad framework for all reacted designs, right? Now let us see in catalytic reactions what is that that is required?

Input again is definitely required because that determines the plant capacity and the kinetics we need now a rate expression and we also had a rate expression for non catalytic reactions, okay. That is mainly in terms of x B and time. Here we will have in catalytic reactions the rate equation will be in terms of minus R A and as a function of the partial pressures or concentrations. Again you need a rate expression but what form it will be you will now see, okay. Then contacting anyway it will come.

If it is a packed bed, if you have a rate expression packed bed catalytic reactor where the solid particles are catalyst now. And the difference between non catalytic and the catalytic is in non catalytic reactions the solid will finally be converted into a product, right? So and it may even disappear like in coal combustion or coal gasification whereas in catalytic reactions the solid will not change. The size is same and if you assume that deactivation is not there so then lifelong you can use this catalyst as a catalyst particle, okay.

So under those conditions somewhat it is easier than non catalytic reactions because the solid here is an inert as far as reaction is concerned. But only it is increasing the rate of reaction inside the particle when the molecules go but it is not participating directly in the reaction, okay. So it is easy for us. That means when I put a packed bed let us say 1 centimetre particles I pack and then if there is a no deactivation till I die I can use. Of course now only I have short span but even if you also start till your end you can always use packed bed, okay.

So like that even fluidized bed or moving bed again all the reactors. That is why I have been appreciating chemical engineering so much because you have the contacting patterns. Any reactor you can bring you can break into only two ideal reactors. So that is why in one sense you do not have to learn much as far as the contacting pattern is concerned. Only you have to learn is mathematics analysis depending on the complications, right? So I mean even non catalytic reactions also I have done only simple things.

And the one of the simplest things what we have done is only single particle and change is only in the particle, there is no gas change. That means there is no concentration change in the gas phase, okay. Normally we can maintain that in industry by sending large amounts of gas particularly when the gas is not very costly like air you just compress and then blow over the coal particles and you do not have to recover anything with that. Nut whereas hydrogen and all that when you use definitely we have to take that also into account.

But concepts are same. Only mathematical analysis will be a little bit difficult that is all. And that is the reason why you know we are giving you six or seven courses in mathematics, in B Tech four five. I think some of the people would have done six and in M Tech also you have mathematical methods in chemical engineering and transport phenomena is nothing but again mathematical course if you do not appreciate the physical phenomena of the processes.

So everywhere you see mathematics in chemical engineering because the processes are complicated, right? So now let us see how we develop this kinetic expression as I have been telling you this you know. Only two reactors and batch that is all. Two continuous and one batch and this also I know. This job we will give to MBA people. They will go to market and then say that so much you have to produce, okay. So then we will know our production.

Then this is where we have to concentrate most of the time depending on what kind of heterogeneous system you have. We have gas solid non catalytic reactions. Liquid solid also very same except that when you have that pseudo steady state assumption that is no more valid. So again mathematically complicated that is all. Other than that you do not have to learn anything new there. For example gas liquid system, same procedures all the time.

Develop your rate expression, go to contacting pattern and you know the input and substitute this kinetics in terms of rate in the contacting pattern equation and then you have to integrate, good okay. So, in the kinetics of catalytic reactions most of the time we know that we have only solid catalyst. We also have liquid catalyst but I think you know that is called homogeneous catalysis, okay. For example biodiesel is one of the examples.

They use liquid biodiesel from seeds and all that they are doing now (())(07:16) and all that. So there the catalyst also is in the form of liquid but the liquid catalyst should be dissolved in one of the liquid phases. You cannot really identify whether there is a catalyst or not. Only through reactions only you can see because it is completely dissolving which you cannot see that, okay. So but we are talking about gas solid catalytic reactions because that kind of reactions are many in industry. Can you give me examples? Gas solid.

Student: F C C.

Professor: F C C, what is the catalyst?

Student: (())(07:48)

Professor: Okay, one more example.

Student: Hydrogen reaction (())(07:54)

Professor: Hydrogen initially actually (())(07:56) I am asking gas solid. Very simple example my favourite example all the time, Kavya?

Student: Ammonia.

Professor: Ammonia what is the catalyst?

Student: Iron.

Professor: Iron catalyst. I think you know the simplest one what I have been telling all the time is sulphuric acid, okay. In one step you have to use catalytic reaction. What is that?

Student: S O 2 2 S O 3.

Professor: S O 2 2 S O 3. And what is the catalyst?

Student: (())(08:20)

Professor: So like that of course many catalyst are used and industry because just to increase the rate of reaction and it is heterogeneous system. So what we imagine again here is one single particle, right? So I may have a particle, okay, something like this. Again beautiful spherical particle we are trying to draw and then we have here the film.

And because most of the time we use porous particle we have to also show that pores. So this may be something like this or okay, it maybe whatever way you want to draw you can try it, okay. So here also I may have. So this may be solid, this may be a solid.

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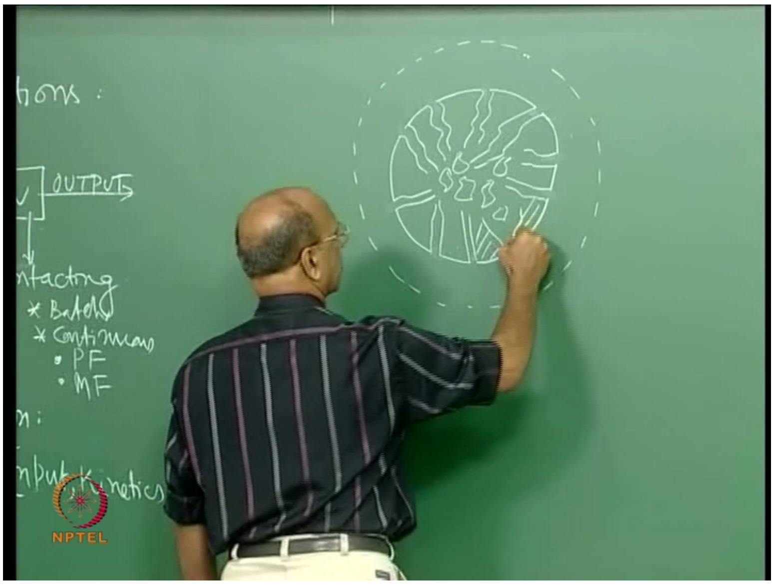

So something like this you will have this solid particle. And now the gas will be flowing like this. This is reactant gas. Now as usual we can imagine what are the number of steps that are required for the reaction to take place. Step 1 is mass transfer of, okay, let me also say that we have a reaction something like, for simplicity again, A going to R. This is catalyst A going to R. That is catalyst.

So now this is actually gas A then step 1 is mass transfer of reactant to the surface, correct? So unless it does that it cannot. So this is adsorption or diffusion we will say, not adsorption, diffusion of A through the pores. And step 3, adsorption now, adsorption of A on the surface. Step 4, reaction on the surface that is step 4. And step 5, desorption of product from the surface.

Step 6, diffusion of product gas through the pores. And step 7 is again mass transfer of products. Mass transfer of products through the film to bulk gas. Seven steps, seven commandments . So all of them are you know series steps or parallel steps or series parallel. All of them are series, okay.

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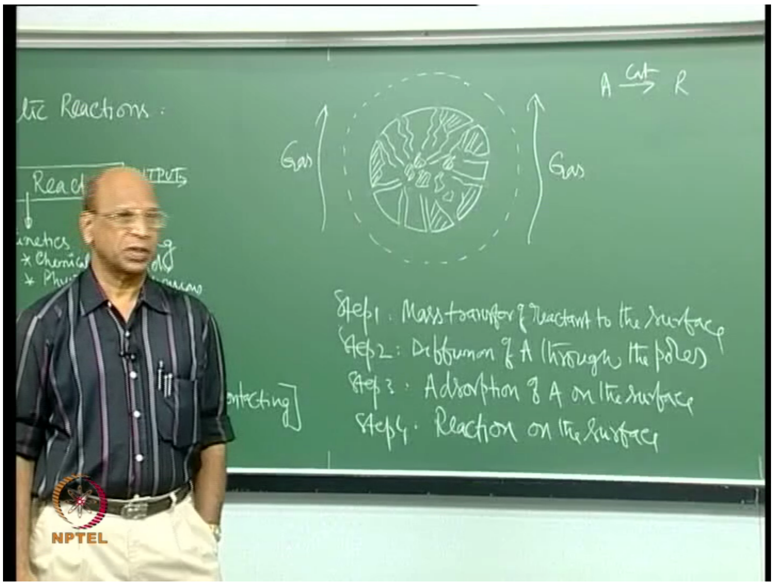

So if I take one molecule, the molecule has to first go through the film, then diffuse through the pores, then get adsorbed. And our imagination is after getting adsorbed in active side then that will dissociate into some kind of intermediate and then the reaction takes place, okay. And after the reaction the product is formed at the same side but now product has to leave the side. Why? It can happily sit there.

Student: Catalyst (())(14:27)

Professor: Catalyst is a?

Student: Not to be used further.

Professor: Yes but why you should leave?

Student: Concentration gradient.

Professor: Yes, concentration gradient because outside you have less concentration of product and inside you have more concentration of product because of the generation there because this is reactant converted to product so that is why it has to leave. So because of the concentration gradient it comes out and then again the diffusion through the pores and diffusion through the film and then comes out, okay good. Out of this how many are mass transfer steps and how many are reaction steps?

Student: One reaction.

Professor: Which is the one?

Student: Step 4.

Professor: Yes, but what about desorption and adsorption? What do you tell? These are mass transfer steps or reaction steps? Yes, so we call them 3, 4, 5 are the generally reaction steps which contains adsorption, desorption and surface reaction, okay. And adsorption, surface reaction and desorption all three. So that is why all three first we take because that is where the reaction taking place. The remaining four are mass transfer steps, right? And through the film we already have the equation.

Same Frossling equation again, same Ranz Marshall correlation here also. Why? I have the particle, surrounding that I have the film then reactant has to go through that and at steady state when the continuous process is going on we also have the products coming out. So now you have again assuming that equimolar counter diffusion, right? So products are coming out, reactants are going in, so kind of dynamic equilibrium is established there in steady state again, okay.

Steady state so that mass transfer coefficient I can find out through correlations. And always mass transfer depends on hydrodynamics. I do not know whether any time you realised that. First of all you should know what is hydrodynamics? Okay. Hydrodynamics means it is the fluid mechanics around the particle or inside the reactor, okay. So, mass transfer coefficients and heat transfer coefficients always depend on hydrodynamics or in general fluid mechanics.

That is why first fluid mechanics we teach before going to heat transfer and then mass transfer, okay. Why it should depend? Because if the particle is stationary and the gas is moving around that or fluid is moving around that, we will have a kind of relationship between the particle and then the fluid. This is the packing. If I use the same particle in fluidized bed again the relationship between the gas how it moves and then you know the solid how it moves is totally different.

So here in a fluidized bed the particle vibrates, particle hits other particles and all kinds of things will happen, okay. It may temporarily jump and then again fall down, all kinds of things. So the mass transfer process or heat transfer process surrounding this will be different when compared to a packed bed where the particle once you put there it is there all the time, it is not changing. But the same thing again if I put in a moving bed that means now packed bed is no more packing, then the entire bed is slowly sliding down.

Then again how the hydrodynamics what we call or fluid mechanics around the particle again different, right? Same thing and then now you can put the same particle in rotary kill. Again heat and mass transfer will be different. So that is why heat and mass transfer coefficients or the process depends on what kind of hydrodynamic conditions what you have.

That is what actually my research area for long so many years. I am always trying to find out in a reactor, before the reaction starts what kind of hydrodynamics are established? And not only this, particularly heterogeneous systems packed bed for example we say void is F or void fraction of solids and void fraction of mixed base liquid or fluid in general, okay. It can be liquid or it can be gas. Then how do I know that? Because it is packing here and it is not moving I know because I can find out exactly what is the voidage.

But the moment I go to fluidized bed where particles are moving how do I know that what is the voidage? The fractions again. Voidage means the fractions, okay. Fraction of solid and fraction of gas, how do I know? And depending on my velocity in the fluidized bed, the bed may expand because normal in a fluidized bed it is open, okay. There is no top distributer whereas in packed bed between two distributors it is slightly packed. So that is why even though you use velocities much higher than terminal velocities of the particles, still particles will not go.

Still it is packed only because you are not allowing it to move at all. It is tightly packed. So that kind of situation will not be there in fluidized bed. So, the particles will expand, the bed will expand so naturally the fractions of gas and also solids will be different. Now just imagine for three phase. You have two continuous phases, gas is continuously going, liquid is continuously coming then you have the solid, okay. And again many varieties are there. Like you have heard of trickle beds, catalytic reactors? Where do they use? I mean in a sense we do not know.

Student: Oil, hydrogen.

Professor: Desulphurisation of you know oils, sulphur is removed using zinc oxide catalyst or so. So there you have hydrogen and also oil as well as the solid catalyst. But you know trickle bed is a packed bed but the other two phases are moving, gas and liquid. But again your fraction of gas and fraction of liquid depends on again what kind of flow rates you have. So that is why hydrodynamics are very important and many people in industry never bother about that.

And because the establishment of volume fractions depend on the flow rates. At a particular flow rate automatically the phases will have certain fraction that is established due to steady state conditions at that particular flow rates. If I change the flow rate again gas volume may change, solid volume may change. Solid volume is constant generally when it is not reacting in the reactor but most of the time catalyst.

But gas and liquid will change because even in fluidized bed you have the solid particles and you are not allowing them to go because even if they are going out like in F C C there is lot of solid particles which are going out. I mean old days F C C process not recent one, okay. So then you collect them and again send back. Now the reason one is first fluidized bed. Anyway they are going out, let me allow to go out. They are going out and again collecting in a cyclone because of deactivation again regenerate and then we will send it back, okay.

So but the old process only normal not first fluidized bed, normal fluidized bed when they use that means the velocities are much lower. Then they will put a cyclone and then try to collect. Not only of course F C C, in any other catalytic process, catalyst should be as porous as possible. The moment you have as porous as possible, what will happen to the mechanical strength of the particle? Decreases. So when mechanical strength decreases because of iteration you will have lot of fines going out.

So that you have to collect in the cyclone and if it is possible again you have to recycle back otherwise you have to take them away and then again make similar particles on them, send it back. So that is why these mass transfer steps in any reactor will be different depending on its own hydrodynamic conditions. That is why mass transfer even though we say that you know we have understood, it is very difficult for a totally new reactor. Now I do not know whether you heard of platinum mesh type reactors .

You have seen mesh where they sew? You know in house also nowadays you know housewife also is doing, okay, to separate that good rice and bad rice. You may have very fine powder rice, not very fine powder, small pieces, okay. And you will have normal rice. So to separate them in houses villages the used to sew, okay. That kind of sews are used as packed bed. One sew above one sew above one sew, it is production of nitric acid in one of the steps.

There because the hydrodynamic conditions are different, mass transfer coefficients like you know Ranz Marshall correlation will not be useful. You have to develop on your own another correlation. So and you know of course we drive cars and then we use cars but we do not know there is a catalytic reaction even in car, okay, in exhaust pipe and that is monolith. Entire catalyst is only one particle.

That particle is simply put into the exhaust pipe, okay. And it is not solid again. You know it is a porous one. It is a wonderful design where you will have this is the cylinder like this, then you have different plates arranged like this and gases go through like this.

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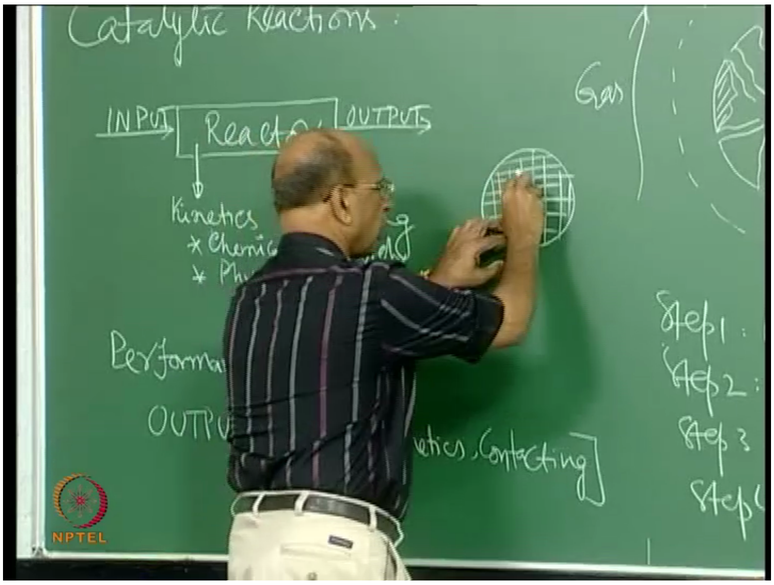

And still good engineers will try to put this one as like this. What is the advantage? Some more surface area. Always chemical engineering job is always how to get more surface area whatever you do, okay.

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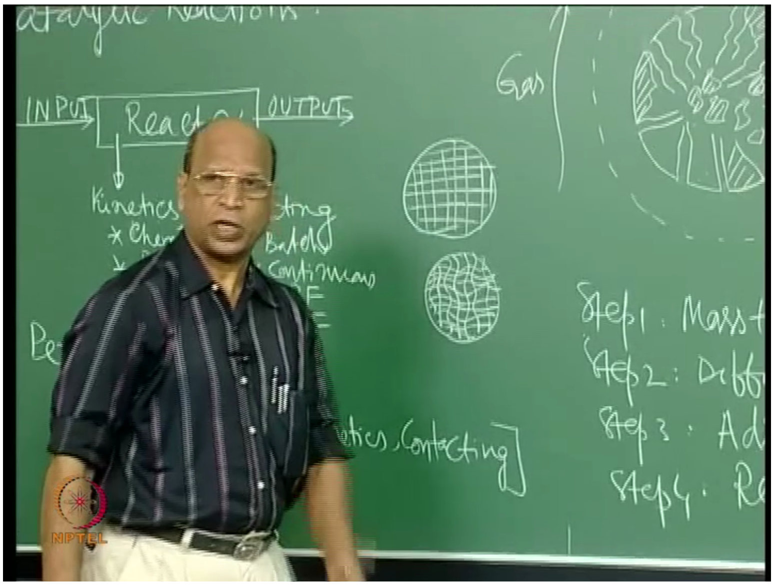

That is why I think you know by the time you come to extraction, you are tired in mass transfer. And maximum amount of time we spend only on dissolution everyone knows that. Afterwards we do not do many operations, okay. Next maximum is only adsorption but in extraction if you go you know what kind of equipment they use? Mixed (())(25:05), of course again packed beds, sew plates. In all that this hydrodynamics is very difficult in liquid-liquid extraction.

Why do you think so? I mean at least try to think. In liquid-liquid extraction it is not that easy to maintain flows through these columns. Why do you think so? Whereas in adsorption, where you have gas liquid system it is easy to do that. It is not that difficult as liquid-liquid. Just can you try to expand your brain why it can be?

Student: Solubility.

Professor: Solubility is fixed when actually liquid-liquid extraction what will not solve in the other, okay. Only one of the components in one phase will only try to go to the other phase. These two are supposed to be immiscible, okay. Anything, we are now right now facing also.

Remember we have liquid solid system but still you know it is like a moving bed type where we want to use that one for, of course you can use it as a biochemical reactor or it can also be used as adsorber to remove collar and all that because it gives a beautiful efficiency as far as adsorption is concerned because it is a steady state process. Normally all adsorbers are unsteady state process because we put the adsorbent as batch. Here we are trying to make this one is continuous.

And when you have solid is continuously coming steady state, liquid is continuously going. So whatever the pollution control board tell us that okay you can you should have 10 PPM in the outlet we can design for that. Whereas in the other system where the solids are in batch condition initially you will get zero because large amount of adsorbent and the same concentration, right? So you will get zero, very pure water.

Then after sometime slowly the concentration in the outlet goes on increasing and then finally it will reach your original concentration in the inlet. So these pollution control board people will not allow you that. So they will say that yes always fix only 10 PPM example, okay. You have not answered me. Why do you think that why? You have to expand I said. You know even if it is wrong answer tell me, no problem. Try to think.

Student: Diffusion.

Professor: Diffusion, who told that? Satyam, yes diffusion of what?

Student: The gas into the.

Professor: How the two phase are (fowin) flowing in the reactor or in liquid-liquid extractor? Of course we have liquid-liquid reactions also. There also again hydrodynamics come. What is the driving force? If I have two liquids what is the driving force if I am not pumping them? How the flow? It is only the density difference. For liquid-liquid systems, most of the time the density difference is not that much so that is why it is very difficult to make them flow the way you want.

And the separation also takes place lot of time because particularly when you have very close densities. Whereas if I have gas and solid, thousand difference. Solid will have normally you know 1000 kg per metre cube and gas will have only 1 kg per metre cube. So then separation is so fast that is why gas solid fluidized bed are very easy to design. Whereas liquid solid fluidized beds are again not easy.

That is what right now we are facing. My research student, you are not able to separate the solids from liquid when it is conducting the experiments on hydrodynamics, okay. So that is why mass transfer and hydrodynamics are very well related, okay. And one has to remember that for every system you have a different correlation. It is not universal the way I was telling you, always Ranz Marshall correlation. Ranz Marshall correlation is only for one particular particle and around that you have yes gas going like that.

Even in a packed bed you have a different correlation. Ranz Marshall correlation is not valid. Only place it may be valid slightly is a fluidized bed. Why? Because in fluidized bed particles are supposed to yes move around independently so the gas may be going around each and every particle. So if no correlation is available for an actual fluidized bed then Ranz Marshall correlation is generally used. That is single particle correlation generally used, okay good.

So now what we do is we take step 3, 4, 5 and combine them as reaction step and this is where what you get is that Langmuir Hinshelwood kinetics, okay. What you do is we take first these three steps and then we develop a rate expression.

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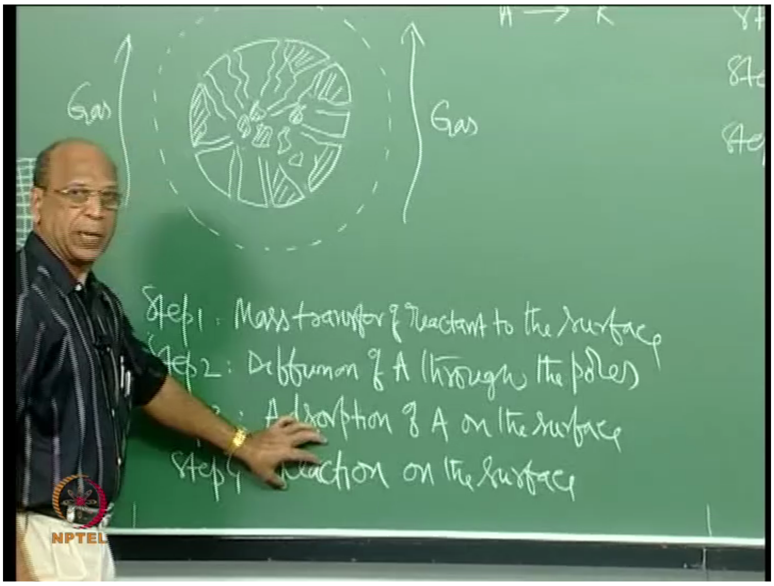

You will get minus R A equal to in terms of you know K A, K B, K C. I think I also told you in the beginning of the course what kind of rate expressions you get for catalytic reactions, okay. Minus R A equal P A minus P B by K divided by you have adsorption, desorption constants, okay. So that is the kind of equations what we are going to develop if you take steps 3, 4, 5. And then once I have that rate expression that means it is totally not affected by these two steps, these two steps.

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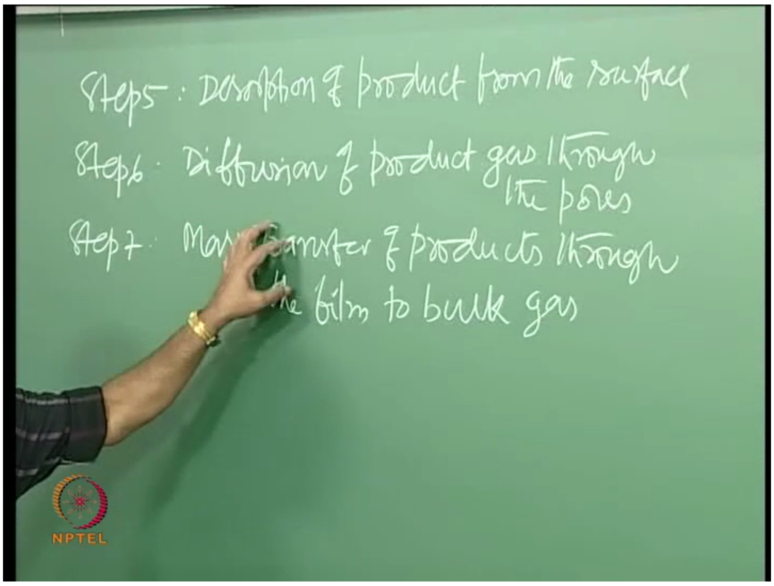

Step5 : Desorption of product from the surface

Step6 · Diffusion of product gas through the pores

Step7 · Ma[illegible]ransfer of products through [illegible]he film to bulk gas

What is the meaning? Mass transfer is not controlling the rate. It is only the reaction, okay. So then once you have this understanding of this 3, 4, 5 steps then you can have how to combine this diffusion and you know diffusion is maybe rate controlling most of the time depending on the pore size of your catalyst. So that means the catalyst particle is able to react because of large surface area that is available in the particle or exothermic reaction, the temperature may be high in the particle so rate of reaction may be fast.

But you do not have sufficient mass transfer through the pores, sufficient reactant coming through the pores for the reaction. So then how do we combine that reaction as well as diffusion? And we have a general thumb rule. Whenever you have this kind of porous particle, the pores through the particle, right and when I have film which will be controlling generally. Diffusion through the pores are controlling. I mean these are the things which you have to remember. There is no choice.

And if you have a good decent interview these are the questions that will be asked. How is the interviewer asking how many mothers, how many fathers, how many sisters, how many brothers? So this is all very good, very well answered so take the job. And then you end up in IT, okay. That is the kind of jobs beautifully they give you, right? Yes but here whenever you have this kind of decent interviews in chemical engineering this is the things only asked. I mean do you have any thumb rule like you know, what step you can neglect.

And you know there are interviews where what are the possible steps in any catalytic reaction? I myself asked many times but I think even PhD interviews also we used to ask.

What is the difference between homogeneous reaction and heterogeneous reaction? Okay. That they will say that answers straight forward comes. What is that? One phase or more than one phase. That is excellent. Then we ask, okay so what? I think if there is more than one phase what will happen?

What is the extra information you require for the design? Stop, okay. So that is why all these things are very important for us also to remember and I am not saying that you know these are very difficult. This is very simple things to remember provided you imagine the process. That is why always I say always in my teaching I try to ask you to imagine what is happening in the process. Automatically mathematics come easily the moment you image in the process, okay.

Most of the time we start with the mathematics and we forget about the actual process, good. So let us take this steps 3, 4, 5 and then develop the equations. For that I think you have to take some continuity notes. We call them as surface reaction models which involves adsorption, reaction and desorption all three, good. Here also we will try you know all 7. All 7 may be rate controlling, closest situation possible but I think you know it is possible then we will derive one equation.

That will give you a wonderful idea, okay. Please check this, physical mass transfer steps are not rate controlling when surface reaction models are developed, okay, or in other words these steps are very fast compared to surface reaction, okay. I think slightly high funda words we will use here. In the bracket you can write that is interface and intraface transport processes are faster. These are slightly high funda words. People who want to impress they say always intraface interface, okay, because again you know our separating have to work.

What is intraface? The moment I said interface (intra) intraface, you all gone like this. So that means you are trying to get. All of us do that, nothing wrong, okay. So intraface is what, interface is what by the way? Yes interface is this and this. Intraface is yes through the pores, okay. So those two, okay good.

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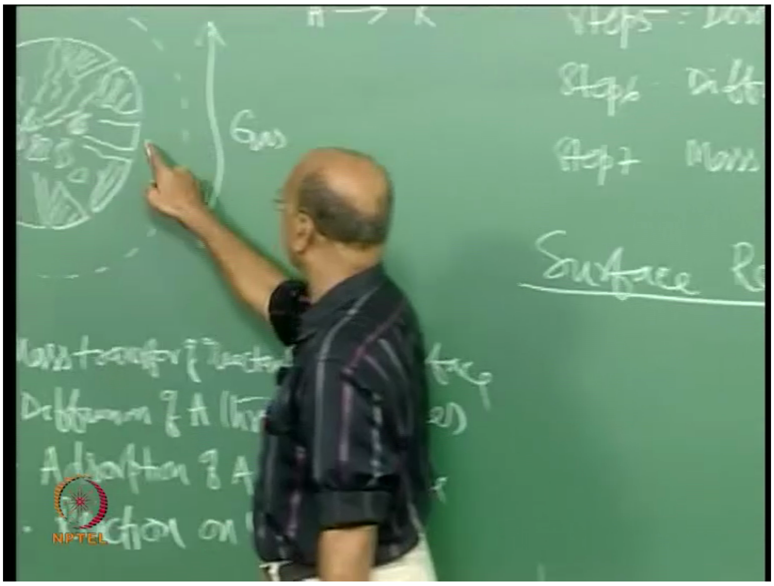

And isothermal condition is assumed, good. Next one you write, surface reaction rates can be expressed in two ways. One is Langmuir Hinshelwood formulation. Please write just below that, in this the rate is expressed in terms of surface coverage data comma and then employing the Langmuir isotherm to relate theta to fluid concentrations.

Second one is Hougen Watson approach. That is the second one just write below that. Hougen and Watson derived rate equations in terms of surface concentrations of adsorbed species and free sites comma and then expressed these concentrations in terms of Langmuir isotherm. I think in your physical chemistry book that theta approach you could have seen when you are deriving Langmuir (iso) isotherm, okay.

But you have seen Hougen Watson book? You have used? I think (())(37:35) you would have never used I think. You do not even know Angad? There are three volumes, volume 1, volume 2, volume 3. Volume 1 is material balance, okay, energy material balance. Volume 2 is thermodynamics, 3 is kinetic. There is no heat transfer. You are talking about Coles and Richardson. Only these three, in volume 3 you have lots of catalytic reaction formulation. Kinetics and catalysis I think that is the title of volume 3 I remember correctly, okay.

Volume 2 is thermodynamics and volume 1 is material and energy balances and those are almost the first books in chemical engineering. And what a wonderful books you know all the books because directly the data from industry were used at that time. I think Shankar was asking me he wanted to give some reactor problems for I think that optimization course or so.

So he wanted to have good kinetic data. Then I told him just go and see catalysis that book by Hougen and Watson.

There are wonderful data given, actual industrial data. Afterwards anyway we went very far from industry and industry also ran away from us and now again we are trying to come together because now I do not know whether you have observed, industry has now intellectual people. I am talking about percentage wise. Because of the competition they have taken the best people that are possible, international competition.

So that is why their processes must be totally new and updated and always they have to be one step ahead when compared to their competitors. So that is why even though 100 percent basic theory they have not understood but wonderful information from chemical Engineering has been used to develop these processes, okay. And also their techniques , academic institutions nowhere can come because of course they have lot of money so they can use those techniques.

And techniques means I am talking about analytical instruments for the analysis and all that because I told you , small 400 ml medicine also maybe costing 1 lakh 2 lakh rupees. So that is why industry has now excellent talent. Now they want to come and then of course again always life is cycle I say. I think you know in the beginning they were together, in between separated. That is also most of the time happens you know.

First love, you come very close together, get married, fight every day, then go away, then children will come, again come together for the sake of children. Everywhere any process you take this cycle thing may happen, okay. So that is why industrial nowadays you know we have how much money that is coming to IIT from either industry or other research laboratories, private laboratories or government laboratories tremendous amount, okay. Anyway so that is why I think this history also sometimes I think you require.

You know Hougen Watson are the people and what is the third name? It is not only two. That is why even I was yesterday I used to push you know these B Tech boys to have chemical engineering quiz and some of us used to give all those questions. And now they also will run away the moment you say chemical engineering. You tell MBA quiz they will run towards that, not chemical engineering. What is the third name? No one remembers, okay. I think very nice. You do not remember even our basic books.

No idea at all, trying to recall. All files are searching in the mind. Ragatz, R A G A T Z. Now you remember these three people. You know because of this and another three people also wrote wonderful book. Who are they three? (())(41:14) is only two I said.

Student: Herriot.

Professor: Herriot is I think is recently yesterday he was born. The original one Herriot I think you know.

Student: Smith and Van Ness.

Professor: Smith and Van Ness only two again.

Student: BSL.

Professor: Yes BSL, Bird Stewart, Lightfoot. Of course there are four others in another mass transfer book. I do not know whether you remember that or not.

Student: (())(41:38)

Professor: Those are three. Faust there is a book. You know that is what you know because of the computers we are going away from the text books also because all your information is only Google. If you want mass transfer correlation you first Google only right? Or heat transfer correlation only Google. I think the beauty is going but anyway again it will come back definitely. Please remember everything will come back to the books again, good okay. So yes take this one.

Even though there is not much difference, next you can write. Even though there is not much difference between these models, Hougen and Watson models are easy to handle in which surface deactivation can be incorporated full stop.

To do justice to both these schools that means Hougen Watson school and Langmuir Hinshelwood school, to do justice to both these schools let us refer them as Langmuir Hinshelwood Hougen Watson all combined formulations. We call LHHW equations, LHHW kinetics, LHHW models all these things. LHHW means Langmuir Hinshelwood Hougen Watson models, okay.

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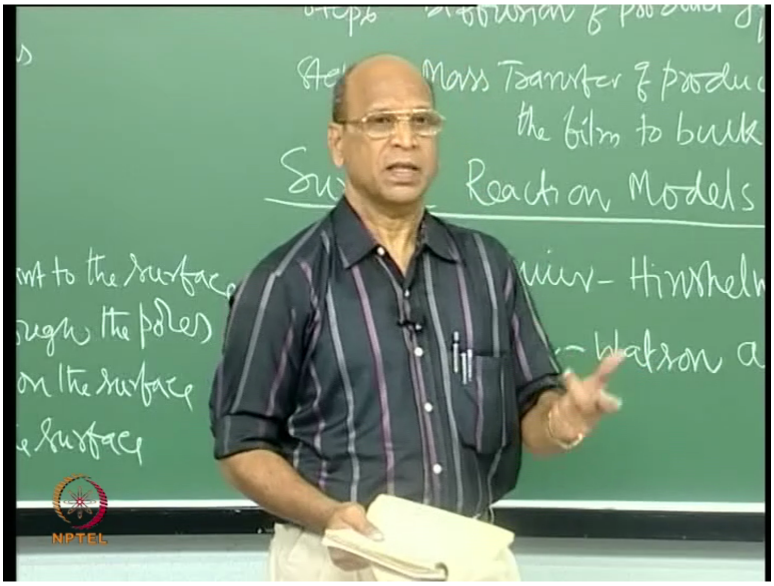

This is what one of the questions I gave also in that zero test where what information you get from LHHW models. What information you get? You get a kinetic expression for catalytic reactions, okay good. Let us first derive Langmuir isotherm. What are the assumptions of Langmuir isotherm? Very good, monolayer coverage, okay. Uniform surface conditions that means I think all surface behaves in the exactly same way, isothermal condition. These are all assumptions. Okay Akshay Kumar lost.

Monolayer coverage, uniform surface activity, isothermal condition, these are the assumptions in Langmuir isotherm. Next one you can write, the surface may be divided into theta and 1 minus theta where theta is fraction of surface covered by adsorbed molecules and 1 minus theta is bare surface that means the surface is free of any adsorption.

So rate of adsorption we call minus r a equal to k into p, the partial pressure of certain gas into 1 minus theta, okay. Rate of desorption equal to minus r d equal to, minus you do not have to put. Can you tell this one? See theta is the surface that is covered with the molecules.

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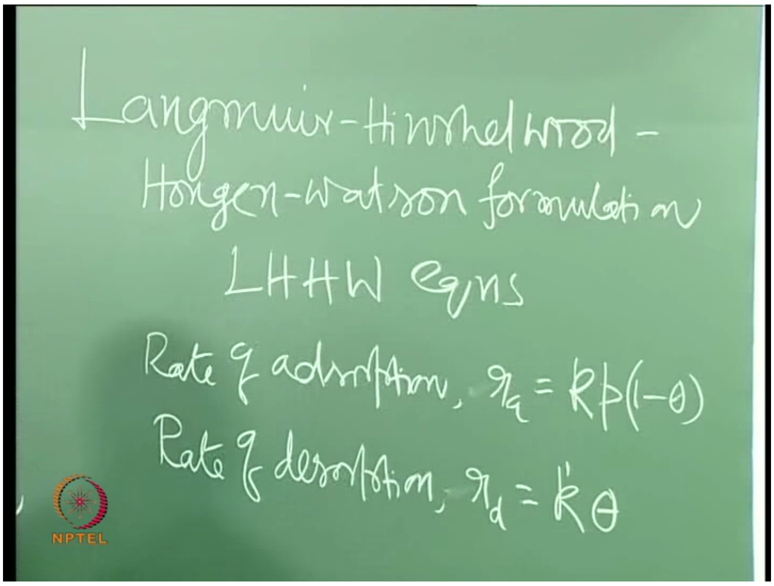

Langmuir-Hinshelwood -
Hougen-Watson formulation
LHHW eqns
Rate of adsorption, $r_a = kp(1-\theta)$
Rate of desorption, $r_d = k'\theta$

Now rate of desorption depends on how many molecules we have on the surface, okay. More coverage means more desorption. And the other one is rate of adsorption depends on what is the free because only monolayer, only one molecule can sit there, okay, at one particular site. So that is why this is proportional to the surface area that is available that is 1 minus theta and that is also proportional to the concentration of that is I think (())(46:07) is concentration partial pressure, okay.

The pressure on the surface of a particular gas, okay. So at steady state so r a equal to r d. We just equate those two and then because this is easy so I thought I will cover this and then leave you. So do you remember the equation? Theta equal to capital K p by 1 plus K p where capital K equal to what? K by k dash, okay.

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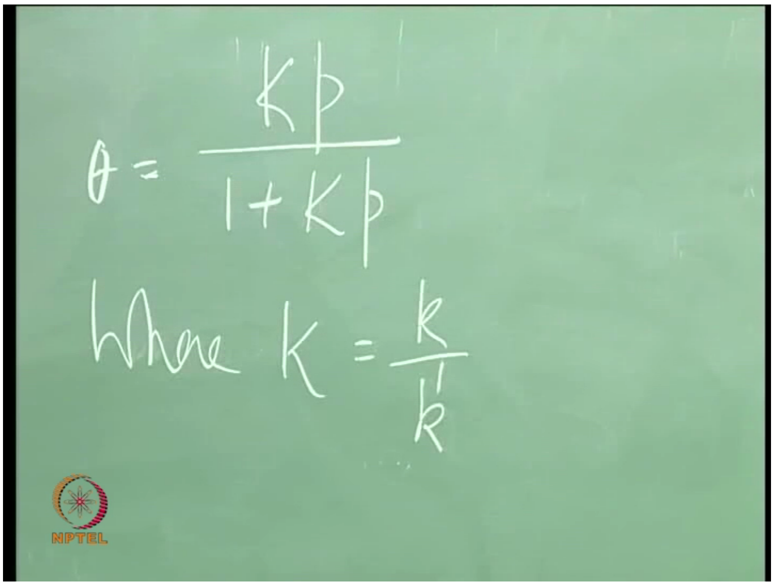

$$\theta = \frac{Kp}{1+Kp}$$

Where $K = \frac{k}{k'}$

Of course sometimes this is also imagined as small v by v where small v equal to volume of gas adsorbed divided by v m equal to volume of gas adsorbed with a monolayer coverage of surface. This is always the fraction, good. Anyway I think we will stop here.

This is what is Langmuir isotherm and even if you derive an equation for Hougen Watson in terms of surface concentrations you will get a similar equation as theta equal to, only one equation I will write, K C into C g is the gas concentration and 1 plus K C C g. This is Langmuir Hinshelwood and this is Hougen Watson.

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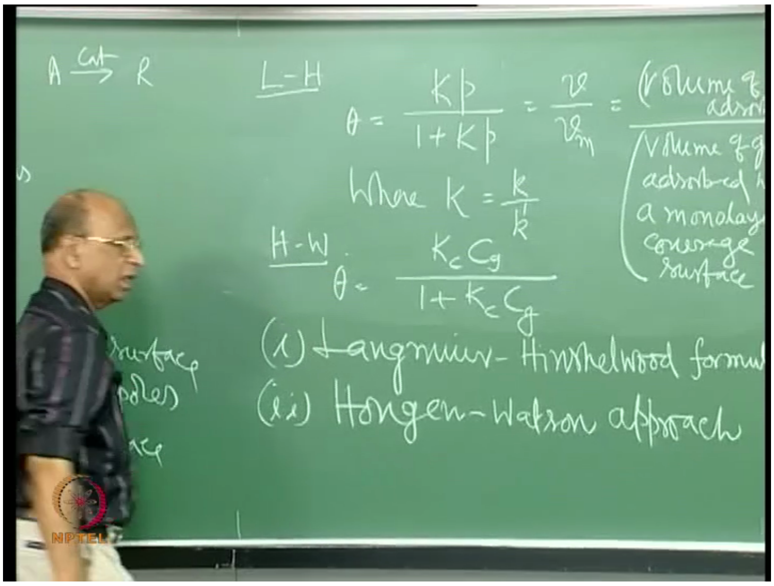

$A \xrightarrow{Cat} R$

L-H $\theta = \frac{Kp}{1+Kp} = \frac{v}{v_m} = \frac{\text{(Volume of adsor}}{\text{Volume of g adsorbed w a monolay coverage surface)}}$

Where $K = \frac{k}{k'}$

H-W $\theta = \frac{K_c C_g}{1+K_c C_g}$

(i) Langmuir-Hinshelwood formul

(ii) Hougen-Watson approach

It is same thing but that is expressed in terms of partial pressures and this K C is written because it is in terms of concentration, okay. Format everything is same, good. So these two, the first equations and then we will actually derive the rate expressions for surface reaction where we have step 3, step 4, step 5 we will come into, okay. Thank you.