Chemical Reaction Engineering 2 (Heterogeneous Reactors)

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Lecture 18

LHHW Kinetic Model Continued Part 1

I think we will continue this LHHW kinetic model. Please take this thing you know as introduction. Following LHHW models let us designate the total concentration of active catalytic centres or sides as S subscript 0 which is a constant for a given catalyst. The next sentence the concentration of unoccupied side is S, these are capital, is S and that occupied by various adsorbed species is S a, S b, S c, etc. Before that we have S not and S, okay. Let me explain this. I think you know happily would have written without even thinking you know what is the meaning.

But the meaning of that is given catalyst will have S not number of active sides, right? So out of that S a, S b, S c are the active sides that are occupied by the species if you have a, b, c. If you have a, b only two. S a, S b like that. Then the remaining sides are S, okay. So now based on this how many sides have been occupied by the species? How many getting adsorbed? How many getting desorbed? All that will come in this and then we will assume that we have a reaction A gas, B gas going to C gas plus D gas. We have the catalyst. It is a reversible reaction, okay.

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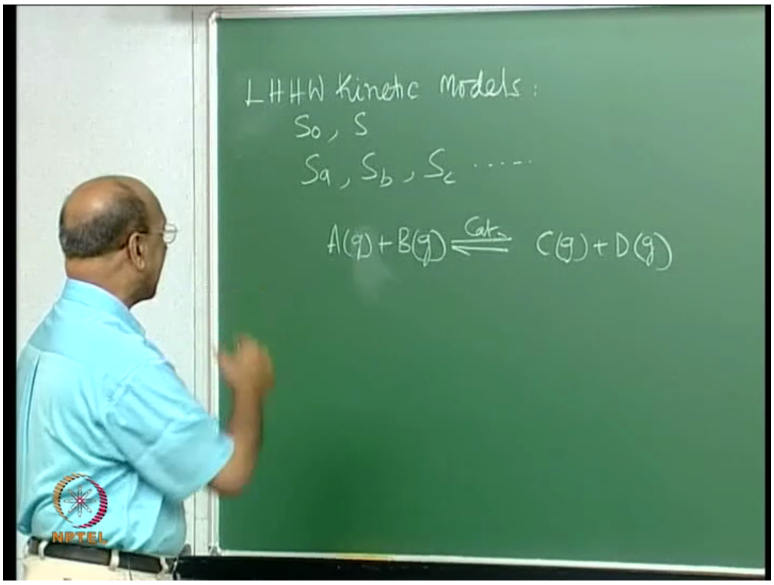

This is the kind of reaction that is going on now on the catalyst. So now we have to develop a rate expression for this stoichiometric equation, okay. So now our imagination for catalytic reaction is that molecule A has to go get adsorbed, molecule B has to also get adsorbed. If they are side by side then molecule A will form some intermediate, molecule B will form some intermediate, both will react and then that is surface reaction step and then desorption of A and now there is no A, desorption of product.

If there is only one product only one will come otherwise if I have C and D and C has to desorbed, D has to desorbed and then reach come through the pores and through the film and reach the bulk. That is what is the overall picture what we imagine for all catalytic reactions, okay. What is that once more? The assumption is that molecules of A will get adsorbed on one side, molecules of B also get adsorbed another side and both of them form intermediate and these intermediate will react and they form the products C and D.

And C and D also they have to be desorbed off after the formation because they are the products where the concentration is high on the surface, low in the bulk. So that concentration difference will make it move through the pores, through the film and all that. So then out of these that means adsorption of A, adsorption of B, desorption of D, desorption of C and also surface reaction we have now five steps. Out of that any one maybe rate controlling, okay.

And maybe adsorption of A alone maybe rate controlling or desorption of D alone maybe rate controlling. All five maybe rate controlling. So how do we know this? We will know only when you first develop your model. The general procedure is writing the main equation, afterwards imagining the steps, adsorption of A, adsorption of B and all that then developing a kinetic model, right? You what you do is in general if it is a new process we do not know what is the rate controlling step. We write all the models.

That means for example here you will have lot of combinations. Simplest one if you take adsorption of A, adsorption of B, desorption-desorption two steps and surface reaction. So we will say that, okay surface reaction is controlling, one model. Adsorption of A is controlling, another model. Adsorption of B is controlling, another model. Then all these models before me. Now you know mathematically I have these models but how do I know which one is really rate controlling? I have to conduct an experiment, right?

And then I have to measure the concentrations of A B. If I know A B C D I can calculate, okay. Or whatever is possible. If I measure C D then A B I can calculate at anytime. So once I have that information concentration versus time data like your normal kinetics then I have to fit this data to the overall kinetic models. So out of that five models one may fit. If all of them are not fitting because each individual one which we have thought you know that is adsorption alone, desorption alone, surface reaction alone then you have to take the combinations.

So that is why it is hell to develop this LHHW kinetic model in catalytic reactions. That is why you happily ask chemist to do that, okay. But I think as chemical engineers also we should do how to do that and we should also develop because these are the microscopic models. Till we are not worried about how the molecules are actually getting dissociated? What are the activation energies? All those things we are not worried here.

We need a microscopic rate which is a function of concentration of A, concentration of B and if it is a reversible reaction then you have concentration of C and concentration of D. That is all what we require as an engineer. But if you go deeper and deeper on the surface what is actually happening? What are the surface energies? Where are these active sides? How do you make these active sides much more active? How do you generate more active sides in a catalyst? All these things again is a big science, catalysis science.

And it is interface between chemical engineers and chemist where both of us work together. We can do much more because the idea is at the end with minimum amount of catalyst how do you produce maximum. I mean as engineers we understand that, okay. But at present what we are trying to do is that let us develop a microscopic model where it gives me a rate expression because this rate expression is necessary for me in my performance equation.

In performance equation I have a term called kinetics and I have another term called input and another term called contacting. So contacting is given by you know the type of reactor I am choosing and kinetic models from this only I have to get and of course input you know how to get it. So that is why now let us write these steps. Step 1 is A, A is the concentration and S is the active side and all the steps are reversible steps. And we can also say this is k 1, k 1 dashed reverse giving me some complex A S, okay.

Then step 2, B plus S giving me this is k 2, k 2 dash. This is B S then the reaction between these two step 3, A S plus B S, this is k 3, k 3 dash. This will be C S plus D S. Those are the complexes. Then step 4 is desorption of C S, k 4, k 4 dash. Now this will be C plus S. And step 5 I hope I will write here is D S, this is k 5, k 5 dash reverse, D plus S.

So if I call these numbers, okay, maybe before that also I have to write one equation. This is S not equal to S plus S a plus S b plus S c plus that is equation 1. This is equation 2 and equation 3, 4, 5, 6, 7.

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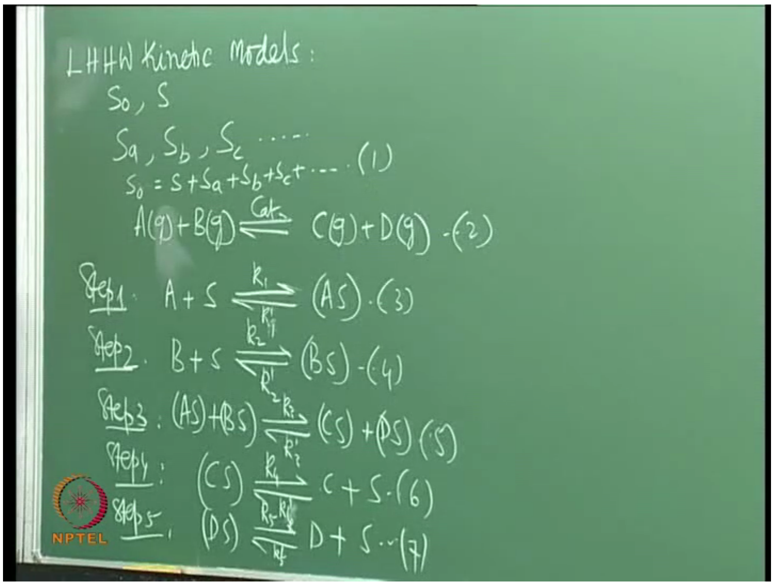

LHHW Kinetic Models:

S_0, S

$S_a, S_b, S_c \ldots$

$S_0 = S + S_a + S_b + S_c + \ldots \; (1)$

$A(g) + B(g) \xrightleftharpoons{Cat.} C(g) + D(g) \; \cdot(2)$

Step1. $A + S \xrightleftharpoons[k_1']{k_1} (AS) \cdot (3)$

Step2. $B + S \xrightleftharpoons[k_2']{k_2} (BS) \cdot (4)$

Step3: $(AS) + (BS) \xrightleftharpoons[k_3']{k_3} (CS) + (DS) \; (5)$

Step4: $(CS) \xrightleftharpoons[k_4']{k_4} C + S \cdot (6)$

Step5. $(DS) \xrightleftharpoons[k_4']{k_5 - k_5'} D + S \cdots (7)$

Definitely you know the meaning of equation 1, right? You know in the notes which I have given you that we have S vacant sides, S a occupied by a b c altogether must be your S not which you have taken in the beginning as a constant for a given catalyst, okay. So out of these again the equation 3 is adsorption step, correct? And next one also is adsorption step. This is reaction step, surface reaction and next one is desorption. Next one also is desorption, good.

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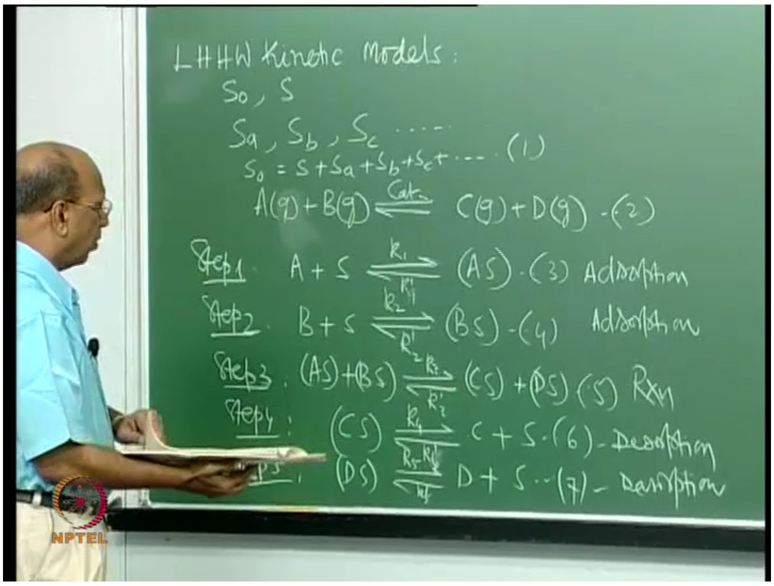

So this is what I have been telling. Any one of the steps may be rate controlling or all maybe rate controlling, okay, two extremes, okay good. So now let us take that surface reaction is the rate controlling step, this step. Surface reaction is the rate controlling step. So we will write a rate expression here r equal to. This one you have to treat it as normal stoichiometric equation, okay.

It is reversible reaction so the rate expression can be written as k 3, concentration of this, concentration of this and minus k 3 dash, concentration of this and concentration of this, okay.

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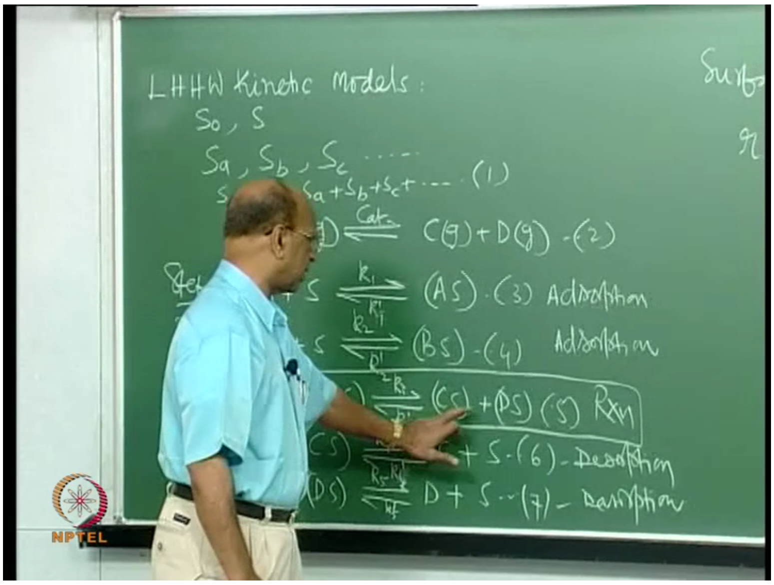

That is what you write there. Then we have k 3 A S, B S minus k 3 dash C S, D S. So this is equation number 8, good. So as usual I think you know I have been telling you this one for all heterogeneous systems this rate should be in terms of measurable quantities. What are the measurable quantities here in these equations? A, because this is the concentration of A in the bulk which you will see that and the B and C and D. And all other things I cannot. Intermediate in the concentration I cannot measure, right?

So that is why we have to now write that equation in terms of measurable quantities. The procedure is universal you know for all heterogeneous systems. Finally then if I am able to express this rate in terms of all measurable quantities then that is called the overall rate, observed rate, measured rate, global rate. All these various names are there I am just repeating again. Good.

So now the general procedure here is that when you take reaction as the rate controlling step, all other steps are so fast always you can see equilibrium of those steps. In fact these, what you have done even for homogeneous systems. Let me recall your memory that you know you have non elementary reactions. Non elementary reactions if A plus B going to C is not actually A plus C going to C. In between there are many steps. That means A maybe first forming an intermediate, B maybe forming an intermediate, then those maybe reacting.

So all these again models you will imagine in non elementary reactions. Procedure is the same there also. You write all that imaginary steps, okay. How A is reacting? Forming the intermediates or B is forming the intermediate and then try to write for each and every equation what you write there as a elementary equation. Elementary means? What is the definition of elementary reaction?

Student: (())(14:12)

Professor: Stoichiometric and then stoichiometric coefficients will be the same, okay. So similarly here when I write an equation, this is what you have written. This first order, this with respect to this first order, with respect to this first order, like this. Then overall second order, overall second order because coefficient one here, one here, one here, one here. So this is the general procedure. Except that rate controlling step you have all other steps as I mean in equilibrium, okay. So that means thermodynamic equilibrium.

So how do you write those equations thermodynamic equilibrium? Okay, I think you may forget later so I think better let me tell this also. When step 5 is rate controlling, okay. Step 3 is fine. Equation 5 or step 3. When step 3 is rate controlling, all other steps are assumed to be under equilibrium. Then from step 1 the thermodynamic equilibrium is A S, A S equal to K 1 which is nothing but your k 1 by k 1 dash, correct right? So this is equation 9.

Then from step 2 this one B S, this is concentration of B separately, concentration of A separately. This is K 2 which is again k 2 by k 2 dash, 10. Then we have step 4, C S by this is K 4 which is slightly changed here. That is k 4 dash by k 4. Just this constant I have just reversed for easy writing, okay. That you have to notice there, okay.

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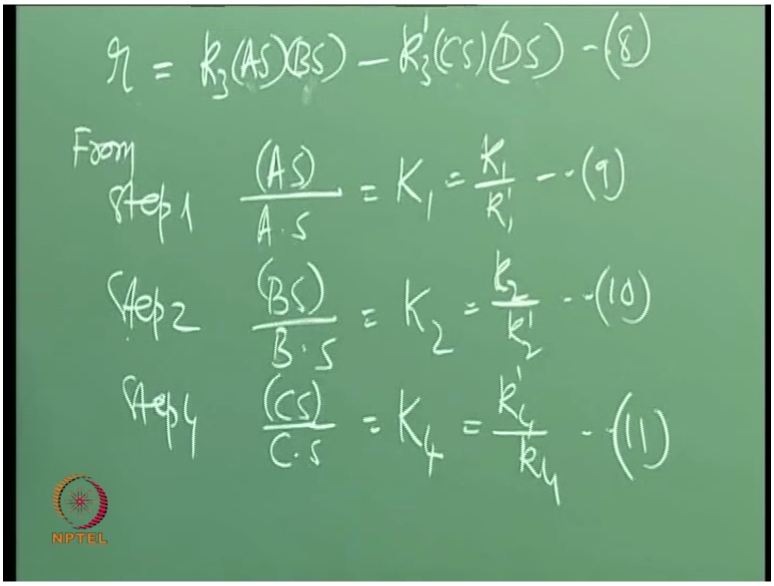

$$r = k_3(AS)(BS) - k_3'(CS)(DS) \quad -(8)$$

From step 1 $\dfrac{(AS)}{A \cdot S} = K_1 = \dfrac{k_1}{k_1'} \quad --(9)$

Step 2 $\dfrac{(BS)}{B \cdot S} = K_2 = \dfrac{k_2}{k_2'} \quad --(10)$

Step 4 $\dfrac{(CS)}{C \cdot S} = K_4 = \dfrac{k_4'}{k_4} \quad -(11)$

I hope you notice that. Normally it will be products by reactants but here I have reversed and then this is defined like that. This is only for easy manipulation of algebra that is all, nothing else, okay. Then step 5 is D S, D dot S. This is K 5 which is equal to k, k 5 dash by yes. This is the one. Good. So now I can write A S, B S, C S, D S here in terms of these equations, correct right? So that means A dot S will come here, B dot S will come here and C dot S here, D dot S there, good. Yes now let us write that.

Substituting equations 9 to 12 in 8 first let us write that and then we can rearrange. I think I will write here k 3, capital K 1 A dot S. Now all this we can have in bracket like this. Then K 2 B dot S minus k 3 dash K 4 C S K 5 D S. Yes this equation also we can call as 13. So this after rearranging a little bit then you will get r equal to K 3 K 1 K 2.

Now I have A B minus K 4 K 5 by K 2 K 1 K equilibrium or capital K also we can write, C D bracket closed. I have now here S square. This is 14, okay, where K equilibrium or K in general capital K I can write as K 3 by K 3 dash, good.

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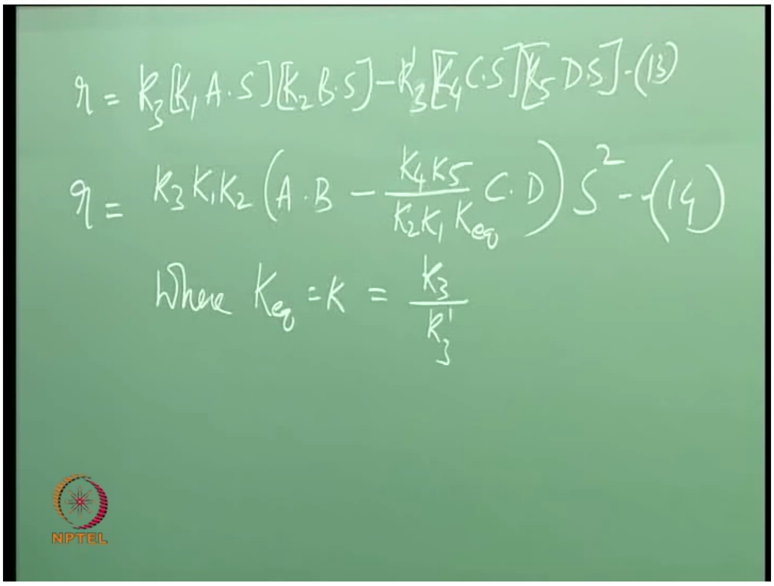

$$r = k_3 [K_1 A \cdot S][K_2 B \cdot S] - k_3' [K_4 C \cdot S][K_5 D S] \quad \text{-(13)}$$

$$r = k_3 K_1 K_2 \left(A \cdot B - \frac{K_4 K_5}{K_2 K_1 K_{eq}} C \cdot D \right) S^2 \quad \text{-(14)}$$

$$\text{Where } K_{eq} = K = \frac{k_3}{k_3'}$$

Still can I use this equation immediately or do I have to do something else? Yes we have to also eliminate the number of you know vacant sides, okay. That can be done because still this one, these constants anyway I have to evaluate only from the experiments, okay. But this S square I can also eliminate by taking this equation 1. Yes equation 1 gives me S not equal to S plus S a, S b, S c, here S d and I can also have here some inert, okay. Inert also occupy some active sides, okay good.

So now I have to substitute for S a. S a is nothing but this concentration A S, okay, B S, C S like that. That is the concentration on the active sides. So that is why if I write this S plus A S, B S, C S, D S and I can also have I S. I is the inert component like for example nitrogen which may not be participating in the reaction, okay.

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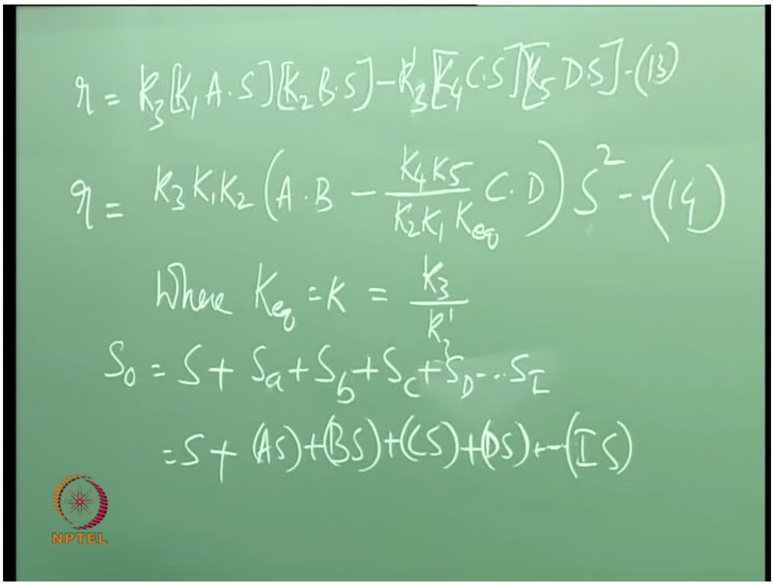

$$r = k_3[K_1 A\cdot S][K_2 B\cdot S] - k'_3[K_4 C\cdot S][K_5 D\cdot S] \quad (13)$$

$$r = k_3 K_1 K_2 \left(A\cdot B - \frac{K_4 K_5}{K_2 K_1 K_{eq}} C\cdot D\right) S^2 \quad (14)$$

Where $K_{eq} = K = \frac{k_3}{k'_3}$

$$S_0 = S + S_a + S_b + S_c + S_D \cdots S_I$$

$$= S + (AS) + (BS) + (CS) + (DS) + \cdots (IS)$$

So this equation now this is S not. This also of course these things I do not know but I have to write that in terms of again known measurable quantities. What are the measurable quantities? Again these equations. A S I know. A S is nothing but K 1, right? Or K 2, B S is nothing but K 2, B dot S, okay. So you have to substitute again equation 9 to 11 here then you get S plus you have K 1 A S, K 2 B S and K 4 C S, K 5 D S, K I yes, okay, I S. This is the equation.

Now you know I have S here, S here, S here, S here, S here, S here. All that S I can take out common, okay. So this equation if I take as this is 15, this is 16. Then equation 16 can be written as S equal to S not divided by 1 plus K 1 A, K 2 B, K 4 C, K 5 D plus K I I. That is the equation. This is equation 17, excellent good.

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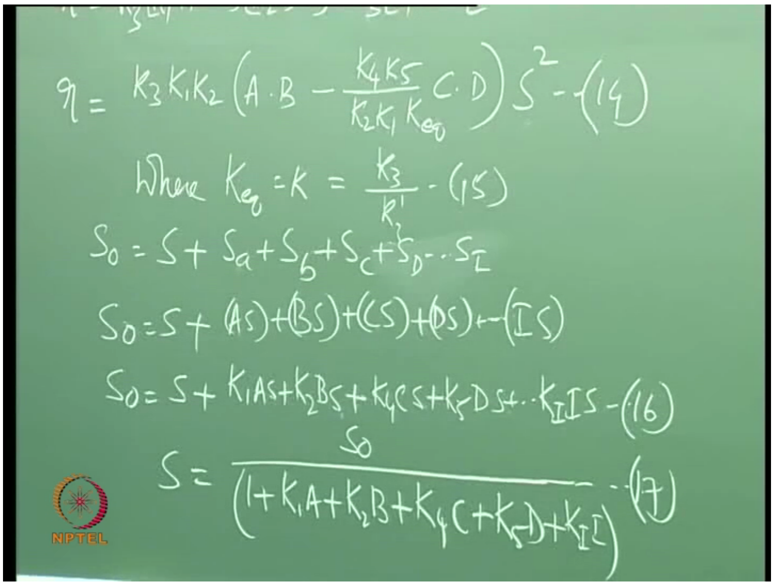

$$r = k_3 K_1 K_2 \left(A \cdot B - \frac{K_4 K_5}{K_2 K_1 K_{eq}} C \cdot D \right) S^2 \text{ -- } (14)$$

$$\text{Where } K_{eq} = K = \frac{k_3}{k'_3} \text{ - } (15)$$

$$S_0 = S + S_a + S_b + S_c + S_D \cdots S_I$$

$$S_0 = S + (AS) + (BS) + (CS) + (DS) + \text{--} (IS)$$

$$S_0 = S + K_1 AS + K_2 BS + K_4 CS + K_5 DS + \cdots K_I IS \text{ -- } (16)$$

$$S = \frac{S_0}{(1 + K_1 A + K_2 B + K_4 C + K_5 D + K_I I)} \cdots (17)$$

So now equation 17 has to be substituted in 14. Now you will see the format which normally you see for LHHW kinetics, okay. So what is that? Please take that substituting equation 17 in 14 what you get is yes r equal to k 3, capital K 1, capital K 2, S 0 square. Now I can write A B minus C D by I write capital K not. This in the bracket. So now all these term 1 plus K 1 A, K 2 B, K 4 C, K 5 D plus K I I whole square, okay. Yes so this is the equation actually. This is equation number 18.

And in the normal form when you write this I can write this as r equal to all this as some k and concentration of A, concentration of B minus concentration of C, concentration of D, K not whole thing divided by 1 plus K 1 C A, K 2 C B, K 4 C C, K 5 C D plus K I C I whole square. This is one format. There is another format also which you will see. Of course this k is all that together. Let me also write that where small k equal to k 3 K 1 K 2 S 0 square, good.

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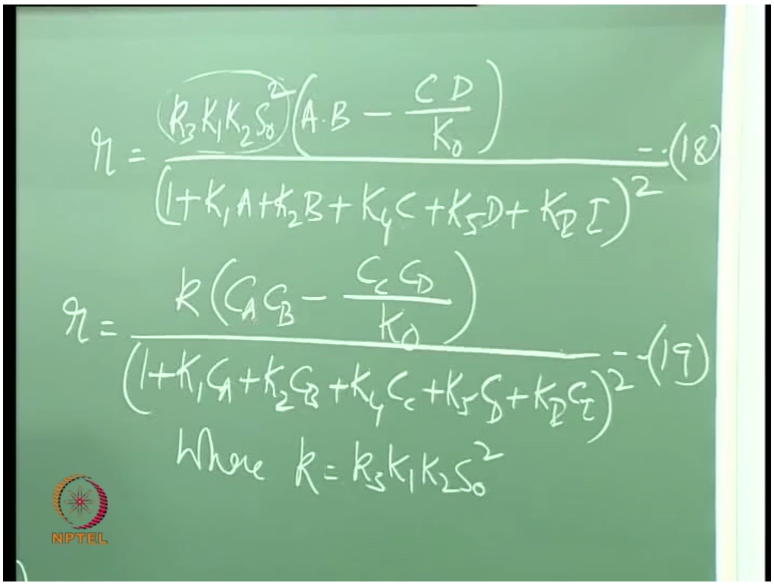

$$r = \frac{k_3 K_1 K_2 S_0^2 \left(A \cdot B - \frac{C D}{K_0}\right)}{\left(1 + K_1 A + K_2 B + K_4 C + K_5 D + K_I I\right)^2} \quad \text{--- (18)}$$

$$r = \frac{k\left(C_A C_B - \frac{C_C C_D}{K_0}\right)}{\left(1 + K_1 C_A + K_2 C_B + K_4 C_C + K_5 C_D + K_I C_I\right)^2} \quad \text{--- (19)}$$

Where $k = k_3 K_1 K_2 S_0^2$

So I can also write this one, this is another format normally we will see as p A p B minus p C p D by K not. I am returning the same constants but constants will be actually different. So 1 plus K 1 p A, K 2 p B, K 4 p C, K 5 p D plus K I p I whole square. This is equation 20, 21. These are the two formats normally you will see in all the books, okay.

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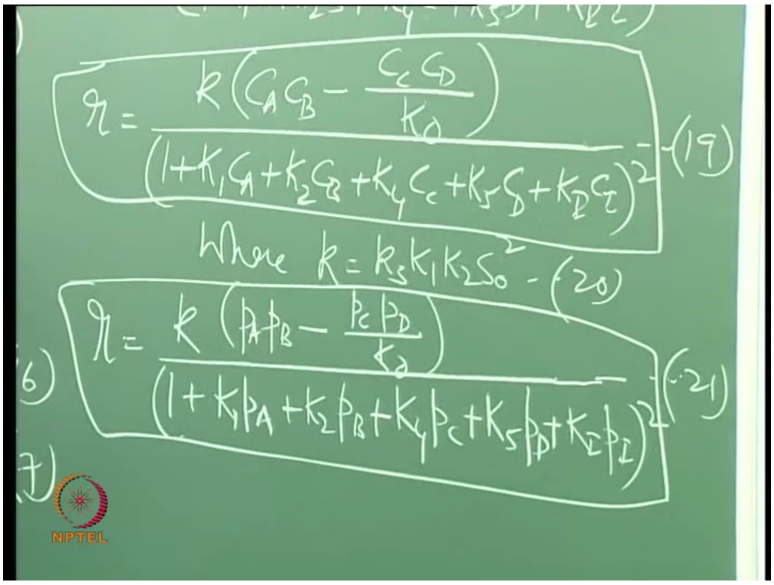

$$r = \frac{k\left(C_A C_B - \frac{C_C C_D}{K_0}\right)}{\left(1 + K_1 C_A + K_2 C_B + K_4 C_C + K_5 C_D + K_I C_I\right)^2} \quad \text{--- (19)}$$

Where $k = k_3 K_1 K_2 S_0^2$ - (20)

$$r = \frac{k\left(p_A p_B - \frac{p_C p_D}{K_0}\right)}{\left(1 + K_1 p_A + K_2 p_B + K_4 p_C + K_5 p_D + K_I p_I\right)^2} \quad \text{--- (21)}$$

Many things can be understood from these equations, right? Many things like this denominator whenever you have a rate expression, you know this is the actual rate expression or this one C A minus C B minus this is normal rate equation. You know when you have A plus B going to C plus D this is the kind of rate equation you will have, right, for reversible.

But in catalytic reactions this is the denominator which comes and that is actually inhibiting the reaction. That is why in biochemical reactions when inhibition is taken into account, some terms are added in the denominator. Those terms are not just like that added but you know through mechanism.

Student: Sir, in the denominator is it 1 or?

Professor: 1 plus.

Student: Concentration is committed to partial.

Student 2: No but the constants here are not same from previous equation.

Professor: That is what I mentioned. That is what I told you. Even though I am writing this impartial thing I am retaining the same constants. That is what I have told, okay. So I know the entire derivation you can also do in terms of partial pressures from the beginning. You will have 1 only. You will not have some other value here, okay. So that is why these constants, make a note, I told that whenever writing that these constants even though I am maintaining the same they are not same because of partial pressures, okay good.

But what is that we can understand here is that you have this square here. Normally that square comes when two active sides involve in the reactions, two active sides. If there are three, like A plus B and also plus C going to the products then three active sides they are involved then you will get here cube, okay, for surface reaction when you have surface reaction. That is why when someone gives you model if they give you in this format and also you see in the step 3 what you have.

That reaction step that will not be there in the denominator, any constant K 3 will not be there in the denominator. So in the denominator you will have only those steps which are not the rate controlling steps. So here, okay, step 1, 2, 4, 5 are not rate controlling steps. They are the fastest steps, right? So that is the reason why you will have in the denominator. Why I am telling all this is when you see a book or you when you see an equation, even now people are publishing papers on this.

When you look at that you can easily find out what could be the rate controlling step from that. With experience even just by seeing you will know what is the mechanism you know based on which that particular equation is derived, okay good. So this is one thing and then what we have to do is now evaluate k, K 1, K 2, K 4, K 5, K I.

That means you have to now conduct experiment and experiment you conduct to find out what is the partial pressure of A, partial pressure of B or concentration A, concentration of B. Then concentration of C and D you can definitely get from stoichiometric equation. One mole, one mole, one mole, one mole that is no problem. Then with time this rate is nothing but minus depending on your base, right? Most of the time for catalytic reactions we base our rate based on weight of the catalyst, okay.

So how do I write that? It is minus 1 by W, d N A by d t. So the number of moles of A changing with respect to time I should know, right? When you know the concentrations you can find out how many moles are changing? Various times you are finding out the concentrations then you know, what is the change in moles of A, right? So you can calculate easily rate once you measure the change in concentration or the change in moles of a particular component. Good.

So that means rate I will know and then corresponding concentrations. Normally it is time and concentrations then you can convert that into rate and concentrations. And once you have that information then you have to go to this particular model and then try to find out K 1, K 2, K 3. There are many methods available for finding out very accurately K 1, K 2, K 3, K 4, K 5 and also other constants, right? There are many methods. That is why again you know here it become purely mathematical techniques.

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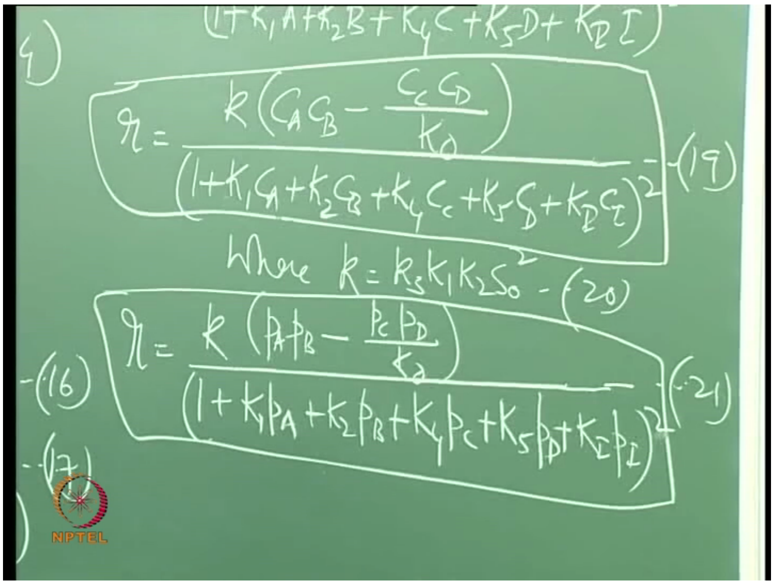

$$(1+K_1A+K_2B+K_4C+K_5D+K_I I)$$

$$r=\frac{k\left(C_AC_B-\frac{C_CC_D}{K_a}\right)}{(1+K_1C_A+K_2C_B+K_4C_C+K_5C_D+K_IC_I)^2} \quad -(19)$$

$$\text{Where } k=k_3K_1K_2S_0^2 \quad -(20)$$

$$r=\frac{k\left(p_Ap_B-\frac{p_Cp_D}{K_a}\right)}{(1+K_1p_A+K_2p_B+K_4p_C+K_5p_D+K_Ip_I)^2} \quad -(21)$$

And old type engineers where the complicated mathematics when they have not used what they did was that they conduct the forward reaction and then avoid as far as possible this term. That is why you know there is a method called initial rates for finding out kinetics. I do not know whether you still remember that or not, initial rates. And these initial rates mainly came from for forward reaction first and then you take the products because you are trying to find out the kinetics, okay.

So then you have to take C and D and then have the backward reaction and those initial rates. So that means separately without this term you should have all this and without this term you should have all this and then conduct one experiment for the entire normal A plus B going to C plus D and then check that data with the initial rate data that is given. That you have checked with. So that is the overall procedure.

And my god to actually find out K 1, K 2, K 3 it takes lot of time but there is a pleasure in doing that. There is real pleasures in doing that you know evaluating these constants and accurately measuring the rate of reaction because all your design now depends on this rate.

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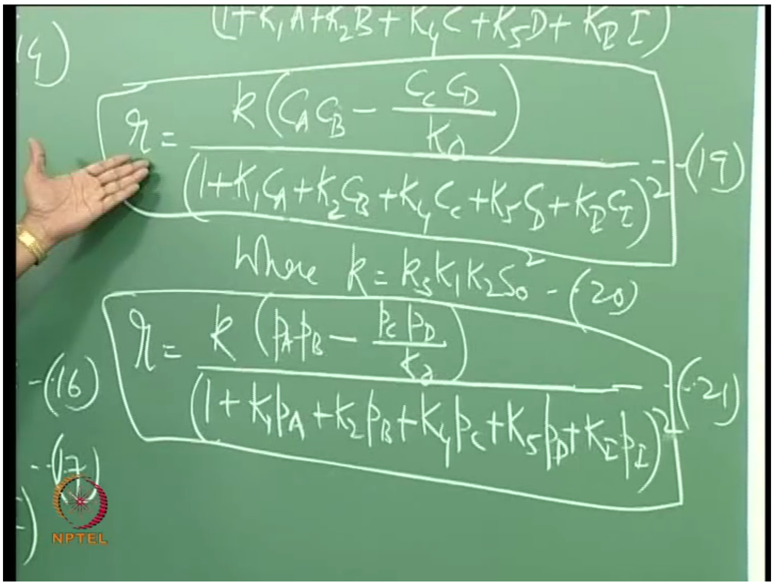

$$(1+K_1A+K_2B+K_4C+K_5D+K_I I)$$

(4)

$$r = \frac{k\left(C_AC_B - \frac{C_CC_D}{K}\right)}{\left(1+K_1C_A+K_2C_B+K_4C_C+K_5C_D+K_IC_I\right)^2} \quad -(19)$$

$$\text{Where } k = k_3K_1K_2S_0^2 \quad -(20)$$

$$r = \frac{k\left(p_Ap_B - \frac{p_Cp_D}{K}\right)}{\left(1+K_1p_A+K_2p_B+K_4p_C+K_5p_D+K_Ip_I\right)^2} \quad -(21)$$

-(16)

-(17)

I can tell you very quickly here if you want to find out weight of the catalyst in the packed bed what is that you know the equation what you use? Equation what you use this F A not equal to d x A by minus r a and this is minus r a for me. This is the equation which you have to substitute here.

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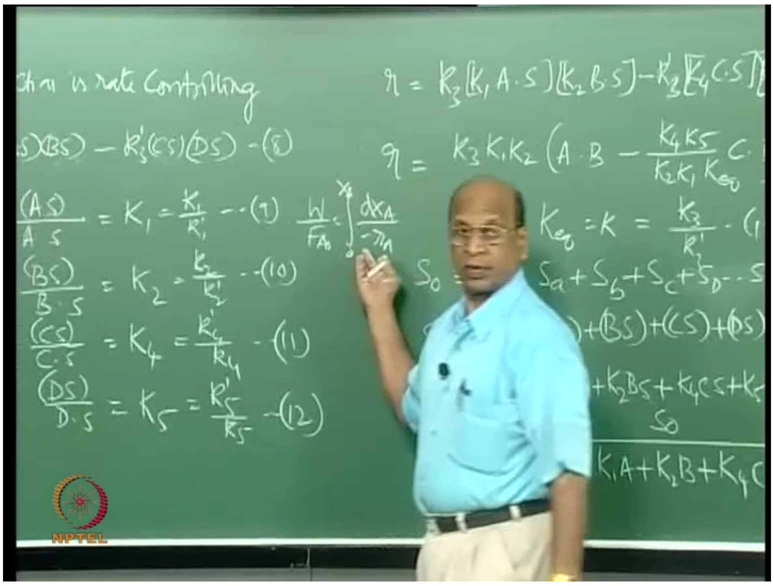

And many times it may not be possible to have an analytical expression. You cannot integrate just like that so that is why you go for either graphical integration or numerical integration or some other technique. Finally to get what is W by F A not. And what is this equation for which reactor? P of r which his packed bed plug flow reactor. All packed beds are treated as plug flow reactors.

So that is why this rate expression finding out is the first step and then I have been telling you in heterogeneous reactions most difficult steps are only finding out the rates, okay. Finding out the rates so this is one thing. I think very quickly I can also tell you another rate controlling step that is let us take adsorption of A rate controlling. Procedure is same again, exactly same.

That means first writing an equation for this alone minus r a equal to this one K 1 into A S minus K 1 dash into A S. So now you have to try to eliminate this A S using all other steps.

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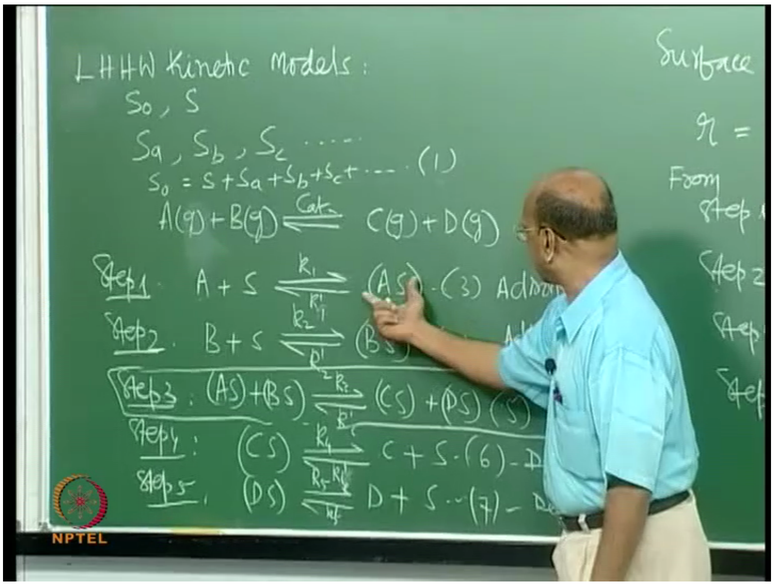

That is all. The procedure is same. So let us do that very quickly. I think we have time or no time. I think because already we have some steps there, okay, so let us take another very simple one, okay. This is adsorption control. I am not taking the earlier one because it takes time. So we have a reaction A going to R or A going to B also we can write because I wrote there A plus B, I do not want to confuse you there. So now here this is the reaction that is going on the catalyst. What is step one the way we imagine? Here I have catalyst.

Step 1 is A plus S giving me A S that is adsorption of A. Step 2 is A S giving me R S. That is the surface reaction step, okay. Then step 3 is R S giving us R plus S. You see this active side is again is ready, regenerated after this step. So now this one as usual I will write k 1 k 1 dash, k 2 k 2 dash, k 3 k 3 dash. Now we take this one is the rate controlling step. So if I take this one as 1, 2, 3.

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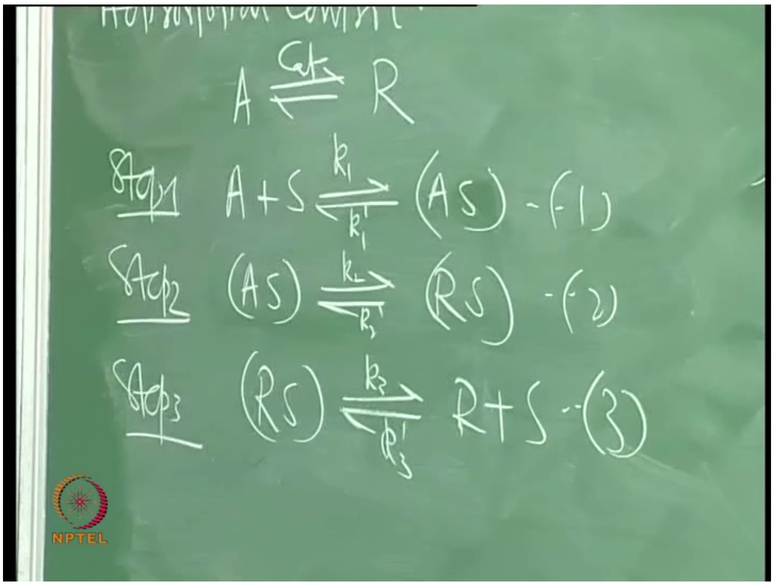

$$A \underset{}{\overset{Cat.}{\rightleftharpoons}} R$$

Step 1 $A + S \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} (AS)$ - (1)

Step 2 $(AS) \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} (RS)$ - (2)

Step 3 $(RS) \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} R + S$ - (3)

So when this is rate controlling step so we have the equation r equal to k 1 A S minus k 1 dash A S, okay good. That is the actual rate expression, 4. Now we have to find out from others two steps because they are under equilibrium the other two steps. So I can write from step 2 what we have is K 2 equal to R S by A S. From step 3 it is K 3 equal to R S by R dot S. So this is equation number 5, equation number 6.

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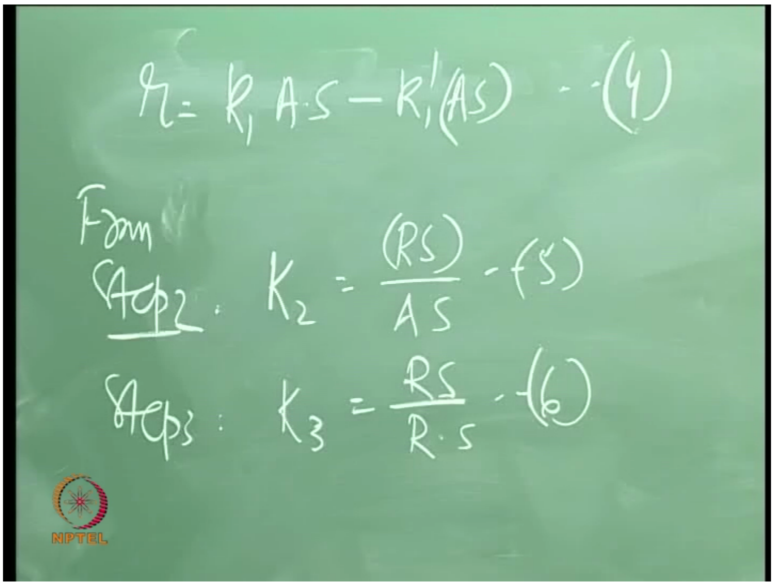

$r = k_1 A \cdot S - k_1'(AS)$ - (4)

From

Step 2 : $K_2 = \frac{(RS)}{AS}$ - (5)

Step 3 : $K_3 = \frac{RS}{R \cdot S}$ - (6)

Now we have to substitute this in this, okay, equation 4. So if we do that we will have r equal to k 1 A S minus k 1 dash R S by from this R S by this also I have bracket. It is very important, step 2. R S by K 2, this is equation 7, right? But still this is unknown to me, R S, right? So now we have to substitute equation 6 in 7 because R S R dot S. Naidu confusing, okay good. So R equal to k 1 A S minus k 1 dash. For this R S I have to substitute capital K 3 R dot S by K 2. This is equation 8.

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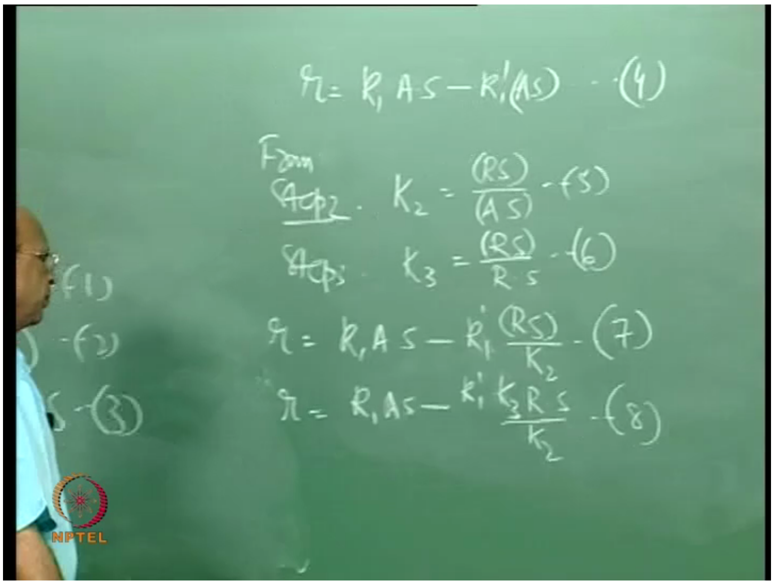

So now I have to write this equation as k 1 S into A minus K 3 by capital K 1 K 2 into R, okay, where I will write here where capital K 1 equal to k 1 by k 1 dash. So this is and S is there already so this is 9, this is 10. What is the other equation? Now I have to eliminate S. Procedure is same. I have to eliminate S, okay. So when I eliminate S, to eliminate S I have S 0 equal to S plus S a S r plus S I inert. So this is equation 11, good.

So now I have to substitute S plus, for S a it is A S plus R S plus inert also if I want to have that there it is I S. So the equation 12. Now I have to substitute for A S, R S, I S, okay. We have the equations here. First one if I want to substitute for A S this will be R S by K 2, right? What is it?

Student: Capital K 1 A S, can we use that?

Professor: Capital K 1 how can you use that?

Student: Okay.

Professor: Yes, capital K 1 cannot come there. Capital K 1 is only for this reaction thermodynamic equilibrium capital K 1, okay. So here when I substitute this I will have here S plus R S K 2 yes plus R S. I am writing that slowly now. I S, this is equation 13. Now these two together, S plus, for R S I have to use this equation K 3 R S, right? So this one is what? K

2. So far R S I have to use K 3. Actually I can take common also there. So this will be 1 by K 2 plus 1 multiplied by K 3 R dot S in fact, okay, plus I S, correct no. K I sorry K I S, okay.

So now S I can take common. So this is S not equal to 1 plus K 3 by K 2 plus K 3 R plus K I, okay, whole thing multiplied by S. That is why I am also running fast, right? Here also I is there, okay, I dot S. S not by 1 plus K 3 K 2 plus K 3 into R plus K I. So that is the one, good. So now I have to substitute there and then you will get . Substitute in which equation? Yes equation 9. Substituting in equation 9 may be I think I have to write here. I will give only one expression. Substituting here also I have to write 13, 14 this is 15.

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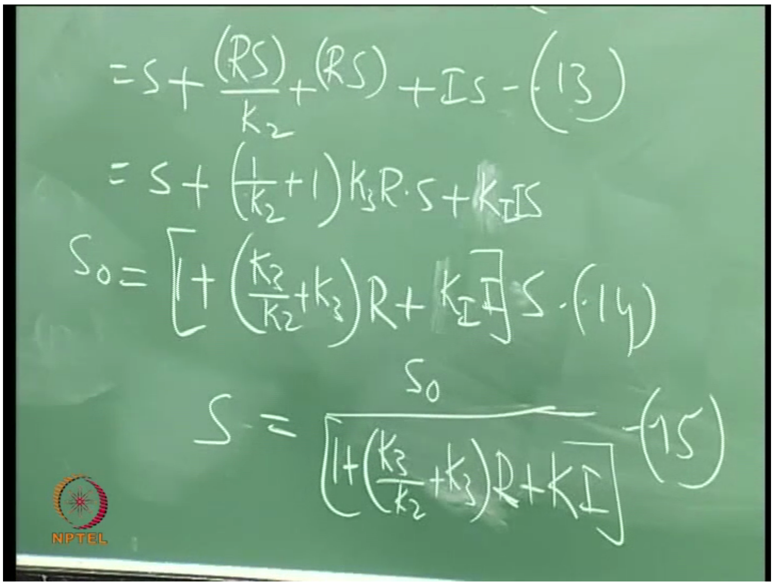

$$= S + \frac{(RS)}{K_2} + (RS) + IS - (13)$$

$$= S + \left(\frac{1}{K_2} + 1\right) K_3 R \cdot S + K_I IS$$

$$S_0 = \left[1 + \left(\frac{K_3}{K_2} + K_3\right) R + K_I I\right] S \cdot (14)$$

$$S = \frac{S_0}{\left[1 + \left(\frac{K_3}{K_2} + K_3\right) R + K I\right]} - (15)$$

Substituting equation 15 in 9 what do you get is r equal to k 1 S not A minus K 3 K 1 K 2 R whole thing divided by 1 plus K 3 by K 2 R plus. So this is the expression. So this is of course one can write also this one as some constant k C A minus another constant for example C R by K not whole thing divided by 1 plus K 3 K 2 K 3 C R plus K I. Of course you can also write this one in terms of partial pressure, okay. Where K not equal to all this, okay.

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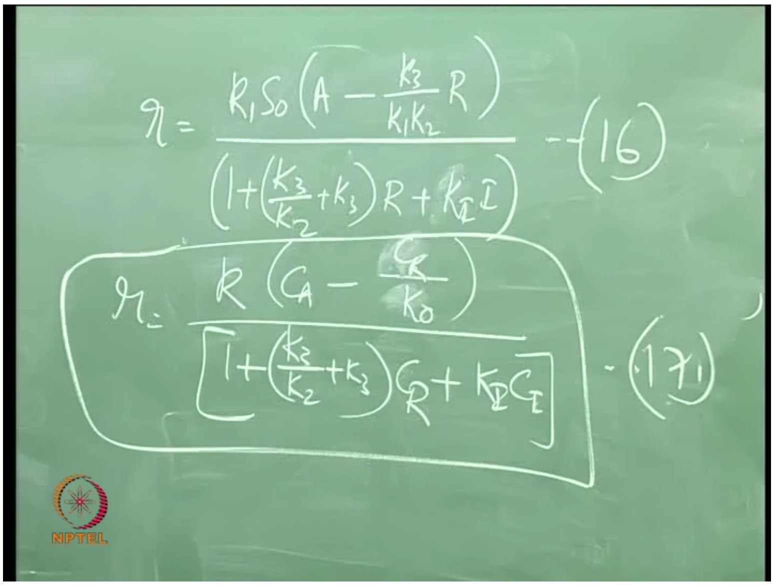

$$r = \frac{k_1 S_0 \left(A - \frac{k_3}{k_1 k_2} R\right)}{\left(1 + \left(\frac{k_3}{k_2} + k_3\right) R + k_I I\right)} \quad --(16)$$

$$\boxed{r = \frac{k \left(C_A - \frac{C_R}{K_0}\right)}{\left[1 + \left(\frac{k_3}{k_2} + k_3\right) C_R + k_I C_I\right]}} \quad -(17)$$

Yes, you can go, okay. Tomorrow we will discuss.