Chemical Reaction Engineering - II
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Lecture – 36
Network of First Order Reactions

So, now let us look at what if there is network of first order reactions so, this is we looked at what is the experimental criteria and what is the Thiele modulus and effectiveness factor and what is their relationship and how to use that information in order to find out whether there is internal diffusional limitations or not for a single reaction.

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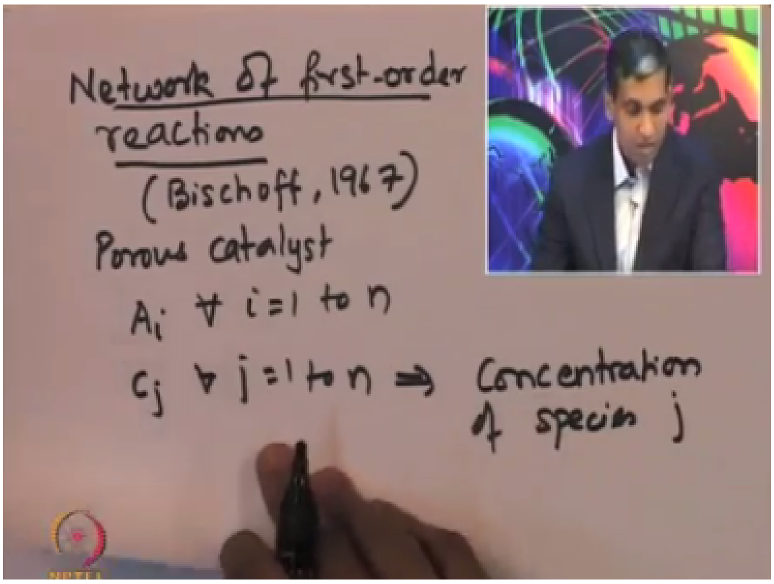

Network of first-order reactions

(Bischoff, 1967)

Porous catalyst

$A_i \ \forall \ i=1$ to n

$c_j \ \forall \ j=1$ to n $\Rightarrow$ Concentration of species j

Suppose, if there is network of first order reactions, then can we develop a; is there a general framework in order to find out what is the effectiveness factor and what is the Thiele modulus for each of these first order reactions and it is very useful in term; in practice because the diffusional limitations of one species can now strongly affect the selectivity of the desired product.

So, therefore it is important to understand what is the Thiele modulus of each of these species; for each of the species and the corresponding effectiveness factor so, let us now look at what is the general framework, so this was actually done by Bischoff in 1967, so now suppose, if the first set of network of first order reactions is carried out in a porous catalyst where all the species which is which are reactants they are; they diffuse into the catalyst.

And moment they diffuse into the catalyst, the reaction happens and some of these species they can adsorbed onto the surface of the catalyst sites and then the reaction happens on the catalyst site and moment the reaction is completed, the product actually dissolves, if it is in the; if it is still adsorbed onto the active sites then it dissolves from the surface and the product leaves the catalyst.

Now, it may be that some of these species directly go into the gas stream and so they leave the catalyst without the desorption step which may be present so therefore, suppose if I assume that Ai are the n species which is participating in this network of first order reactions, so Ai for all i going from 1 to n, so there are n species which are present and n species which is participating in this network of first order reactions.

Now, if Cj for all j going from 1 to n is the concentration of the species, if Cj is the concentration of species j for all values going from j = 1 to n so, now the local rate for species Ai because it is a network of first order reactions.

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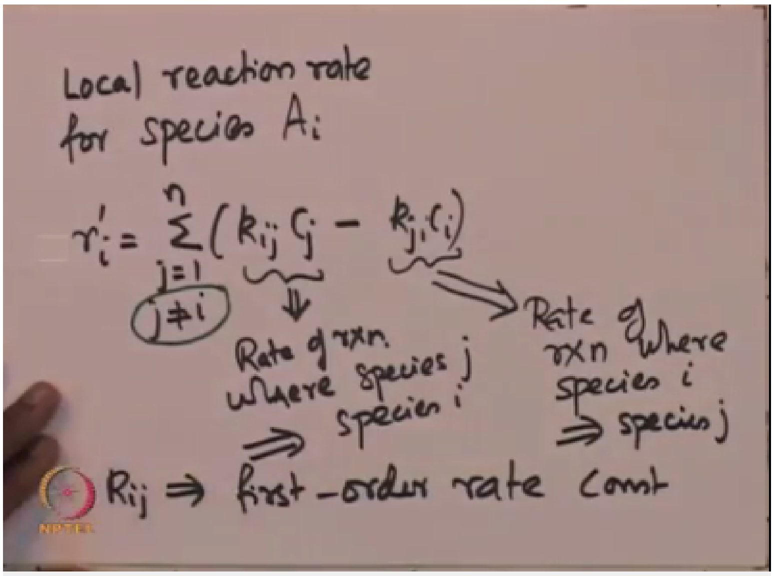

Local reaction rate for species A_i:

$$r'_i = \sum_{\substack{j=1\\ j\neq i}}^{n} \left(\underbrace{k_{ij} C_j}_{\Downarrow} - \underbrace{k_{ji} C_i}_{\Rightarrow}\right)$$

Rate of rxn where species j ⇒ species i

Rate of rxn where species i ⇒ species j

R_{ij} ⇒ first-order rate const

So, the local reaction rate for species Ai is given by ri which is the rate ri that will be sum j = 1 to n, okay and j! = I, Kij * Cj - Kji * Ci. Now, Kij, so this term here corresponds the; corresponds to the rate of reaction where species j is converted to species i so, basically here the reactant is species j and the product is species i now, the second term here is this corresponds to the rate of reaction where species i leads to formation of species j, species i acts as a reactant and leads to formation of species j, so that is the reaction rate.

So, this is the rate of reaction where a species i lead to formation of species j and the first term corresponds to the rate of reaction where the species j is consumed and species i is the product that is formed. So, now if I assume that all Kij, they are all first order rate constants and they have units of time inverse and it is important to note that the that there cannot be a situation where the species j is converted to itself that is why this summation does not include; this summation should not include the ith species.

So, therefore it is represented as j! = i that is this summation is for n - 1 species with the j = i is not included in this summation so now, if we write a; if we assume that the diffusivity of each of this species is Di.

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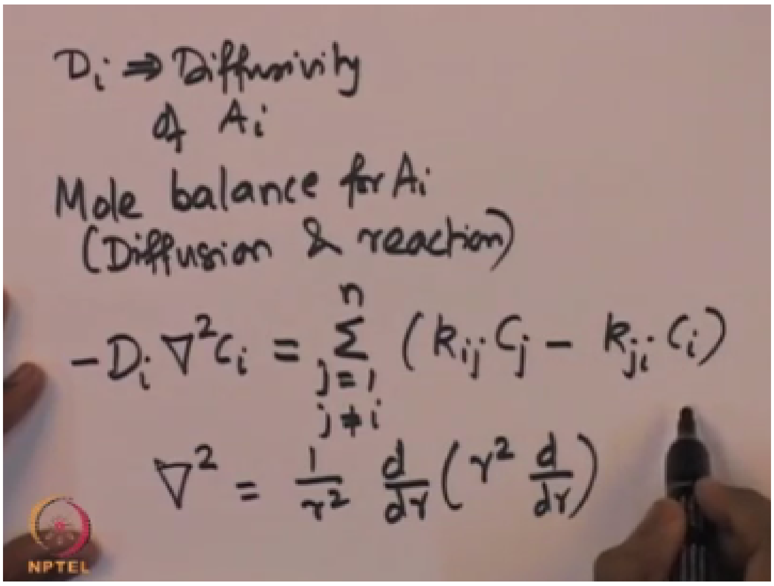

$D_i \Rightarrow$ Diffusivity of A_i

Mole balance for A_i

(Diffusion & reaction)

$$-D_i \nabla^2 C_i = \sum_{\substack{j=1 \\ j \neq i}}^{n} \left(k_{ij} C_j - k_{ji} C_i \right)$$

$$\nabla^2 = \frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{d}{dr} \right)$$

So, if Di is the diffusivity of Ai, Di is the diffusivity of species Ai then, one can write a mole balance for species Ai, so one can write a mole balance that incorporates diffusion and reaction, mole balance for Ai incorporating diffusion and reaction that incorporates diffusion and reaction, so the mole balance will be -Di * del square i, so this is the Laplacian in particular coordinate system whichever coordinates in which the reaction is the whichever coordinates the pellet is actually designed or the geometry of the pellet.

And that should be equal to 1 to n j! = i Kij Cj – Kji Ci now, del square suppose, if it is spherical coordinates, if it is a spherical catalyst then, del square will be 1/ r square * d / dr * r square d / dr, so that is the Laplacian in spherical coordinates, if the catalyst were to be a spherical particle and remember that the first term here corresponds to the species reactant being j and the product which is formed as species i.

And the second term corresponds to the reactant being species i which is being consumed in order to form a product j, so that is the nomenclature that will be used for demonstrating the Thiele modulus and effectiveness factor for network of first order reactions. Now, this mole balance is valid for each and every species i for all n species and so one can write this in a vectorial form.

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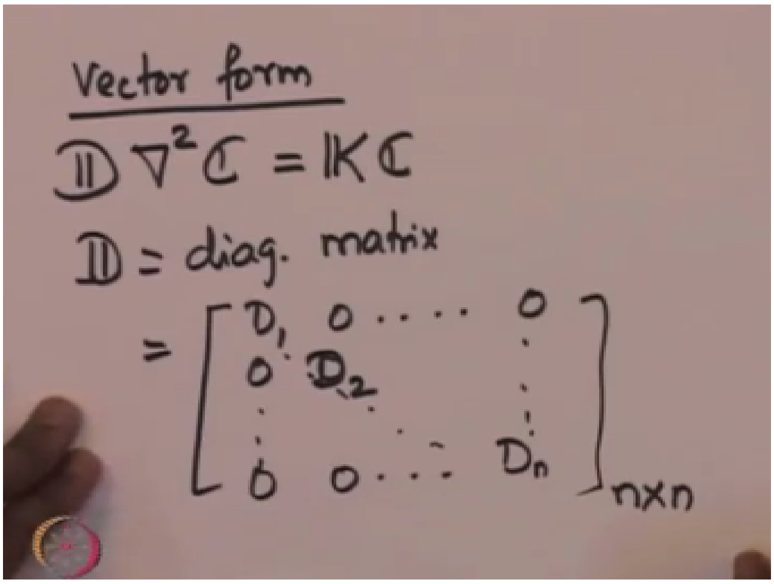

Vector form

$$\mathbb{D}\nabla^2 \mathbb{C} = \mathbb{K}\mathbb{C}$$

$\mathbb{D}$ = diag. matrix

$$= \begin{bmatrix} D_1 & 0 & \cdots & 0 \\ 0 & D_2 & & \vdots \\ \vdots & & \ddots & \vdots \\ 0 & 0 & \cdots & D_n \end{bmatrix}_{n \times n}$$

In the vector form, this can be written as the diffusivity D multiplied by the Laplacian diffusivity matrix D multiplied by Laplacian of the concentration vector C that should be equal to the rate constant matrix K multiplied by the concentration vector C so, now the diffusivity matrix is essentially a diagonal matrix, it is a diagonal matrix and that looks like D1, Dn, D2, so it is an n cross n matrix where the diagonal elements are the diffusivity of each of the molecular n molecular species.

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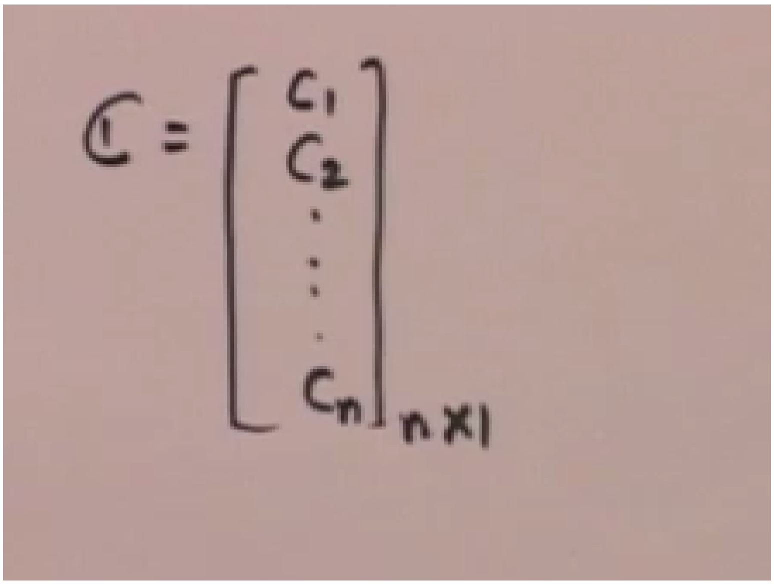

$$\mathbb{C} = \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_n \end{bmatrix}_{n \times 1}$$

Now, similarly the concentration C, the concentration vector can be written as the concentration vector C is essentially a vector of concentration C1, C2 etc. up to Cn so that is a n cross 1 vector, it is a n rows and 1 column, so n cross 1 vector where containing the concentration of this n species which is actually participating in the network of first order reactions then, one can look at the rate constant matrix.

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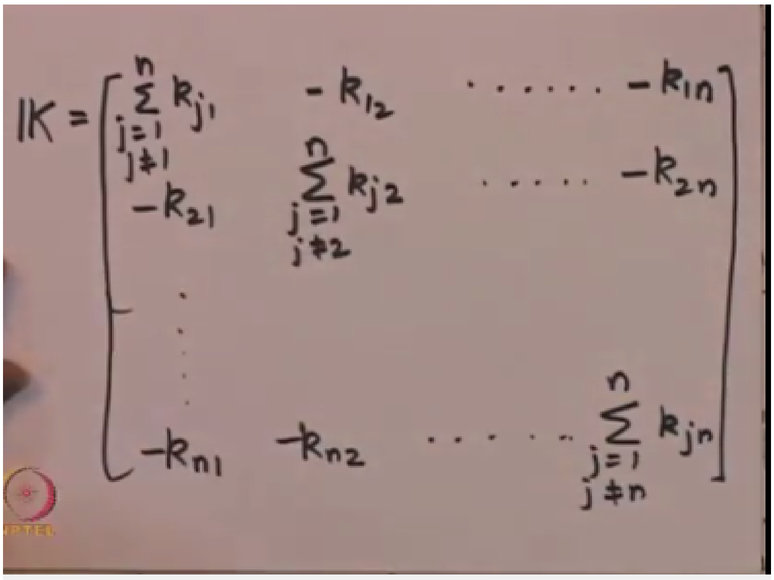

$$\mathbb{K} = \begin{bmatrix} \sum_{\substack{j=1 \\ j \neq 1}}^{n} k_{j1} & -k_{12} & \cdots\cdots & -k_{1n} \\ -k_{21} & \sum_{\substack{j=1 \\ j \neq 2}}^{n} k_{j2} & \cdots\cdots & -k_{2n} \\ \vdots & & & \\ -k_{n1} & -k_{n2} & \cdots\cdots & \sum_{\substack{j=1 \\ j \neq n}}^{n} k_{jn} \end{bmatrix}$$

So, the rate constant matrix is essentially looks like this, so where K is rate constant matrix and that is given by sum j = 1 to n Kj1 where j!= 1 - K12 all the way up to – K1n and the second term will be K21, this will be sum j = 1 to n Kj2, where j! = 2 – K2n and similarly, we can fill this matrix and that will be – Kn1, -Kn2 and that will be sum j = 1 to n, j! = n Kjn, so that is the rate constant matrix.

So, this contains all the information about the rate constants for; first order rate constants for all the reactions which is involved in the network that is being considered so now, one can actually find out so because of the presence of diffusion because of the diffusional limitations, the observed kinetics based on the observed reaction rate can be different from the what is the actual true kinetics.

So, the kinetics is falsified because of the presence of the diffusional limitations and that can actually be expressed in terms of vectorial form for the network of first order reactions.

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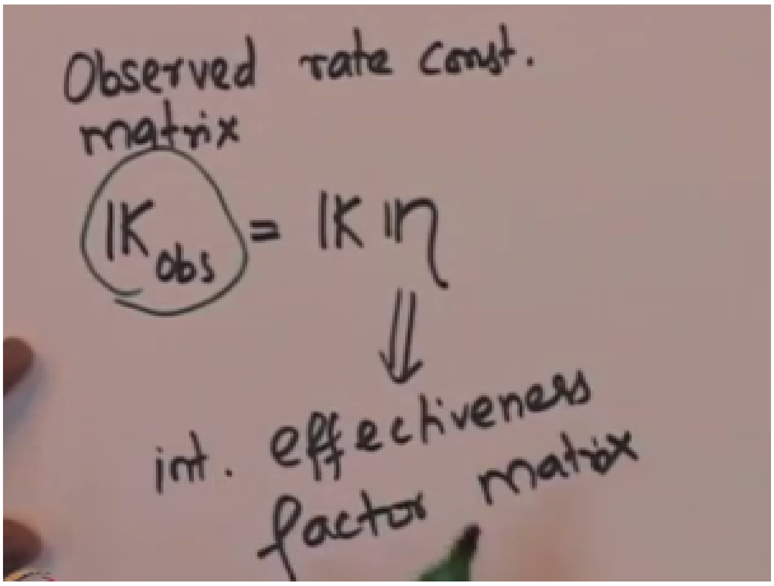

Observed rate const. matrix

$$\boxed{\mathbb{K}_{obs}} = \mathbb{K}\,\eta$$

$\Downarrow$

int. effectiveness factor matrix

And that is given by; see the observed reaction rate constant matrix; observed rate constant matrix is given by suppose, if K observed is the observed rate constant matrix, so that should be equal to the true rate constant matrix which is what we just wrote in the last slide and multiplied by the corresponding effectiveness factor matrix, so this is the internal effectiveness factor matrix.

In the presence of the internal diffusion, the reaction rate that is observed is actually falsified and the observed reaction rate which is given by this matrix which contains; it is an n cross n matrix containing all the reaction kinetics rate constants and that is given by the true rate constants multiplied by the corresponding effectiveness factor matrix, so what is this effectiveness factor vector?

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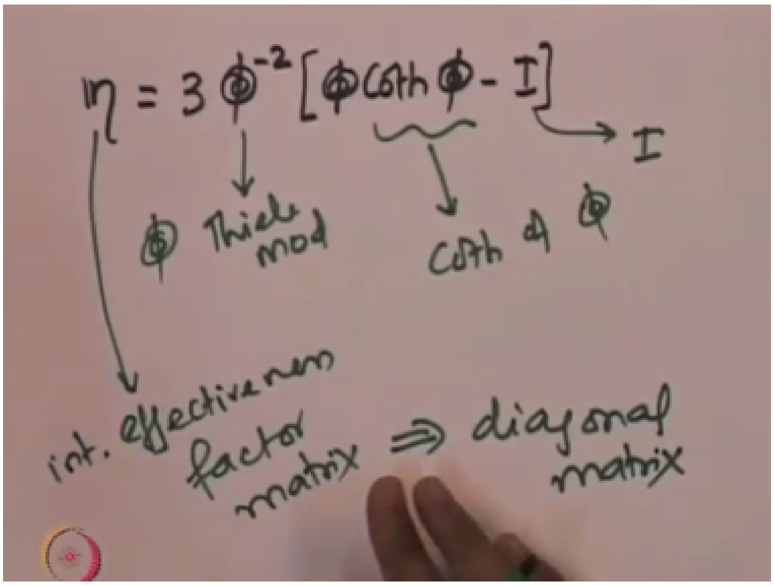

So, it can be defined as the; if we solve the equations and find out what is the effectiveness factor, so the effectiveness factor matrix is given by 3 that is the matrix of Thiele modulus, it is the square of the inverse, inverse of the square of the matrix of Thiele modulus multiplied by matrix of Thiele moduli and took cot hyperbolic of the; it is a matrix of cot hyperbolic minus the identity matrix, so this is the Thiele modulus, so phi is the Thiele modulus matrix.

And this is the cot hyperbolic of the Thiele modulus matrix, so that is the matrix of cot hyperbolic and it is a diagonal matrix and the I is the identity matrix and eta is the effectiveness factor matrix, eta is the internal effectiveness factor matrix and this is essentially a diagonal matrix and this is diagonal because the Thiele modulus matrix turns out to be a diagonal matrix and the cot hyperbolic function of the diagonal matrix also is a diagonal matrix.

And therefore, the effectiveness factor matrix is also a diagonal matrix consisting of the individual effectiveness factor of each of these networks of reactions.

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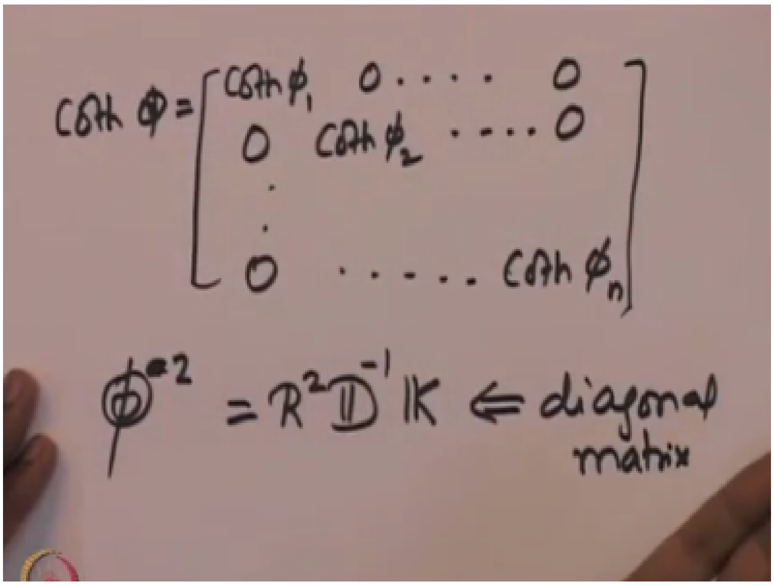

$$\coth \Phi = \begin{bmatrix} \coth \phi_1 & 0 \cdots & 0 \\ 0 & \coth \phi_2 & \cdots 0 \\ \vdots & & \\ 0 & \cdots\cdots & \coth \phi_n \end{bmatrix}$$

$$\Phi^{*2} = R^2 \mathbb{D}^{-1} \mathbb{K} \Leftarrow \text{diagonal matrix}$$

So, now the cot hyperbolic of the Thiele modulus matrix that is a matrix is given by it is a diagonal matrix, it is the cot hyperbolic of phi 1, 0, cot hyperbolic of phi 2, etc. cot hyperbolic of phi n, so that is a diagonal consisting of the cot hyperbolic of each of the Thiele modulus corresponding to each of these species and the overall Thiele modulus matrix which is again a diagonal matrix.

It is the square of that is given by R square which is the length scale of the catalyst multiplied by the diffusivity matrix which is again a diagonal matrix inverse of that multiplied by the corresponding rate constant matrix first order; network of first order reaction rate constant matrix. So, this is again a diagonal matrix and so the network of the; so once we know the Thiele modulus matrix, we should be able to find out what is the cot hyperbolic.

And we can substitute that in the expression for the relationship between the Thiele modulus matrix and the effectiveness factor matrix and from that the effectiveness factor matrix can be found out and using that one can actually find out what is the actual observed kinetics and express that in terms of the true kinetics. So, from experiments if we measure the actual kinetics and from the effectiveness factor.

We will be able to use that expression to find out what is the true kinetics of the network of first order reactions. So, this is important because the diffusional effects strongly affect the selectivity of the product that is desired.

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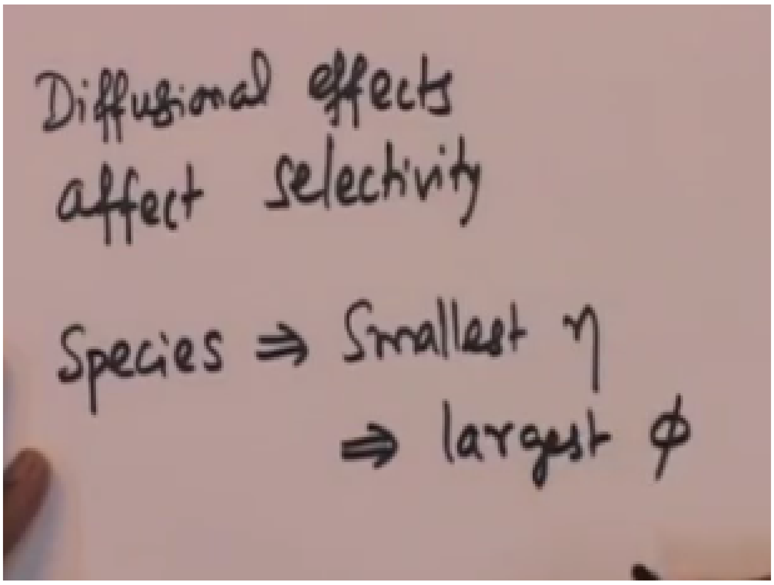

Diffusional effects
affect selectivity

Species $\Rightarrow$ Smallest η
$\Rightarrow$ largest ϕ

So, the diffusional effects; they affect selectivity and so because the effectiveness factor matrix is a diagonal and the Thiele modulus matrix is also a diagonal matrix, one can easily deduce that the species with that has smallest eta, smallest internal effectiveness factor will actually have the largest Thiele modulus, so species n whose Thiele modulus is the largest will have the correspondingly smallest effectiveness factor that can be deduced simply from the expressions.

So, now let us look at what are all the experimental limiting cases from what; how to deduce these limiting cases from the experimental data, so if you want to summarize what are the features of the experiments or what are the information from the experiments that needs to be used in order to deduce whether a particular limiting case exists in a given heterogeneous catalytic reaction, so that can be summarized quite nicely depending upon the dependence of the rate on various parameters or various system parameters.

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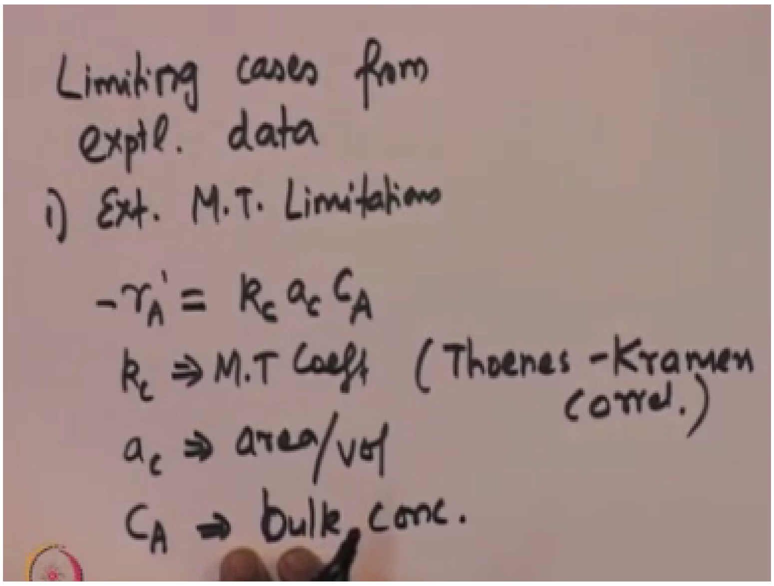

Limiting cases from
exptl. data
i) Ext. M.T. Limitations

$-r_A' = k_c a_c C_A$

$k_c \Rightarrow$ M.T Coeff (Thoenes-Kramen corrl.)

$a_c \Rightarrow$ area/vol

$C_A \Rightarrow$ bulk conc.

So, let us look at the limiting cases from experimental data, look at the limiting cases from experimental data so suppose, if we look at the external mass transport limitations, then the reaction suppose, if the reaction is controlled by the external mass transfer then the reaction rate - rA is given by the mass transport coefficient Kc multiplied by the area per unit volume of the catalyst into the concentration of the species; the bulk concentration of the species.

So where Kc is the mass transport coefficient and this can typically be estimated using various correlations; appropriate correlations for example, one could use a Thoenes Kramen's correlation, so one could use a Thoenes Kramen's correlation in order to estimate what is the mass transport coefficient and the ac is the area per unit volume of the catalyst and CA is the concentration; bulk concentration of the species.

Now, if we look at this the dependence of the mass transport coefficient on various system parameters, so we could now look at the Thoenes Kramen correlation because the mass transport is given by these correlations, so let us take an example and look at the Thoenes Kramen relationship.

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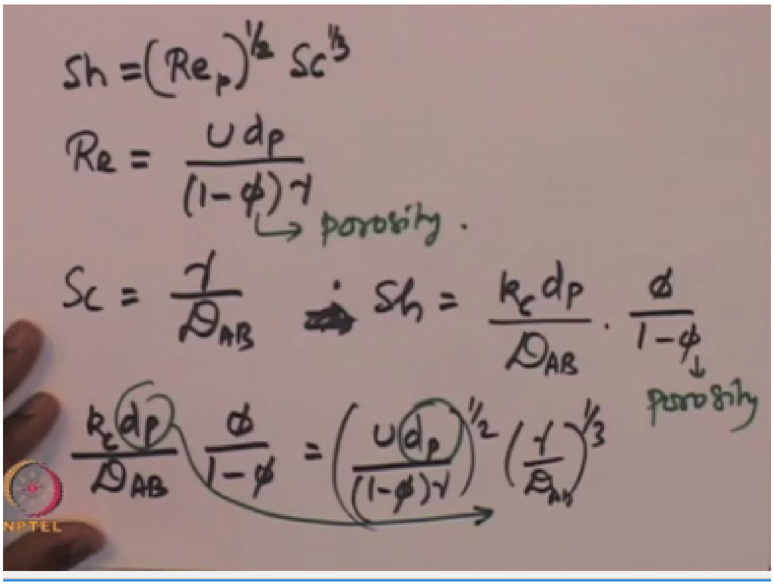

$$Sh = (Re_p)^{1/2} Sc^{1/3}$$

$$Re = \frac{u d_p}{(1-\phi)\nu}$$

porosity.

$$Sc = \frac{\nu}{D_{AB}} \quad \therefore \quad Sh = \frac{k_c d_p}{D_{AB}} \cdot \frac{\phi}{1-\phi}$$

porosity

$$\frac{k_c d_p}{D_{AB}} \frac{\phi}{1-\phi} = \left(\frac{u d_p}{(1-\phi)\nu}\right)^{1/2} \left(\frac{\nu}{D_{AB}}\right)^{1/3}$$

So that will be that is given by the Sherwood number = the Reynolds number based on the particle diameter, so to the power of 1/2 multiplied by the Schmidt number to the power of 1/2 so that is the dependence of the Sherwood number or the Reynolds number of the part; based on the particle diameter multiplied by the Schmidt number. What is the Reynolds number?

Reynolds number is given by the superficial velocity u multiplied by the diameter of the particle dp divided by 1 - porosity into the kinematic viscosity remember that phi here is not Thiele modulus, this is the porosity; porosity of the bed, of the catalyst bed in which the reaction is being conducted and the Schmidt number SC is given by kinematic viscosity divided by the diffusivity of that species, molar diffusivity of that species.

And so from here and Sherwood number is given by mass transport coefficient Kc multiplied by the diameter of the particle dp divided by the corresponding diffusivity * phi/ 1 – phi, once again here phi refers to the porosity of the bed, so from here we can substitute these expressions into the Thoenes Kramen relationship, so this is the Thoenes Kramen relationship, so from here we can see that Kc dp/ DAB * phi/ 1 - phi that should be =u * dp divided by 1 – phi * nu to the power 1/2 * nu / D to the power of 1/3.

So, now from here we can deduce that the mass transport coefficient Kc is a function of square root of dp which appears in the Reynolds number term and then if we bring this dp, if we divide this expression by dp, so we will find that we can bring this to the denominator.

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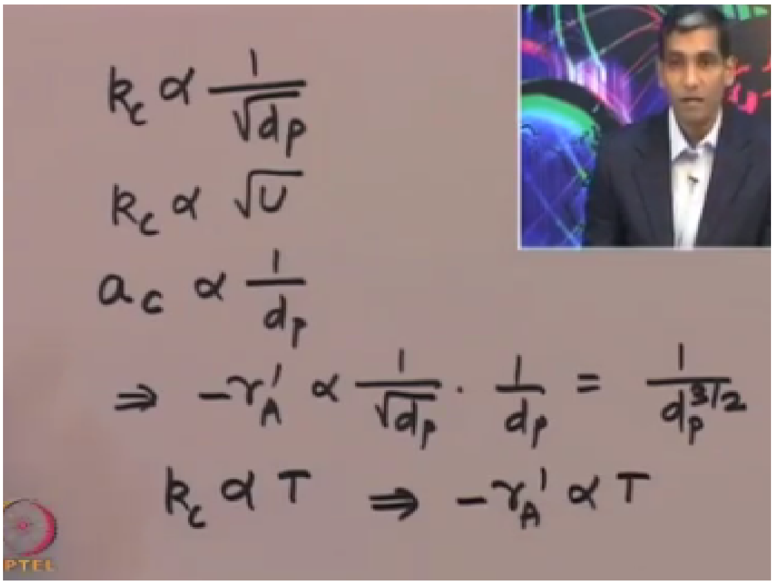

$$k_c \propto \frac{1}{\sqrt{d_p}}$$

$$k_c \propto \sqrt{U}$$

$$a_c \propto \frac{1}{d_p}$$

$$\Rightarrow -r_A' \propto \frac{1}{\sqrt{d_p}} \cdot \frac{1}{d_p} = \frac{1}{d_p^{3/2}}$$

$$k_c \propto T \Rightarrow -r_A' \propto T$$

And we will find that the mass transport coefficient Kc is now a function of; is now a function of Kc is now proportional to 1/ square root of dp, now in addition to this, the mass transport coefficient is proportional to square root of the superficial velocity now, the surface area per unit volume of the catalyst is essentially proportional to 1/ dp because it is the surface area per unit volume.

And therefore, we can say that the reaction rate; the reaction rate of that particular species is proportional to 1/ square root of dp * 1/ diameter of the particle and that is = 1/ dp to the power of 3/2 and the mass transport coefficient Kc is proportional to the temperature at which the reaction is being conducted, so which means that the reaction rate is now proportional to temperature.

So, what we have looked at in this lecture so far is we have looked at the generalized criterion for determining what is the; whether based on the experimental data whether the internal diffusion controls the overall catalytic reaction; heterogeneous catalytic reaction and then we had looked at what if there is a network of first order reactions, what is the general framework for finding the effectiveness factor and Thiele modulus of various species that participate in a network of first order reaction.

And then we initiated discussion on how to use experimental data and to identify what are the various kinds of limitations and how the rate depends upon various systems parameter and so we will continue with this in the next lecture, thank you.