Heterogonous Catalysis and Catalytic Processes
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Lecture – 29

Good morning, last time I was talking about effeteness factor in a pellet and we have derived the expression for a slit cylindrical pore; the effeteness factor based on the Thiele modulus calculation. And, there after we discussed it for a spherical pellet.

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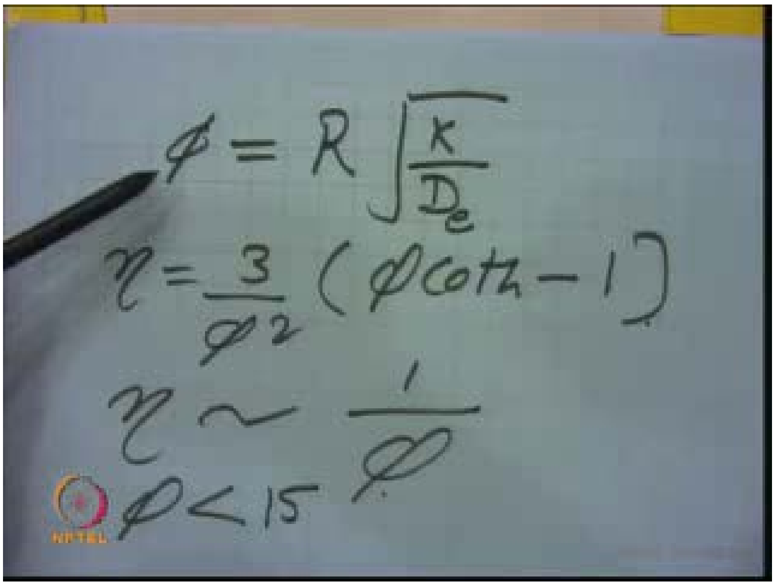

$$\phi = R\sqrt{\frac{K}{D_e}}$$

$$\eta = \frac{3}{\phi^2}(\phi \coth - 1)$$

$$\eta \sim \frac{1}{\phi}$$

$$\phi < 15$$

So, as I discussed last time that the thiele modulus which dictates about the diffusion resistance in a pore of the catalyst or in a catalyst pellet. And, phi was defined something like R under root of K by D; if you look at just a first order reaction. Where, K is the rate constant here based on the volume of the catalyst; right. So, that there can be the different units; it can be K double dash based on surface area of the catalyst or it can be mass basis also. So, when it is mass basis, it will be k dash; that is K prime multiplied by the density of the catalyst. If it is based on surface area, it will be K double dash times the surface area of the catalyst per unit mass and then multiplied by the density of the catalyst. So, that we have discussed.

These are the difective effective diffusion coefficient, when you discuss or talk a pellet. R is the effective radius; so, in some cases you may see as I discussed R is basically the characteristic length and defined by V p by S x. So, in some case, you may see R by 3 also; so, that depend. So, R here the eta what we defined is 3 upon phi square phi cot hyperbolic phi minus 1. This was the definition which we made last time and that is the Thiele model effeteness factor in a pore. So, depending upon this eta is inversely proportional to phi, when there is a strong pore diffusion. So, this is what has been shown in this graph; that if you have a plot of effecteness factor verses Thiele modulus for the case of isothermal conditions. Then, the initially when the phi is low; so, generally when the phi is low, 1 can say phi is less then 10 or less then 15 to be safer side. And, then it will be a reaction which is free from diffusion resistance, right. So, eta will be large number.

So, theoretically when there is no diffusion resistance, then eta will be 1 and this is what the initial portion of this curve here, right. So, there is no limitation of internal diffusion in a pore of a catalyst. But when there are diffusion limitations like, may be a particle size may be a problem, porosity may be a problem or the temperature; that is the rate constant is very very high like. So, temperature because at high temperature the rate of reaction is very very high right and I defined you the definition of effeteness factor is global rate divide by intrinsic rate.

So, that may also affect the performance because of this change in the Thiele modulus. So, this is what has been shown here; at high value of phi which could be because of various reasons. As I said size of the pellet, the porosity is very very low, the reaction order may be also high right; like this here. For a same Thiele modulus you can say here if the order is high, then diffusion limitations are severe; that is effeteness factor is low. So, effeteness factor is the consequence of diffusion resistance and this is related to your rate.

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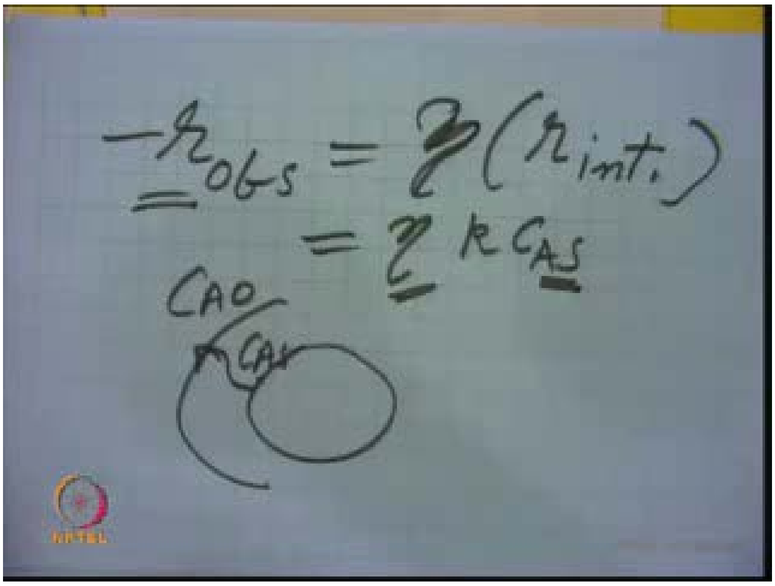

$$-r_{obs} = \eta (r_{int.})$$

$$= \eta k C_{AS}$$

So, observed rate will be effeteness factor; that is eta multiplied by the rate which is measured at the surface condition which we said intrinsic rate, right. So, if I know suppose the reaction is first order and you know the concentration at the surface; then, this can be written simply k time C A S. So, experimentally 1 can measure this observed rate. Here you have to predict the resistance phase and then find out the concentration which is given in the bulk that is C A 0.

And, then what is the concentration at the surface of the catalyst. If there is something like that the film which I am talking here C A 0 and this is C A S; so, this may be different. But then the film resistance is negligible, then this is equivalent to bulk concentration. So, that is something again related to another effeteness factor which is known as overall effeteness factor. So, I will discuss that point little later.

So, 1 thing is clear from this graph that when the thiele modulus is very high, the strong diffusion resistance. So, this is the z1 where the diffusion resistance is very high; it is a not very good of design right. So, 1 need to control the size of the pellet, 1 needs to control the experimental condition in order to avoid the diffusion limitation in the pore. And, this 1 can do once he understand the basic theory of the catalyst preparation right, selection. That is the hydro based on hydrodynamic conditions, select the particle size and then decide what should be the optimum particle size for the given reaction and optimum superficial velocity in a catalyst. So, optimum conditions need to be identified.

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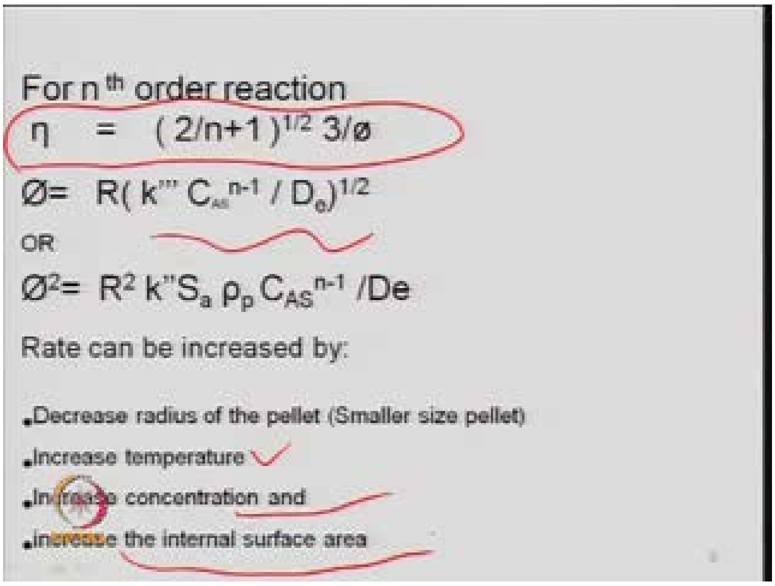

For nth order reaction

$$\eta = (2/n+1)^{1/2}\, 3/\phi$$

$$\phi = R(k''' C_{AS}^{n-1} / D_e)^{1/2}$$

OR

$$\phi^2 = R^2 k'' S_a \rho_p C_{AS}^{n-1} / De$$

Rate can be increased by:

- Decrease radius of the pellet (Smaller size pellet)
- Increase temperature
- Increase concentration and
- increase the internal surface area

So, for first order reaction you have already seen; that phi is R under root K by D. If you do it for second order; it becomes phi for second order reaction will be R under root of K C s to the power n minus 1 something like this. For any nth order reaction, so divide by D. So, K by D times; this times C S to the power n minus 1 by 2 something like that, right.

So, what I mean to say for any n th order reaction the Thiele modulus change. So, and that you can derive when you, when I have written the differential equation, then I told you that minus R A; so, minus R A is equal to K C A to the power n. And, that should be divided; now, C A times C S to the power n minus 1 and that is 1 term which is associated with the phi. So, phi is basically R which is here, phi square basically; when I said m into l is phi right and that is K by D in the first order pore diffusion reaction. But when in this case, it is simply when I write phi square; so, this is R square times K by D times C A S to the power n minus 1 something like this, right.

So, eta is inversely proportional to phi; you are saying that, right. So, for any n th order reaction when you do it, you can do the derivation of the equation just for 1 exercise just take the second order case where you have the differential equation for second order. And, then simplify the equation. So, all the time you will have the C S to the power n minus 1; when it is n th order reaction, right. So, this is what the expression given here, the effeteness factor, if you solve; when you have calculated this thiele modulus, then eta, effeteness factor which is calculated again based on the same equation something like this. That is global rate divide by the intrinsic rate.

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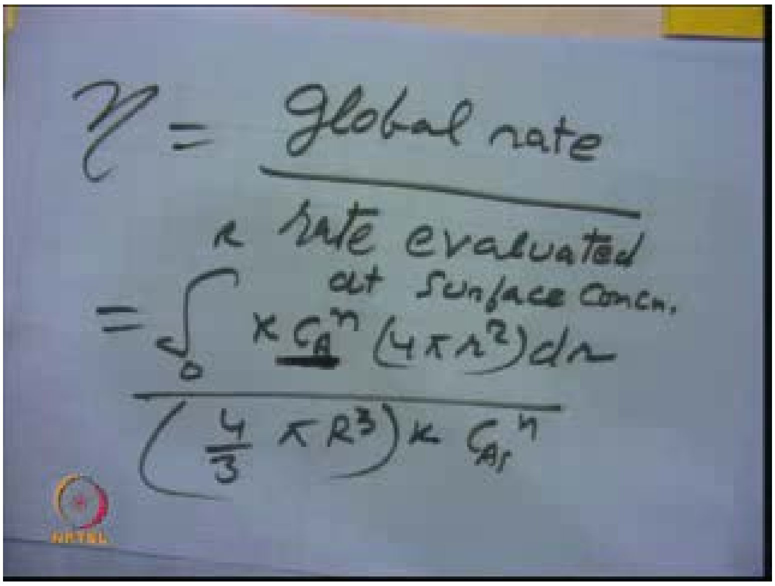

$$\eta = \frac{\text{global rate}}{\text{rate evaluated at surface concn.}} = \frac{\int_0^R k\, \underline{C_A}^n (4\pi r^2)\, dr}{\left(\frac{4}{3}\pi R^3\right) k\, C_{As}^n}$$

So, there also the global rate, when you write; so eta definition says simply global rate divide by rate evaluated at surface concentration. So, it means global rate is again K times whatever the concentration which is being calculated and integrating over the surface. So, if it just spherical pellet, then you are d1 it like this 4 pi r square d r right and evaluated for the surface.

So, only term changes here C A to the power n now, right. And, same thing will be for the intrinsic rate; so, that can be defined 4 by 3 pi R cube, if you are writing per unit volume basis times of volumetric rate constant times the C S to the power n, correct. So, integrate this expression and solve them. Then, you will see that the rate of reaction which is here based on 4 by 3 pi r cube volume; if you write in based on mass, it will be multiplied by density. So, per unit mass, then it will be K dash times C A to the power n right.

So, what I mean to say the integrate this equation which you have obtained for C S for n th order reaction. So, for second order you can try, for third order you can try and then 1 can generalize the expression for any n th order reaction. So, effeteness factor for any n th order reaction which has been defined here is 2 divide by n plus 1 to the power half times 3 upon phi. For any n th order reaction the effeteness factor will be calculated based on this expression. So, for n is equal to 1 this becomes 1 right; for n is equal to 2 this will become 2 plus 1, 3; so 2 by 3 to the power half right and so on so. So, this is what the definition for effecteness factor for any nth order reaction. Why we are doing this? Because I want to discuss something, the consequence of diffusion resistance in a pellet right.

So, there will be a kind of disguised kinetics right or falsified kinetics which is, just you know now that this phi which is defined by R right times K C S to the power n minus 1 divide by D E and square root of whole term right. That is basded on here volumetric constant. If you write it based on surface, then K double dash times S A; S A is meter square per gram right, D E T surface area rho p density of the pallet which can be the bulk density also, if it is in the bed right.

Then, rate will be defined based on the total volume of the reactor basis. C S is the concentration right to the power n minus 1 and divide by D e; that is your diffusion, that is coefficient d e effective diffusion coefficient and this is thiele modulus square right. So, something which is defined based on the kinetic rate divide by diffusion rate and evaluated the surface concentration.

So, based on these 2 and based on this; now certain observation are that if you want to reduce the limitation, diffusion limitation in a pellet; then, reduce the radius of the pellet. That is used smaller pellet in the catalyst bed right. So, that is 1 very important thing; that do not take very large size particle when you do the kinetics or do the experiment with the catalyst effeteness, right.

So, however either hydrodynamic condition are also equally important. Because if you have very fine powder then pressure drop may arise in the reactor. So, you have to the catalyst size right that is 1 thing. Temperature. So, when the temperature is high rate constant k will be high. So, your thiele modulus value will be high in 1 way right. So, that but high temperature the diffusion coefficient will also increase right accordingly. So, you have to look at the effect of the temperature.

So, generally what very high temperature. Very high temperature meaning that when you are beyond the thermodynamic limits right; the 1 thing is that the minimum temperature is required to activate the rate of reaction. So, in that case first you identify what are the temperature conditions required, pressure condition required for reaction? And, then when you do the kinetic though study of the reaction at excessively high temperature right especially when you screen out the catalyst. The basic idea is that at that time your kinetics is very high and their possibility may be that diffusion may control the rate right.

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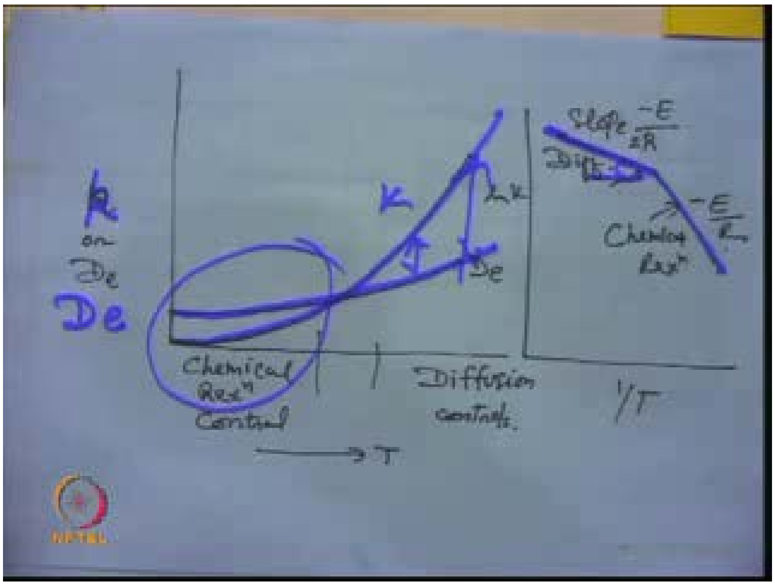

So, that if you look at just a graph which is something here which gives you the idea about the rate constant k or effective diffusivity D e. And, you can see here the D e goes like this with temperature. And, this graph shows the variation of k with temperature. Because k is k 0 e to the power minus e upon R T right; these also given in the same fashion sometimes we write it d 0 e to the power minus e d by R T something like that right.

The activation energy for diffusion reaction or diffusion is lower compare to the kinetics. So, kinetic control reaction may have a activation energy 200 kilo joule per mole but diffusion control reaction will have activation energy less than 20 kilo joule per mole. So, if the variation or effect of temperature will be more dominating in this case; the kinetic right, this is your k value. So, it means the lower temperature z 1, this is your chemical reaction control right. And, then the higher temperatures suppose the experiments are carried out in this z 1. Then, the variation of temperature or rate on temperature may be not be significant; that time the diffusion may be a dominant term.

So, because k is very high at that time compare to this d you see here the gap is widening right. So, it is a contribution of the 2 resistance basically; the diffusion resistance and the chemical reaction resistance. And, especially when there are the 3 phased reactor, 2 phase reactor we will see the terms; which talks about the diffusion and mass transfer and the kinetic terms, right. So, this is 1 thing. And, if you look at the slope because this l m k verses 1 by T very standard method of calculating known as a arrhenius plot right. So, l m k verse 1 by T; if you look at here this slope is E upon R here for the chemical reaction control right; whereas this slope is E upon 2 R which is for diffusion control. I will just discuss that little later, right.

So, the slope of diffusion control reaction is lower compared to this right. So, that is the meaning what I said at activation energy for kinetic control reaction will be higher compared to the diffusion control reaction. So, it means the temperature has some role when you look at the kinetics. So, very temperature your rate may be very high, right.

o, in that case the diffusion may be the controlling. Concentration is again important especially for the positive order reaction. So, higher concentration it means the diffusion may be dominating and surface area that is again an issue. So, you have to look at the surface area is very high right it is good basically. So, increase the internal surface area. So, in order to eliminate the diffusion resistance side or in order to enhance the rate; one can look the particle size, look at the temperature, the concentration and the internal surface area. So, all these will increase the rate right.

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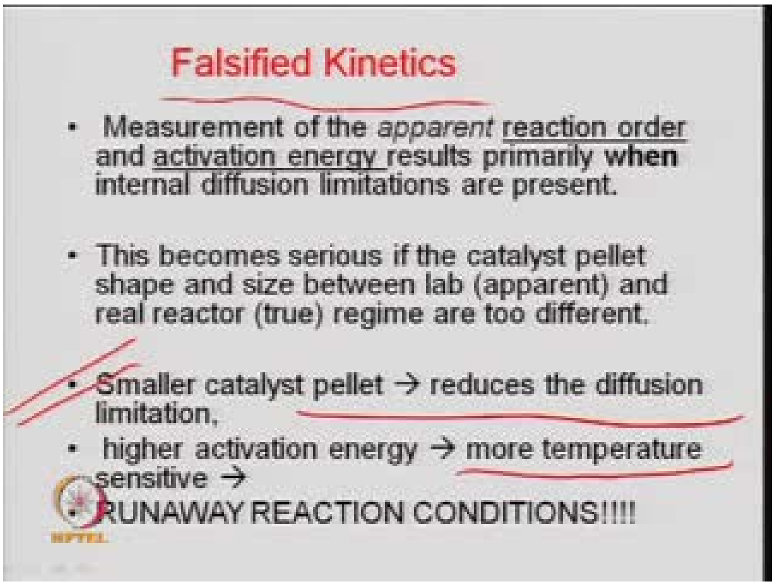

Falsified Kinetics

- Measurement of the *apparent* reaction order and activation energy results primarily when internal diffusion limitations are present.
- This becomes serious if the catalyst pellet shape and size between lab (apparent) and real reactor (true) regime are too different.
- Smaller catalyst pellet → reduces the diffusion limitation.
- higher activation energy → more temperature sensitive → RUNAWAY REACTION CONDITIONS!!!!

Then, when there are diffusional influences right; then you have to look at some kinetic study. Because the kinetics generally as I said you have to avoid the diffusion resistance in the pellet right or in a reactor. But if these studies have not been done carefully or properly; then it may happen the diffusion resistance has some influence on the overall rate of reaction. What is the consequence or what are the consequences let us see here. The first thing is that we call it Falsified kinetics, right. So, measurements of the apparent reaction order.

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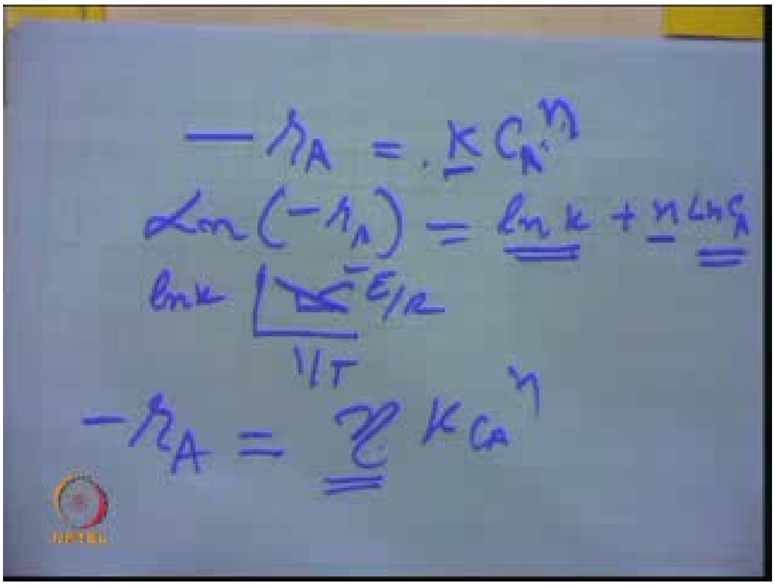

Because in general when you write a reaction you simply say minus r A is equal to K C A to the power n is simple power law model, right. Then, how do you do? You just take suppose L n of minus r A right is equal to L n of k plus n L n of c A right; 1 can regress this right equation or 1 can use the some graphical methods or either method can be. So, this is your temperature dependant term k and this is your concentration dependent term and this is order of reaction. So, basically when if you plot this verses C A it will give you a straight line. And, from that 1 can find out k and n right very simple method. And, then you plot k at different temperature what I have shown earlier.

So, you plot L n k verses 1 by T and you get a slope; and this will give you the activation energy. So, that has been studied in the homogenous kinetics; the approach is similar right the only that here this K and C A they may be affected because of diffusion resistance. Because I told you that now your observed rate is there is some diffusion resistance it is eta times k C A to the power n something like this; where eta is in this case because there were no diffusion resistance. But in this case if there are the consequences of diffusion resistance; then this eta is also in picture right. And, eta is 1 by phi and phi is related to concentration right. So, that may change or alter if you do if you do not know what is the value of this it may affect this right. So, let us see how does it change.

So, this is important that apparent reaction order and activation energy which you get just from the effect of concentration and effect of temperature carry out the experiment; and do the regression method. So, these become serious if the catalyst pellet that is shape and size between lab and the actual reactor; and there is a variation. So, if there is a gap say you have not taken care of selecting a proper particle size; then diffusion may affect the rate.

So, if this happens then your commercial reactor or reactor which you have the you are saying; that it is first order reaction actually, it may not first order reaction. It will be different same thing the activation energy I told you if it is diffusion in first; the activation energy will be lower. Because diffusion control reactions suppose purely diffusion control reaction the activation energy is 20 kilo joule per mole right or may be 30 low.

When the kinetic controls it can be of the order of 100 or 200 kilo joule per mole. So, if the combination of to it means the activation energy is lower. But when you look at a commercial reactor and you have designed it based on that activation energy or that order of reaction. Then, result will be different the final productivity or the conversion data will not match with the lab data. So, that is what I told that a smaller the catalyst pellet you reduce the diffusion limitation. If the activation energy for the reaction or temperature required for reaction is high. Because higher temperature favors the reaction of higher activation energy.

So, kinetic control reaction they are they will have the activation energy higher than the diffusion control. So, you have to just take care of that right and they are more temperature system. So, if that is the case then there may be a runaway condition, transient condition, unsteady state condition because of hot spot formation right. And, that may be a kind of that is uncontrollable situation; when you have a runaway condition especially when you have a exothermic reaction in the catalyst.

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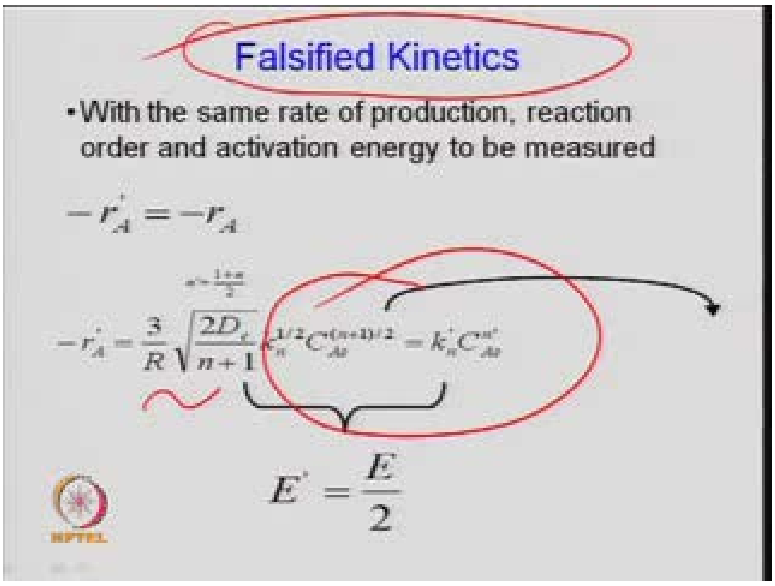

Falsified Kinetics

- With the same rate of production, reaction order and activation energy to be measured

$$-r_A' = -r_A$$

$$n' = \frac{1+n}{2}$$

$$-r_A' = \frac{3}{R}\sqrt{\frac{2D_e}{n+1}}\,k_n^{1/2}C_{As}^{(n+1)/2} = k_n' C_{As}^{n'}$$

$$E' = \frac{E}{2}$$

So, what is Falsified kinetics just quickly I have written here that all of you know this. So, I will go quickly.

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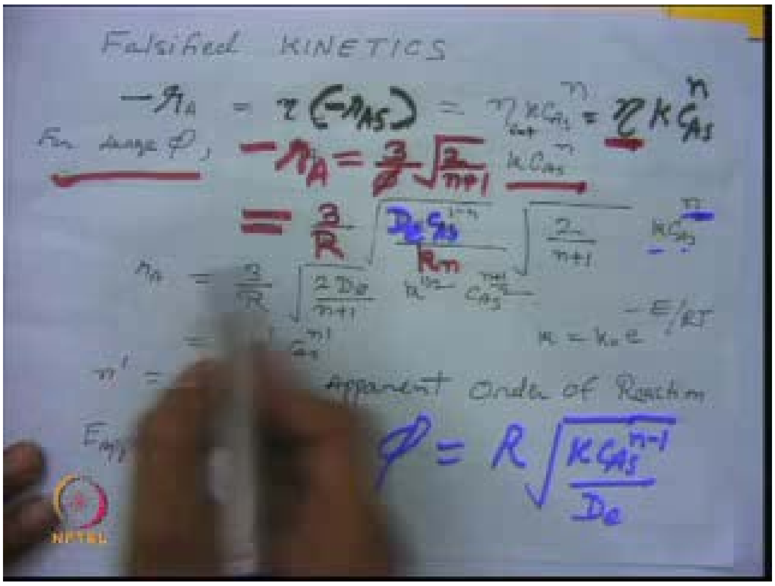

Falsified KINETICS

$$-r_A = \eta(-r_{AS}) = \eta k C_{AS}^{n} = \eta k C_{AS}^{n}$$

For large ϕ, $-r_A = \frac{3}{\phi}\sqrt{\frac{2}{n+1}}\,kC_{AS}^{n}$

$$= \frac{3}{R}\sqrt{\frac{D_e C_{AS}^{1-n}}{k_n}}\sqrt{\frac{2}{n+1}}\,kC_{AS}^{n}$$

$$r_A = \frac{3}{R}\sqrt{\frac{2D_e}{n+1}}\,k^{1/2}C_{AS}^{\frac{n+1}{2}}$$

$$k = k_0 e^{-E/RT}$$

$$= \quad C_{AS}^{n'}$$

$n' =$ Apparent Order of Reaction

E_{app}

$$\phi = R\sqrt{\frac{kC_{AS}^{n-1}}{D_e}}$$

So, minus r A what you have defined now is effeteness factor times this rate which is evaluated at the surface condition minus r A s, right. So, minus r A s is the rate which is evaluated at the surface condition; and we are talking any nth order reaction. So, this is your eta times k times c A s to the power n right; where your eta is the effeteness factor. Now, if you look at here your if I say that the reaction is controlled by diffusion large phi value right. If it is phi is low eta is 1 no problem but the phi has some value. Then, this eta will be define; eta see I told if you have a cylindrical pellet, spherical pellet roughly for high value it ((Refer Time: 21:54)). It is inversely proportional to the phi theilie modulus. So, that is what now minus r A rate of reaction. If you look at here that is simply equal to phi divide by phi times for nth order reaction I told you the definition this is the eta 2 divide by n plus 1.

So, for any nth order reaction this eta which is generally 3 upon phi and along with that value right times k c s to the power n as usual. Now, phi value; phi is r under root k c s to the power 1 minus 1 divide by D e. So, this is your substitution of phi. So, this is 3 upon R times this is R under root of k. So, this is your k for any nth order reaction k subscripted as n times; this is your D e effective diffusivity times C A s to the power 1 minus n. Because this n is already there; 1 is n and this is your n minus1 by 2 right. So, what is effectively your phi value is written like this; R under root of k C A s to the power n minus 1 divide by effective diffusivity, right.

So, this is c A s to the power n minus1 when you take it to the right c A s to the power n minus 1 and this is your C S to the power n already right. So, if you take it inside. So, this has become 2 m basically right. So, just solve this is n minus which is c s to the power n minus 1 that is with negative sign minus 1 minus 1 can write divide by 2; and this is your n right. So, n minus 1 minus n divide by 2. So, basically this becomes 1 minus n; c s to the power n minus 1. So, k at by D C S to the power n minus 1 that has been taken to numerator here first. So, 1 minus n and then added to this C S to the power n right. So, this is K C S to the power n. Now, take this n and 1 minus n by 2; so add them. So, finally, you have eta R which is 3 divide by R. So, let me write it here.

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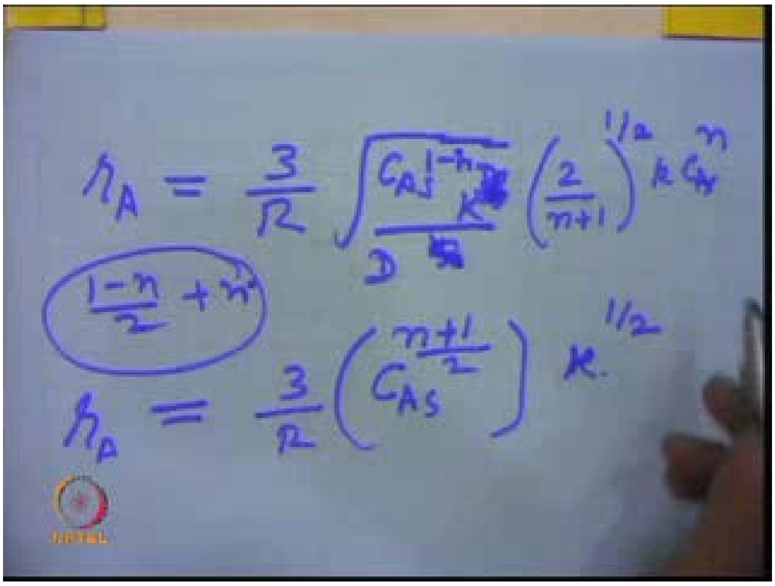

$$r_A = \frac{3}{R}\sqrt{\frac{C_{As}^{1-n}\,k}{D}}\left(\frac{2}{n+1}\right)^{1/2} k\, C_{As}^{n}$$

$$\frac{1-n}{2} + n$$

$$r_A = \frac{3}{R}\left(C_{As}^{\frac{n+1}{2}}\right) k^{1/2}$$

So, your r A is equal to 3 divide by R times c A s to the power 1 minus n times D e effective diffusivity divide by rate constant for nth order reaction times; whatever your 2 divide by n plus 1 to the power half times k times c A s to the power n, right . So this is your expression where this is your 3 upon phi. So, this value is your phi and this is again whatever the k C A s to the power n. And, this is related to eta power the nth order reaction I told you 2 over n plus 1 to the power half. So, this is 1 minus n by 2. So, what is 1 minus n by 2 plus n right which is your C S power total right. So, 2 n minus n so n so and this will remain here right. So, that is simply you 1 minus this is 2 n. So, this 2 n minus n and this will become 1.

So, n plus 1 by 2 right. So, what is the term which is written based on this 3 upon r. So, I am just combining now this c A s to the power n plus 1 by 2 right overall rate of reaction which I am calculating. So, this is your concentration dependent and second is your temperature dependent; that is your k and written to the power half like this right. So, this is your temperature dependent term.

So, k is here and D is here right. So, is in the numerator rate constant and this D in the denominator here. So, K C S. So, let me just explain it again. So, this equation is 3 upon r which is phi defined r under root k c s to power n minus 1 right. So, that is k is already there and this c s to the power n minus 1 times the second term. So, eta which is defined; so let me do it here again eta which is defined 3 upon phi.

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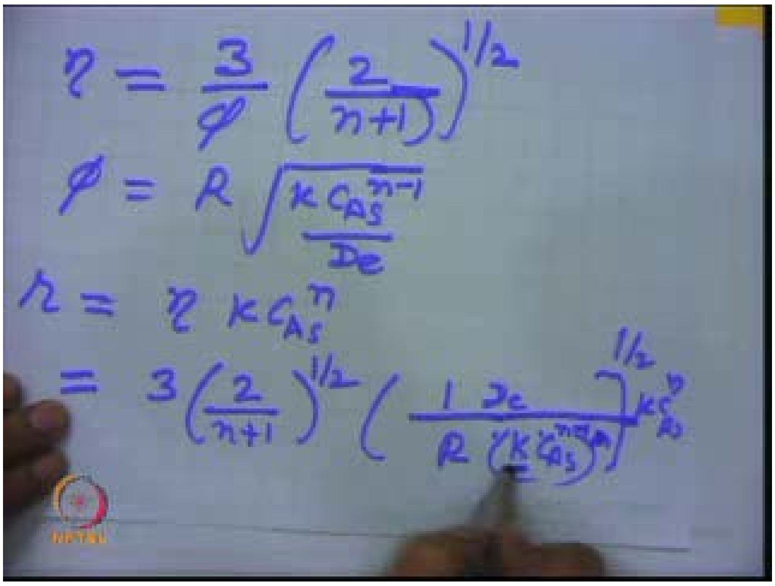

$$\eta = \frac{3}{\phi}\left(\frac{2}{n+1}\right)^{1/2}$$

$$\phi = R\sqrt{\frac{k C_{As}^{n-1}}{De}}$$

$$r = \eta k C_{As}^{n}$$

$$= 3\left(\frac{2}{n+1}\right)^{1/2}\left(\frac{1}{R}\frac{De}{(k C_{As}^{n-1})}\right)^{1/2} k C_{As}^{n}$$

So, it times 2 over n plus 1 to the power half right; this is your eta value. And, phi is defined R under root of k C A s to the power n minus 1 divide by D e this right. Now, we are defining your rate which is k eta times k s C A s to the power n. So, eta is 3 upon phi; so, this became now your 3 divide by phi. So, I am substituting the value of phi; so 3 times 2 divide by n plus 1 to the power half and this phi which is now will become 1. So, phi I am writing divide by r under root of k c s 2 the power n times D e divide by D e to the power half is it correct. And, then times k c s to the power n right. So, we have solve this already.

So, c k c s to the power this is k c s to the power n minus n minus 1 here right k c s to the power n minus 1. Now, this when you solve c s to the power n minus 1 it goes to the numerator. So, that is 1 minus n by 2 and this k at this k is there. So, in the numerator you have k to the power this is k to the power half k, k to the power 1 here and this is your k to the power minus half. So, that is k the expression which you get which is a temperature dependent term.

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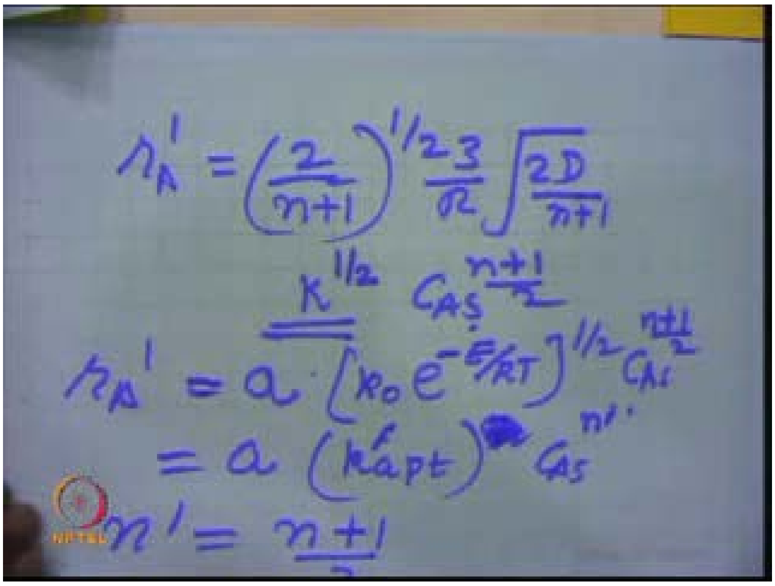

$$r_A' = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{R}\sqrt{\frac{2D}{n+1}}$$

$$\underline{k^{1/2}} \quad C_{As}^{\frac{n+1}{2}}$$

$$r_A' = a\left[k_0 e^{-E/RT}\right]^{1/2} C_{As}^{\frac{n+1}{2}}$$

$$= a\left(k'_{apt}\right)^{\text{[illegible]}} C_{As}^{n'}$$

$$n' = \underline{n+1}$$

So, the numerator will have now effectively minus r S dash is equal to whatever 2 over n plus 1 to the power half. So, other terms are already there which is written here right in this form 3 upon r and then 2 times D divide by n plus 1. So, that is again a term and times the I am interested in this term k to the power half and c s to the power n plus 1 by 2. So, this is what I want to show you here this expression right. And, basically these calculations is simply eta upon phi and substitute the value of phi which is your R under root k by D when you do it for first order reaction. And, R under root k c s to the power n minus 1 divide by D e right. And, eta is 2 upon n plus 1 to the whole to the power half right and times 3 upon phi. So, substitution of these values.

So, what I mean to say finally that this is the constant term, this is your temperature dependent term which is k to the power half now here. And, second is your concentration dependent term which is your c s to the power n plus 1 by 2 right. And, now my rate r A dash is some say approximated if whatever the A constant other terms are constant. So, temperature dependent term which is k defined as some k 0 e to the power minus e upon R T right. So, e upon R T and whole to the power half right; this is temperature dependent.

Second term is the concentration dependent c s to the power n plus 1 by 2. Now, this is temperature dependent term and when you take the log of this L n of minus r A right. So, that is the disappearance if I write. So, L n of minus r A is equal to half of this activation energy right; that is you get the activation energy in terms of. So, if I write it a times whatever the apparent activation energy I will write it now; k apparent rate constant right which is half to the power times. This is your apparent c A s n dash which is apparent order of reaction basically right. So, I will so apparent order of reaction is basically n plus 1 by 2 right. So, what I mean to say because of the falsified kinetics. So, I can write it k apparent I will not put half here basically. So, k apparent times c s to the power n dash. So, n dash is your n plus 1 by 2.

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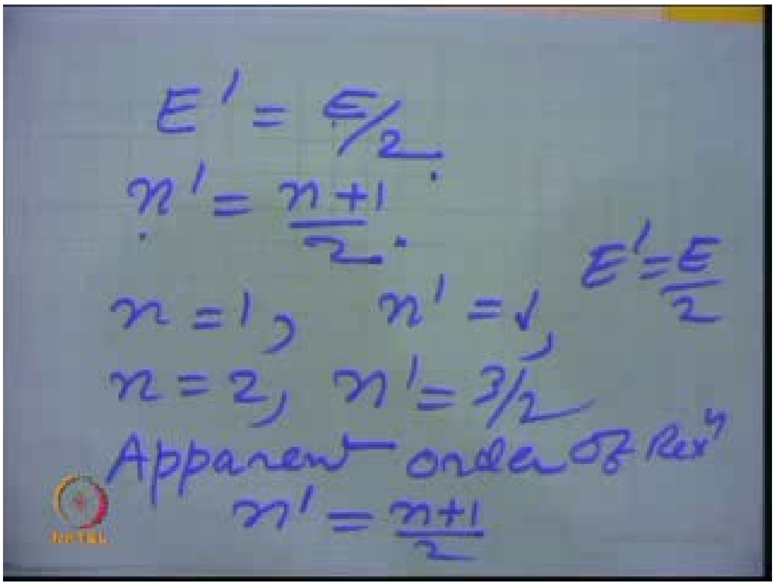

$E' = E/2$.

$n' = \frac{n+1}{2}$.

$n = 1, \quad n' = 1, \quad E' = \frac{E}{2}$

$n = 2, \quad n' = 3/2$

Apparent order of R_{ex}^{n}

$n' = \frac{n+1}{2}$

And, e dash is your E by 2. So, what is e dash? E dash has been calculated because you are calculated the effect of temperature now from here that will be from arrhenius plot. So, arrrhenius plot gives you the slope which I discussed before like this E upon R right. But in this falsified kinetic if you take the slope it comes to be E by RT to the power half. So, it means E upon 2 R right. So, if the apparent activation energy n dash has become now n plus 1 by 2. And, apparent order of reaction and apparent activation energy has becomes E by 2 right. So, this means suppose your reaction is first order then n dash becomes for n is equal to 1; n dash is not changed. So, n dash is also 1 right. So, order has no problem but activation energy E dash has become half of the actual activation energy. Suppose active on a actual activation energy 100 kilo joule per mole in this case if the diffusion is controlling; you will get 50 kilo joule per mole. So, that is totally false information.

So, what is the consequence of diffusion resistance is that your apparent order for n is equal to 2 this change see n dash is equal to now 3 by 2; 1.5 order actual order is first order reaction sorry second order. But you will get it 1.5. So, it means the rate of change of concentration this should have been the square of the power. Now, it is just 1.5; temperature dominancy which we have seen now that is just half of the original or actual activation energy which should have been for a kinetic control reaction right. And, this is known as falsified kinetics right. So, basically the logic is that what we are talking in terms of kinetic controlled reaction or when you study the kinetics of a reaction. Because kinetics is very important; you need to size a reactor, you need to commercialize the reactor in terms of the diameter right; and height of the reactor and based on the size of a particle.

So, you have to make certain assumption when you look at or you design. And, those assumptions suppose you are assuming a plug flow reactor right. So, it means the L by D the ratio should be high; same thing there should not be any channeling there should not be any x ray dispersion. So, these are separate which one needs to study and access the dispersion number or picakellet number and then talk what is the RTD right. Hydro dynamic study based on that or RTD study then looks at the deviation from the ideal reactor that is one thing.

But second thing is also especially important in the catalytic reaction; that you have to look at your size of the catalyst small reactor verses the large reactor right. The diameter of the reactor and your lab reactor verse the size of the catalyst particle. And, the same thing when you look at in a commercial reactor right. And, when you speak about the kinetic even you evaluate the model parameters you have to also ensure that this is actually the actual kinetics. So, that this endues should not disguise you right; it should be n only pure n right. And, same thing for k dash it should be the pure k. It means the reaction should be free from the diffusional resistance. So, that is the meaning of falsified kinetic. Basically we have calculated the rate by introducing the factor which is effeteness factor right.

So, but when there is then you should know that activation energy which is apparent activation energy; this is known as true activation energy. So, this is your true activation energy divide by 2; same thing here n is known as true order of reaction, and n dash is known as apparent order of reaction. So, we use this word like apparent kinetics. So, apparent order of reaction; that is your n dash which is n plus 1 divides by 2. So, sometimes we have some criteria or parameters by which one can identify whether diffusion is controlling or not or are we sure whether the diffusion limitation have been removed from the reactor or not right. So, these limitations need to be removed right.

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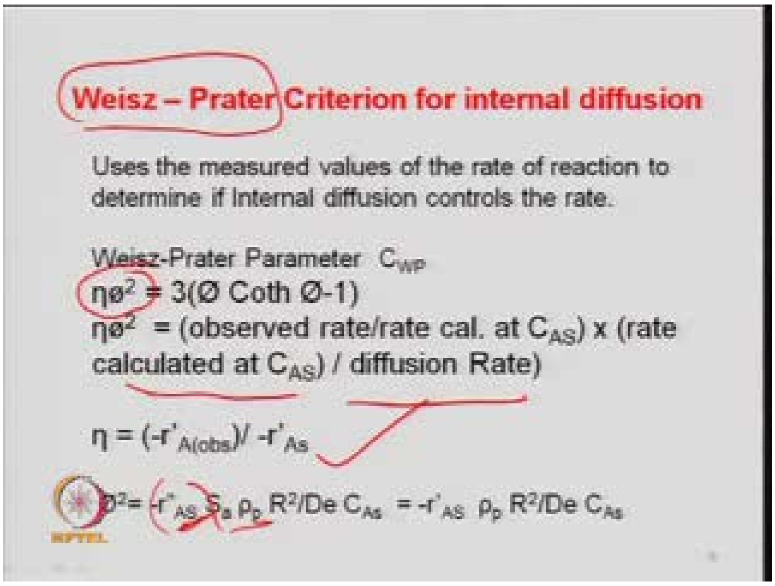

Weisz – Prater Criterion for internal diffusion

Uses the measured values of the rate of reaction to determine if Internal diffusion controls the rate.

Weisz-Prater Parameter C_{WP}

$\eta\phi^2 = 3(\phi \text{ Coth } \phi - 1)$

$\eta\phi^2$ = (observed rate/rate cal. at C_{AS}) x (rate calculated at C_{AS}) / diffusion Rate)

$\eta = (-r'_{A(obs)})/ -r'_{As}$

$\phi^2 = -r'_{AS} S_a \rho_p R^2/De\, C_{As} = -r'_{AS} \rho_p R^2/De\, C_{As}$

So, for that the criteria which is provided by Weisz- Prater right known as Weisz- Prater criterion. And, basically this is use for the internal diffusional resistance right. So, the definition is same but you have done so far that thieli modulus. Thieli modulus you know now square of the thielie modulus is talking about the kinetic rate divide by the diffusion rate. In other words diffusion resistance to the kinetic resistance. And, effeteness factor is your global rate divide by the intrinsic rate right.

So, if you take a parameter which is your eta times pi square because you have already defined your phi right. So, phi has already been defined so eta times phi square. So, substitute the value of eta, substitute the value of I square. So, this number comes out to be 3 times phi cot hyperbolic phi minus 1 this is the right hand side. But we are just talking in terms of the known parameter.

I have already talk talked about the effeteness factor, I have already talked about the phi square thielie modulus; and these are defined based on the global rate and intrinsic rate. So, you can see here the eta is your observed rate or global rate divide by rate which is calculated at the surface condition, surface concentration right; phi square is again rate which is calculated at surface concentration. And, divide by that diffusion rate we have written last time remember D times c A s minus 0 divide by that d z or length of the pore right d L. So, eta is your R observed divide by intrinsic that is measured the surface condition; phi square we have already defined. So, r A s if you define based on the surface area here. So, s a times rho p times R square because R under root k by D for first order reaction based on volumetric rate constant.

So, here it based on surface area. So, s a times rho p times R square divide by D e right times that is this is divide by D e times c A s because I have written here r A s. So, just you have to r A s rate which is defined as k times c s right and this is your definition of thielio modulus.

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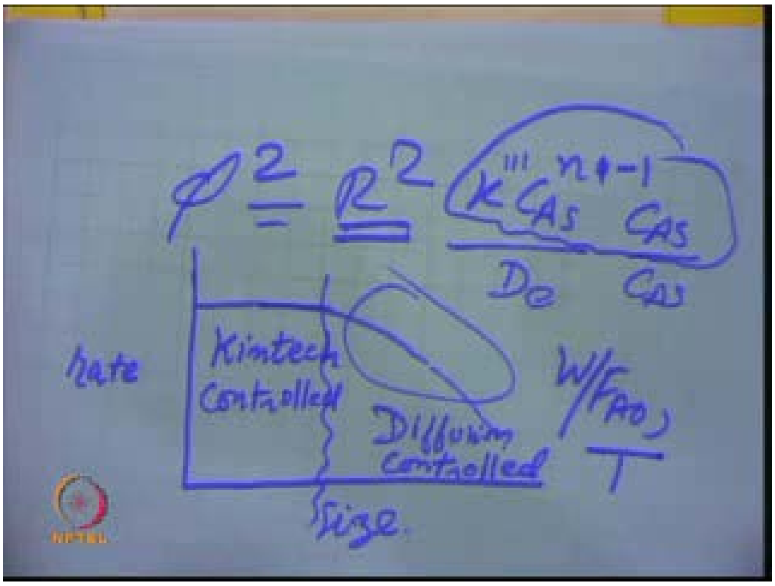

Now, again you have to look at here that phi square is defined simply R square times k for any nth order reaction c A s to the power n minus 1 divide by D e right. So, if I multiplied by c A s and divide by c A s. So, this is your now k c s to the power n right; and that is what written here, this is rate which is you related at the surface condition. So, we have divided by C A s here other terms are same. Because this is based on the volumetric rate constant when I write it is similar to k triple time right. And, I have already talked about the relationship between all these terms right. So, 1 can write in the k dash times rho b or k double dash times s a times rho p. So, same equation has been written in the form of R a dash also, r a dash times rho p times R square divide by D e times c A s right. So, just to co relate that eta phi square we have defined here the in terms of r A s.

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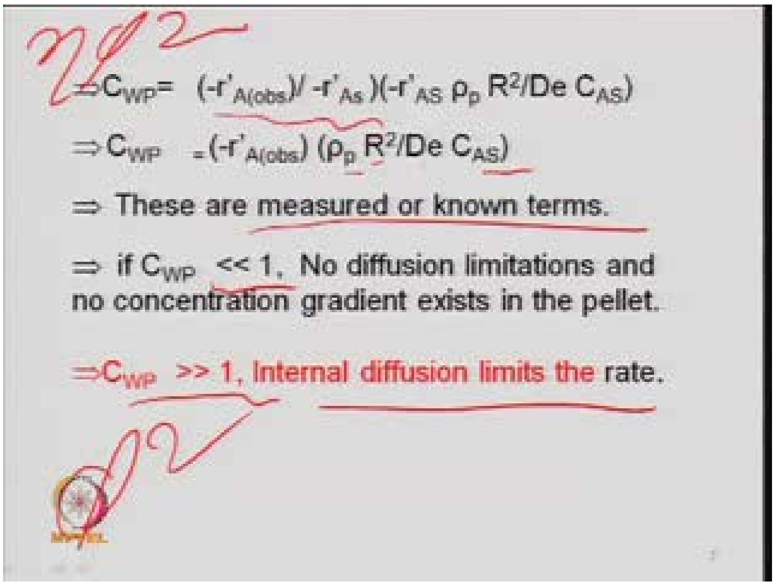

$\eta\phi^2$

$\Rightarrow C_{WP} = (-r'_{A(obs)}/ -r'_{As})(-r'_{AS}\ \rho_p\ R^2/De\ C_{AS})$

$\Rightarrow C_{WP} = (-r'_{A(obs)})\ (\rho_p\ R^2/De\ C_{AS})$

⇒ These are measured or known terms.

⇒ if $C_{WP} << 1$, No diffusion limitations and no concentration gradient exists in the pellet.

$\Rightarrow C_{WP} >> 1$, Internal diffusion limits the rate.

ϕ^2

Now, if you look at further this C w p which we is your eta phi square. Now, you already defined your phi square and eta. So, r observed divide by r intrinsic that is actual rate divide by rate which is measured at the surface condition. So, this is your eta and this is your phi square which you have already defined now. So, r a dash based on mass times rho b times r square divide by D e times c s. So, what is your C w p because these 2 terms gets canceled r a s, r a s right So, this and this cancels. So, r observed times rho p times r square divide by D e times c A s. So, these terms are now known. These are known terms because if you have eliminated the mass transform resistance. Then, your c a 0 is equal to c s right experimentally one can verify that. And, there are similar criteria for mass transform also or external mass transfer limitation.

So, C w p which is defined in terms of observed rate times rho p. So, observed rate is known experimentally you measure that right; when you have pass the feed you can see for a given condition of reaction what is exact mass? And, then one can calculate the conversion and then one can define the rate right; that is what I told conversion verses w you p not you can have a plot. And, then take the slope you can have the rate right and one can use the same thing that t p d type experiments or t p r type experiments using the reactant fiedi stock. Then, also you can measure them right turn over numbers or turn over frequency. So, these are now known terms. So, if the criteria says now or waste criteria says that if your c w p that is eta into phi square that is defined. Now, based on this so these are now calculated numbers if this is much more less than 1; then the diffusion is not controlling the rate.

So, if c w p is much more less than 1 then diffusion is not controlling. It means kinetics may be rate controlling right and if this c w p is much more greater than 1; then internal diffusion controls the rate right. So, same approach what has been defined based on phi square. So, earlier we were talking only on phi square right but phi square if you look at phi square you define kinetic rate divide by diffusion rate or something like what this. So, here the terms are not known right; b is a parameter, k triple prime because you have to do kinetics first. So, this is not known as a priory right and c A s concentration again you have to calculate from this way; so that is right. But the terms are not known in terms of the known variable.

But here most of these term can be defect diffusivity you can co relate from the coalition right or experimentally one can check. So, parameters are almost known. So, this is generally used to check or to confirm whether the diffusion is controlling the rate or not. But the lab scaled I told you already earlier also that you o the experiment with different size particle right.

That you know now that your phi is related to radius of the particle right. So, what you do in the lab scale generally you calculate the rate; observed rate or conversion as a function of the particle diameter that is size of the particle. So, you know that when the particles are larger in size your thielio modulus will be high. And, thielio modulus high means, your eta will be low right; eta will be low means conversion will decrease. So, under identical condition. Identical condition means, fix your w F A naught and all a space time fix your temperature right and carry out the experiment with different size particle; that is 1 m m particle 2 mm particle 1.5 m m particle. But after avoiding the mass transfer resistance right. And, you will see that the rate is initially like this that is for smaller particle when you have fine powder. And, you are increasing the size; then it will go like this and finally it will start dropping right.

So, this is the zone which says that the rate is independent of particle size right. So, when the reaction is in diffusion control region then the rate should be independent of particle that is when the reaction is in diffusion control region. Then, rate will drop with particle size as you increase the particle size the rate is decreasing because you have this term. And, when this is in kinetic control region then rate will be independent of particle size. So, this is your kinetic control region and this is your diffusion control. So, diffusion control react region this one; where the reaction rate is controlled by the diffusion resistance right. And, here you will see your falsified kinetics that is n dash is n plus 1 by 2 right e dash E by 2. And, here you will see just the pure kinetics; that is n and the only pure activation energy right true activation energy.

So, you need to check it experimentally by looking the rate at different size particle and verify that. Another consequence is the mono isothermal point effeteness factor because of the diffusion right. So, one thing is clear here that; when you write a non isothermal point effeteness factor you are writing a your material balance equation which you have already seen for the isothermal case. But beside that you need to write a energy balance also right.

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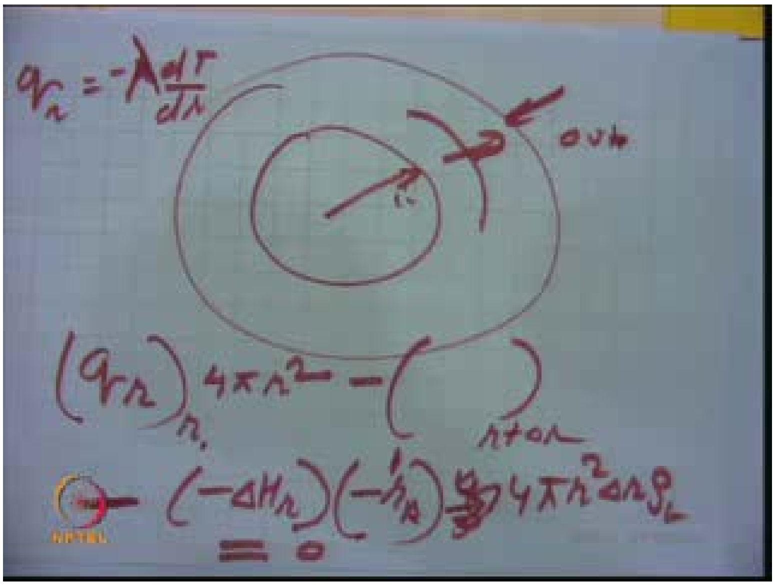

So, energy balances again for a spherical point catalyst you know something like this you will write a shell balance as usual you have done. So, this is your 4 pi r square; so I am just assuming that inward is this right. So, but sign convention just like for a diffusion again I am writing input is here and output is here. And, how heat will transfer because of the conduction right. So, conduction means your q r flux is minus k d T by d r right or I will use lambda here; where lambda is the thermal conductivity of the material right.

So, q r you know the equation now flux q r evaluated at r is equal to r times the area of the shell. So, 4 pi r square right minus the same thing heat out at r plus delta r right. So, that is again q r the same term evaluated at r plus delta r right; input minus output minus disappearance of heat. Because of chemical reaction or generation of heat. So, I will write it minus delta H r exothermic heat of reaction right multiplied by the rate of reaction minus r A right and r A dash r A double dash whatever you want to write. So, if you write r A dash it will become 4 by 3 pi r cube. So, I will write it based on the volume of the shell note not the whole pellet. So, that will become 4 pi r square delta r right. So, 4 pi r square delta r is a volume of the shell and since you are writing it per unit mass. So, multiplied by the density of the catalyst mass per unit volume. So, rate per unit mass and this is the heat generated. And, since you are talking steady state; so that should be 0.

So, what I mean to say I am not going in detail of this but you need to write a energy balance. And, one thing is clear it should be clear in your mind that when the reaction is exothermic. Then, the temperature inside the reaction is taking place inside the pellet right. So, the temperature at the surface will be lower and in the pellet it will be higher. And, you know your rate of reaction is proportional to the rate constant right; and that has the activation energy term k 0 e to the power minus e by RT.

So, it means when temperature is high inside the pellet the rate inside the pellet will be higher. And, what is your definition of eta global rate divide by intrinsic rate; that is actual rate divide by the rate which is measured at the surface. So, inside temperature is high when the reaction is exothermic; then rate inside will be higher here compared to the outer surface? So, effeteness factor for the non isothermal pellet can be greater than 1 right. So, this is what shown here in this graph right.

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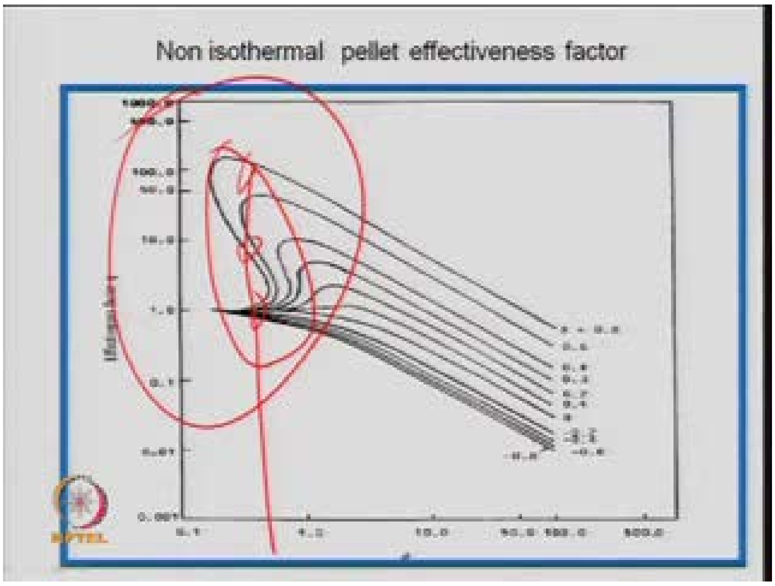

Non isothermal pellet effectiveness factor

And, this gives you a kind of runaway condition, this gives you kind of ensitivity here see for 5 less than 1 these are there are 3 values 1, 2, 3 same values of phi. And, these are what the instability Transnet condition and cause the runaway. And, this will happen right for exothermic reaction in a pellet right and their the temperature inside the pellet will become higher. And, that will cause the hot spot formation also right that runaway conditions; I told catalyst type will go down. So, these are some problems in the catalytic reactors especially when the reactor reaction is exothermic. So, partial oxidation when you do say material partial oxidation right; it is the exothermic process compared to the reforming which is highly endothermic.

But the problem is that total of these kind of reaction exothermic reaction are very difficult. So, industry face problem when you look at the design of these kind of reactor. Because heat is to be removed from the catalyst surface simultaneously right otherwise it will damage the catalyst. So, the equation which is just you need to write a contribution of energy balance equation which is written here first. So, if you look at here the details of this I will just shown here very quickly; I will go through this.

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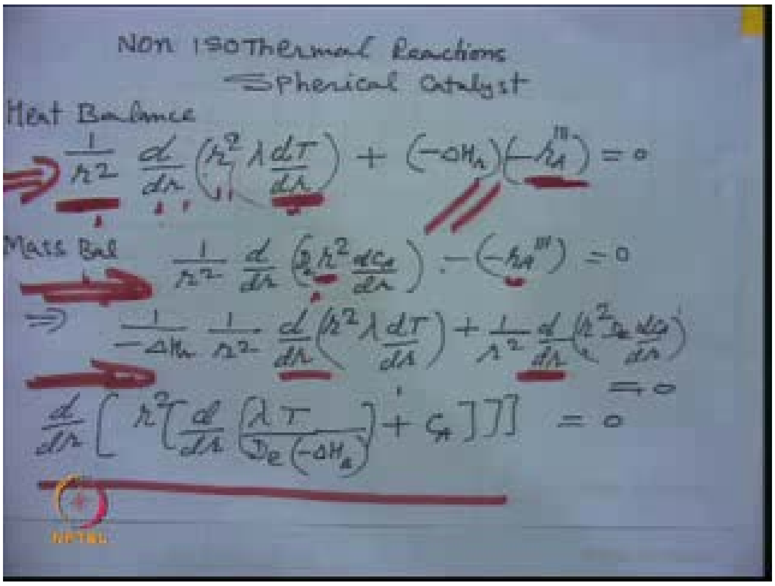

Non isoThermal Reactions

Spherical Catalyst

Heat Balance

$$\Rightarrow \frac{1}{r^2}\frac{d}{dr}\left(r^2\lambda\frac{dT}{dr}\right) + (-\Delta H_r)(-r_A''') = 0$$

Mass Bal

$$\Rightarrow \frac{1}{r^2}\frac{d}{dr}\left(D_e r^2\frac{dC_A}{dr}\right) - (-r_A''') = 0$$

$$\Rightarrow \frac{1}{-\Delta H_r}\frac{1}{r^2}\frac{d}{dr}\left(r^2\lambda\frac{dT}{dr}\right) + \frac{1}{r^2}\frac{d}{dr}\left(r^2 D_e\frac{dC_A}{dr}\right) = 0$$

$$\Rightarrow \frac{d}{dr}\left[r^2\left[\frac{d}{dr}\left(\frac{\lambda T}{D_e(-\Delta H_r)}\right) + C_A\right]\right] = 0$$

So, overall your reaction which is now if you just write this equation which is written here. Now, 4 pi r square q r is minus lambda d t by d r at r; same thing evaluated at r plus delta r right minus delta H r in to minus r A dash times 4 pi r square delta r right. So, that is equal to 0. So, divide by 4 pi r delta r 4 pi delta r and take the limit 0 r delta r tends to 0 the same way as we did earlier. So, quickly I have written it here. So, your equation becomes 1 upon r square because this is this r square has come because you are divide by 4 pi r square. So, 1 upon r square and d over d r of r square already inside. Because that r square you cannot take out right d over d r of r square q r. So, basically this is lambda d T by d r is q r. So, this is term which is because of the contribution of the 2 terms which is shown here.

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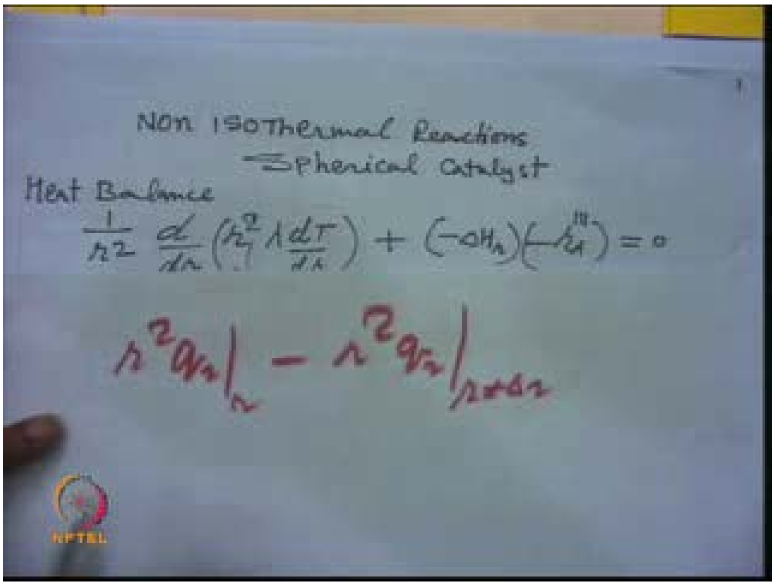

Non isothermal Reactions
– Spherical Catalyst

Heat Balance

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \lambda \frac{dT}{dr}\right) + (-\Delta H_r)(-r_A''') = 0$$

$$r^2 q_r\Big|_r - r^2 q_r\Big|_{r+\Delta r}$$

If I just write it here r square q r at r minus r square q r at r plus delta r. So, these thing you must have read before right so 4 pi r square q at r that was the term which is written here. And, when you divide by delta r; so divide by delta r and take the limit delta tends to 0 right. So, this will become d over d r of r square q r which is here the 2 term. So, d over d r of r square q r. So q r is mi lambda d t by d r right. Because I am taking input positive output negative right; that signs convention choice is yours.

So, ((Refer Time: 52:02)) law of heat conduction has been used here. So, last term because we have already divided now 4 pi r square delta r; so that term is simply delta H r times minus r a triple dash. So, I have written it here volume basis if you write r a dash it will be multiplied by density right catalyst density, pellet density. So, this is your equation for energy balance one equation; that is second 1 is mass balance equation which is written again that we have already done before. So, based on the same thing that is you diffusion d c by d r. So, 4 pi r square times w a r at r same thing at r plus delta r and minus the disappearance because of chemical reaction.

So, minus r a dash times 4 pi r square delta r times rho v. So, same expression you will get which you have already done before like this. So, 1 upon r square d over d r; so this is your fixed law of diffusion d d c by d r since the pellet is spherical. So, r square r square the same term here right minus r a triple dash times 0 because it is disappearance because of chemical reaction. So, if you do not have this term you have studied these thing in your transfer phenomena course also r square q r is a constant for heat transfer and here also r square w r a constant for diffusion flux. So, there is no chemical reaction.

So, now you can write your r a dash from this equation into this equation just to co relates the heat equation right. So, minus r a triple dash from here can be substituted in this. So, you have the equation which will become something like this. So, just as exercise you can you solve it and then check the final value right. So, then this is simple mathematical transformation of minus triple r a triple dash from this equation into this. Because we are interested in co relating the variation in t as a function of r right.

So, once you have this equation you can just look at that; and this equation will come something like in this form. Because your all the term this is also d over d r of r squared lambda d t by d r here it is d over d r of r squared d d c a by d r. So, these all terms have been clubbed together in one differential form. So, one is your concentration term another is your temperature dependent term right; just a interpretation from this differential equation which is written in this form here. And, here it is again the term inside the bracket they are similar right.

So, r square q r or r square w a r flux right. So, based on the mass flux and based on the heat flux. So, if you do it further so very quickly I have done integration of this or solution

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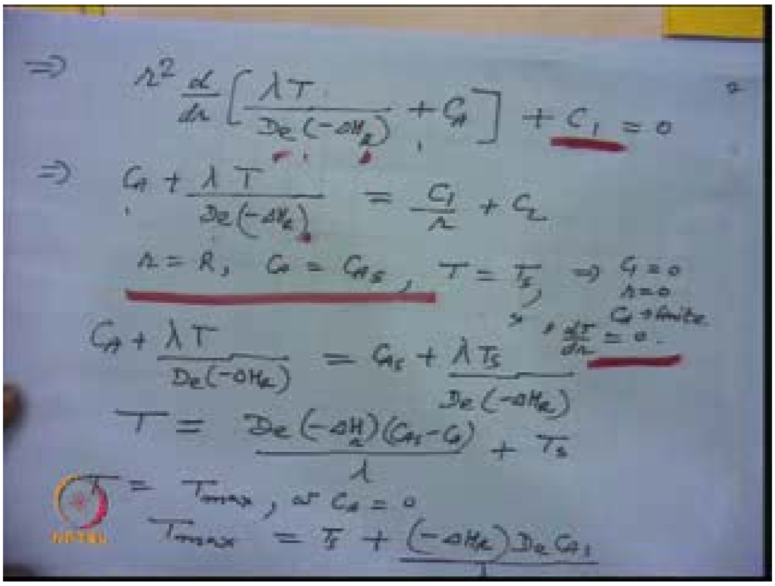

$$\Rightarrow \quad r^2 \frac{d}{dr}\left[\frac{\lambda T}{D_e(-\Delta H_R)} + C_A\right] + C_1 = 0$$

$$\Rightarrow \quad C_A + \frac{\lambda T}{D_e(-\Delta H_R)} = -\frac{C_1}{r} + C_2$$

$r = R,\ C_A = C_{AS},\ T = T_S \Rightarrow C_1 = 0$

$r = 0$

$C_A \to$ finite

$\frac{dT}{dr} = 0$

$$C_A + \frac{\lambda T}{D_e(-\Delta H_R)} = C_{AS} + \frac{\lambda T_S}{D_e(-\Delta H_R)}$$

$$T = \frac{D_e(-\Delta H_R)(C_{AS} - C_A)}{\lambda} + T_S$$

$T = T_{max}$, at $C_A = 0$

$$T_{max} = T_S + \underline{(-\Delta H_R) D_e C_{AS}}$$

So that is the equation which you have drawn now; so r square d over d r of lambda T times D e minus delta H r this is from this equation; same equation which is written here. And, so lambda T D e times minus delta H r plus c A and the first integration has been done right. Because it is a function this is a whole term is a constant; so is equal to a constant. So, one can take c 1 on the other side also just for simplification. So, what are boundary conditions? So, one will be for concentration, another is for temperature right; concentration boundary condition you have already seen right. And, temperature boundary condition means r is equal to R surface temperature is known T s that will be your original condition right T is equal to T s surface. And, r is equal to 0 at the center because of symmetry d T by d r is 0 right. It is similar thing there we said concentration is finite right. Here we are saying that d T by d r because of symmetry it will be finite or one can say temperature is finite, it cannot be infinite right.

So, but the only thing that since it is exothermic. In exothermic reaction it can increase also; so it is advisable to use the boundary condition which is d T by d r is 0 at the center. So, this equation which is written here based on this boundary condition. So, your equation is now first integration has been done and now do the second integration. So, this is C A plus lambda T d divide by D times minus delta H r is equal to now integration of this. Because this will go to here on the other side c upon r square right integration of this gives you minus c 1 upon r. Now, we have taken it on the other side.

So, this choice is yours how you take on that side or this side right; simple mathematical integration of this differential equation. So, basically the first has been done here because this is d over d r of this. So, if you integrate this. So, whole term is a constant right that is written here right. And, second term is which is again in terms of this. So, I will continue it next time and then I would like to conclude it in the next lecture.

Thank you.