

**Chemical Reaction Engineering**  
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**Module No. #04**  
**Lecture No. #18**

**Gas-solid Catalytic Reactions – External diffusion**

Friends! Now, we will start discussion on transport phenomena and chemical reactions. If you recall, so far, we talked about the kinetics of various types of reactions, complex reactions in particular. Now, let us see how we bring in transport phenomena, particularly, when you have heterogeneous reactions.

Heterogeneous reactions imply that you have more than one phase, gas and solid or liquid and solid or gas liquid and solid and the reaction is occurring by interaction of reactants between these phases. Moment you have phases, you have boundaries which separate these phases and the moment you have boundaries, there is a resistance for transfer across the boundaries and hence, the rates of the processes may actually go down because of these resistance for transfer apart from the kinetic limitations that are present in the system. So, what we are going to do is, we are going to start looking at Gas-solid catalytic reactions to begin with and then, we will turn our attention to non-catalytic reactions and then Gas-liquid reactions.

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The image shows a video frame of a presentation. The slide content is as follows:

Topic 6: Heterogeneous reactions

- Gas-solid catalytic reactions
- Gas-solid noncatalytic reactions
- Gas-liquid reactions

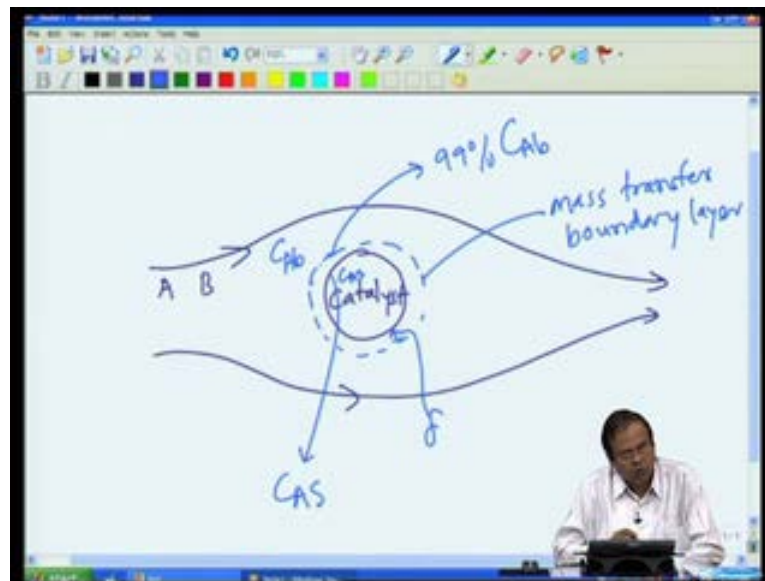
Below the text is a hand-drawn diagram in red ink. It depicts a central circular catalyst pellet with the word 'Catalyst' written inside. To the left of the pellet, three horizontal arrows point towards it, representing the flow of gas. The word 'Bulk' is written above the arrows. The entire diagram is enclosed within a hand-drawn red boundary.

In the bottom right corner of the video frame, a man in a white shirt is visible, sitting at a desk and looking towards the slide.

Now, to refresh our memory, what is the situation when a Gas-Solid catalytic reaction takes place? For example, we discussed earlier that this is my catalyst pellet, then, this catalyst pellet is present in the flow of gas. So, this is a gas which is flowing, this is catalyst and I am going to look at what happens to this gas as it tries to approach the catalyst, what are the transfer processes. You will recall that we have talked about external transfer, that is, from the bulk to the surface. We also said that there is a boundary layer. We will talk about that in a minute. Then, from surface to inside the catalyst, then, your chemical reaction, then again diffusion backward into the bulk.

While we discussed about these chemical reactions so far, we would now start discussing about this transport in the bulk to the surface and from surface to the inside of the **Catalyst** pellet. So, let us look at what happens **when** we have the catalyst which is exposed to the gaseous reactants and products.

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Once again, this is my catalyst. It is a porous catalyst. So, reactions are going to take place inside, but for time being, we will focus only on what is happening outside. Let us say that there is a gas which is flowing past this solid catalyst. It is a situation of flow past a solid surface. So, our reactants are for example, for product A and the product B is **flowing** past this catalyst surface.

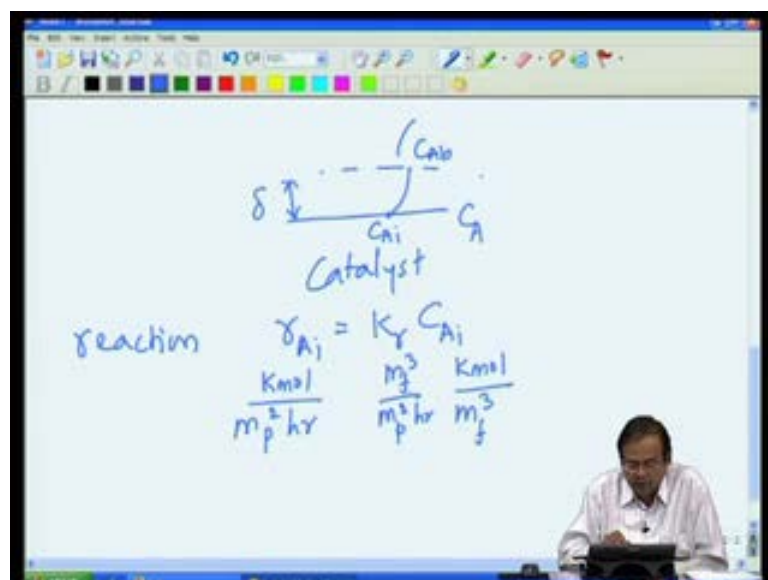
Now, when we talk about flow past a surface, we talk about hydrodynamic boundary layer because what happens is that the velocity of the gas for example, on this surface is 0 and it is flowing with certain velocity  $V$  outside in the Bulk. So, there is a transition of velocity from the bulk to the surface and we say that the hydrodynamic boundary layer is a layer where this velocity is ninety-nine percent of the bulk velocity.

So, if you say that this is a bulk velocity, this velocity at the surface is ninety-nine percent of the bulk velocity and from there, it drops down to 0. When it comes to mass transfer, we will apply the same idea, that is, instead of hydrodynamic boundary layer, we will say that we have a mass transfer boundary layer. What is the characteristic of this mass transfer boundary layer? It is similar manner to what we talked about in the velocity, that is, if concentration of A in the bulk is  $C_{A b}$  to denote that it is a bulk concentration, then the layer having a thickness  $\delta$ , let us say. So, this thickness is  $\delta$  such that the outside edge of this layer, the concentration is ninety-nine percent of  $C_{A b}$  and at the surface, now the concentration cannot be 0 or it may be 0 in certain

cases, but it is not necessary unlike velocity which is 0 at the surface, concentration may be something different. So, let us say that concentration is  $C_A S$ .

So, concentration at this surface of the catalyst is  $C_A S$ , concentration at the outer edge of this boundary layer of thickness  $\delta$  is  $C_A b$ , ninety-nine percent for all practical purposes, we will take it as  $C_A b$ . Now, we can visualize what is happening as the  $A$  from this boundary layer, there is a concentration difference. It has to be there. If the concentration difference is not there, then, there cannot be any diffusion because the driving force for molecular diffusion is the concentration difference. So, there is a concentration difference and that is what is resulting **into** the reaction.

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So, let us now enlarge this and say that this is my surface, this is my catalyst and this is one edge of the boundary layer having thickness  $\delta$ , the concentration at this point is  $C_A b$  and at this point, it is  $C_A i$  and there is a drop in concentration from the outer edge to the boundary.

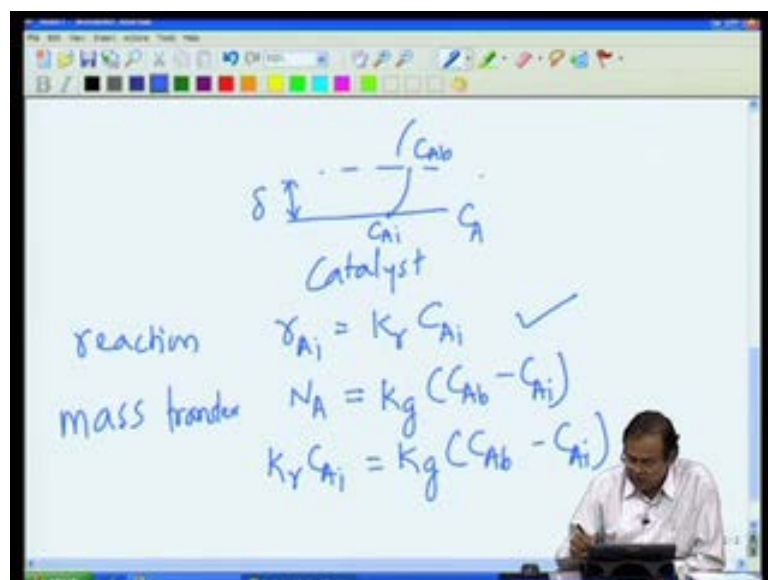
So, now, let us try looking at what is happening on the surface. Right now, we will say that the reaction is taking place only on the surface because we have not brought in the internal diffusion yet. So, let us say that the reaction is taking place on this surface and it

is a first order reaction. So, on the surface, the reaction at a rate  $r_A$  is equal to let us say some rate constant  $K_r$  times  $C_{A_i}$ .

We do not know what this  $C_{A_i}$  is at the moment, but let us say that concentration is some concentration  $C_{A_i}$  and the reaction is taking place with that rate. We should keep in mind that the units of rate are, let us say in kilo moles per meter square of the particle because we are talking of surface area of the particle. So, that is why that subscript  $p$  over here per hour. Now, the concentration of the species  $C_{A_i}$  is in kilo mole per  $m^3$  cube. That is the concentration is kilo mole per volume of the bulk phase. That is the fluid phase. Fluid is in all these phases. So,  $m^3$  cubed.

Therefore,  $K_r$  must have unit of  $m^3$  cube by  $m^2$  square per hour. Why I am pointing out this is we should always keep track of the proper dimensions because any equation that you write, the dimensions of both left hand side and the right hand side must be equal. Now, the reaction rate constant over here has units of  $m^3$  cube per  $m^2$  square hour. It is same length  $m$  and  $m$  on numerator and denominator, but  $3$  subscript and  $2$  subscript over here

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Now, let us see what happens to the mass in this boundary layer. This is the rate at which reaction is taking place, but there is also a rate at which material is or A is coming to the

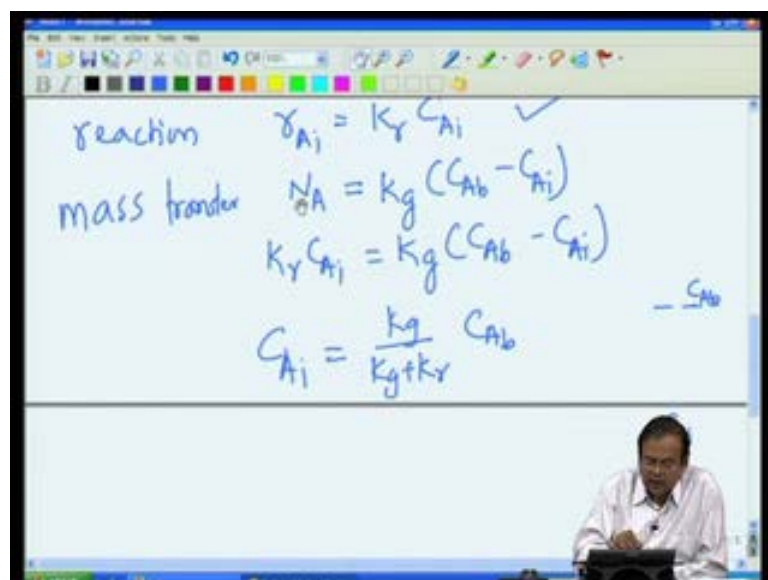
surface and that is because of external diffusion as we call it. So, mass transfer rate, the flux in A if you neglect the curvature effects and write the diffusion equation, we can show this as mass transfer coefficient  $K_g$  times the driving force  $C_{Ab}$  minus  $C_{Ai}$ .

So, what is happening? Let us say that **this** is my surface the gas is flowing from the bulk or the boundary layer thickness to the surface and it is reacting on the surface. Now, if I assume that this surface has no capacity to store mass, then the rate at which A is coming to the surface and the rate at which it is reacting must be equal or in other words, the reaction rate and mass transfer rate must be equal or we can write  $K_r$  into  $C_{Ai}$  must be same as  $K_g$  into  $C_{Ab}$  minus  $C_{Ai}$ .

Equality of mass transfer: what is the assumption that we made? The assumption that we made was that if surface is infinitely small, no volume just the surface, it has no capacity to store mass. So, accumulation is not there. So, the reaction rate must be same as the rate at which the material is coming to the surface.

If we take these two equations and simplify little bit, that is, if we take these **this** two equations, **this** equation in particular and simplify.

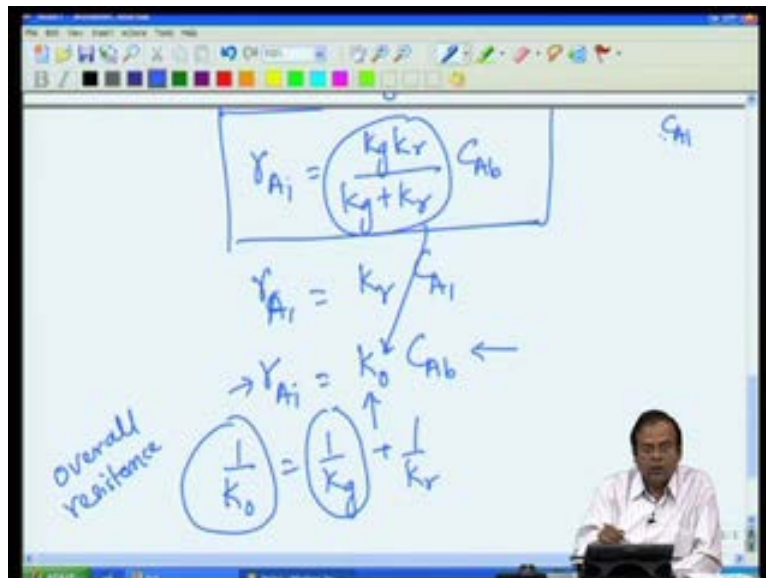
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We will get **from** solving for  $C_{Ai}$ , we will get  $C_{Ai}$  equal to  $K_g$  by  $K_g$  plus  $K_r$   $C_{Ab}$ , that is, concentration at the interface is some fraction of the concentration at the bulk. So,

just imagine that this line which you are seeing here is my interface, that is, the surface of the catalyst. So, concentration here is  $C_{A_i}$ , this is, somewhere my boundary. So, that concentration is  $C_{A_b}$ . So, this concentration  $C_{A_i}$  is a fraction of this bulk concentration and that fraction has both mass transfer coefficient as well as reaction rate constant into it. So, if we now take this  $C_{A_i}$  and plug it back into my rate or in either this equation or this equation, it does not matter.

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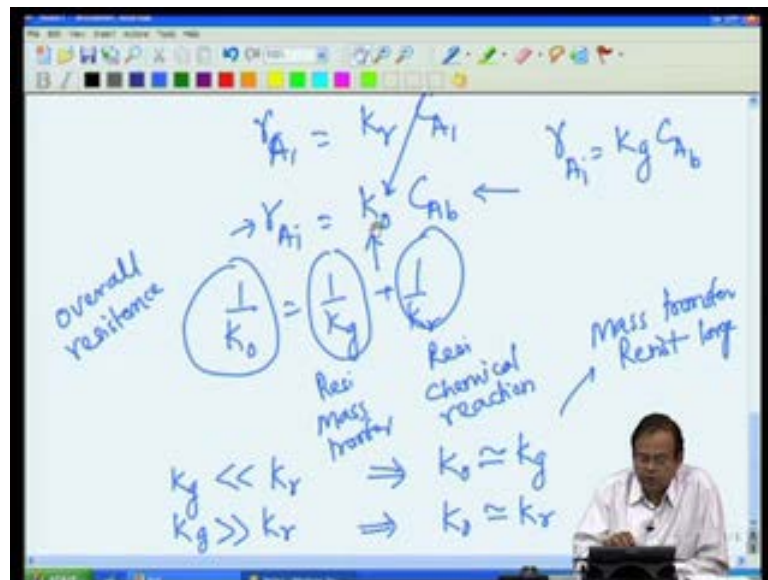
We will get the rate of my reaction as  $k_g k_r$  by  $k_g$  plus  $k_r$  into  $C_{A_b}$ . Rate is also equal to  $k_r$  into  $C_{A_i}$ . That is my interface, but I am not interested because I do not know what the interface concentration is. So, I am interested in finding out what is the relationship between the rate of reaction and the bulk concentration and this is that relationship.

Now, we can compare these two and you will see that these are not same. Of course, this constant is not same because this concentration is also not same. So, what can we write this reaction rate? So, first thing we notice here is that  $k_{naught}$  is  $k_g k_r$  by  $k_g$  plus  $k_r$ . So, this is  $k_{naught}$ . So, reaction was first order kinetics with the surface concentration. It remains first order even with the bulk concentration, but this is not true and for **all** cases, this is true only for first order case. For second order case, it is not necessary that your rate constant is same.

So, **what** it practically means is that when you do these reactions, this is the rate that you are going to measure and you are going to measure the bulk concentration. So, if you try to estimate the kinetic rate constant, you will get the value  $K_{naught}$  and not  $K_r$  because to get  $K_r$  you will have to measure the surface concentration which we do not know.

But, what is a relationship between  $K_{naught}$ ,  $K_r$  and  $K_g$ ? We can write this as  $1 \text{ over } K_g \text{ plus } 1 \text{ over } K_r$ . This will immediately strike a call. Those of you who remember your electrical engineering lectures, resistances in series, they add up. So, coefficient or inverse of coefficient is like resistance. So, this is measure of overall resistance.

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This quantity is the resistance due to mass transfer.  $1 \text{ over } K_g$  and this quantity is resistance or equivalent of that due to **chemical** reaction. Transfer coefficient and resistance are inverse of each other. Now, we can clearly see that if mass transfer resistance is high compared to chemical reaction; that means, mass transfer value  $K_g$  is very much lower than  $K_r$ , that is the situation where mass transfer resistance will be high. So, what we see here therefore is that this is a situation of resistances in series, overall resistance as an addition of resistance due to mass transfer and resistance due to chemical reaction.

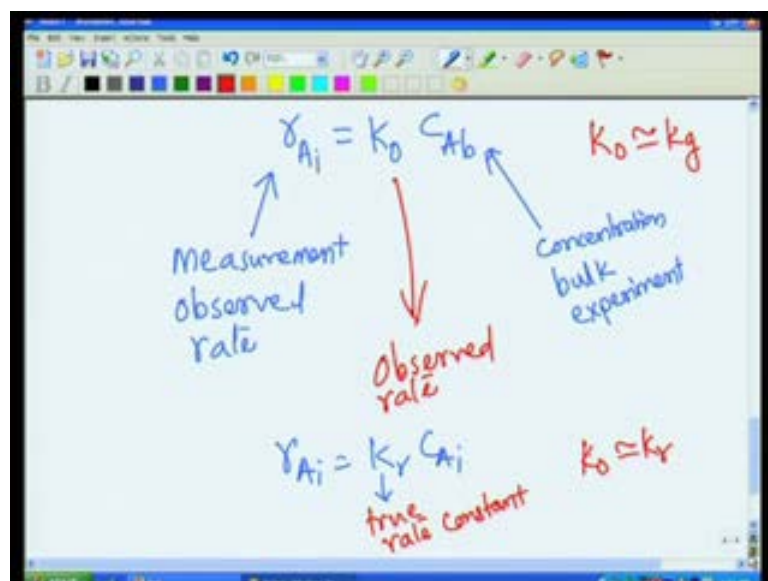


So, resistances are inverse of transfer coefficient. So, higher the resistance, lower is the value of transfer coefficient. So, let us say that our mass transfer coefficient is very much smaller than the reaction rate constant. So, for this particular situation, what will we get is  $1 \text{ over } K_g$  will be very much large compared to  $1 \text{ over } K_r$  to the extent that we can neglect  $1 \text{ over } K_r$  and this would imply  $K_{\text{naught}}$  is almost equal to  $K_g$ .

This, when mass transfer resistance is large, what does it imply? If you go back to our reaction rate,  $r_{A_i}$  is  $K_{\text{naught}}$  into  $C_{A_b}$ , it is actually  $K_g$  into  $C_{A_b}$ . So, the rate constant that we will measure is not the reaction rate constant  $K_r$ , but the overall mass transfer process is very slow compared to the chemical reaction.

What about the other situation? If  $K_g$  is very much greater than  $K_r$ ; that means, now reaction is very slow. This would imply  $K_{\text{naught}}$  is almost same as  $K_r$ . So, when the mass transfer resistance is very small compared to the chemical reaction resistance, then the kinetic rate constant that we will measure or  $K_{\text{naught}}$  is same as the **actual** kinetic rate constant. So, once again, we note that  $K_{\text{naught}}$  is an effective rate constant which is influence by both mass transfer coefficient  $K_g$  and the reaction rate  $K_r$ . I will also emphasize that, because of mass transfer resistance, our reaction or our rate overall observed rate constant is different. Now, let me reiterate this point because this is an important idea which we will be using time and again.

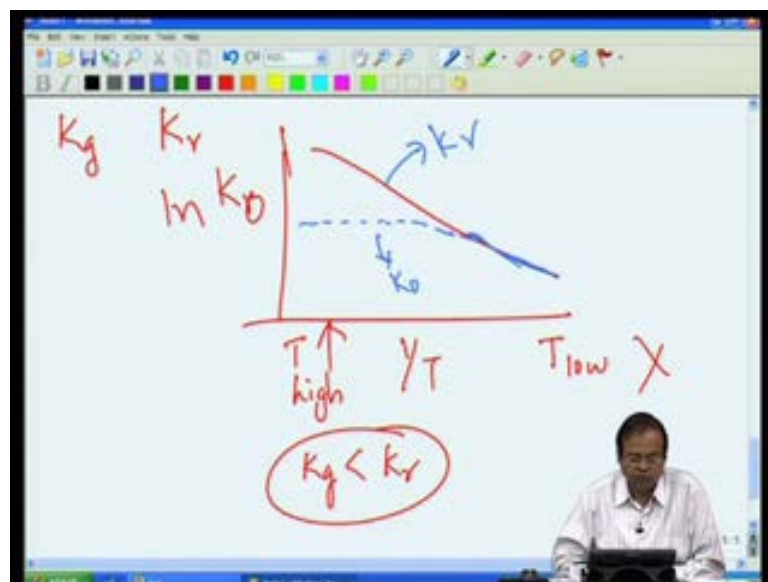
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We said that rate of reaction is  $K_r C_A^b$ . When I actually do the experiments, I will be measuring these rates. So, these are my measurement rates which we also called as observed rate. This is what I will actually measure. This is concentration in the bulk, which again is experimentally measured quantity. So, when I do experiments, I measure this rate  $r_A$  for this particular concentration  $C_A$ .

If I do some linear fit, I will get the rate constant which is actually the observed rate constant. Why it is observed rate constant because, if you recall, true reaction rate is  $K_r$  into  $C_A^b$ . So, this is true rate constant, but I will measure or I will observe  $K_{og}$ . Are these two same? They are if mass transfer resistance is very small. So, if  $K_{og}$  is very much similar to  $K_r$ , that is when mass transfer resistance is negligible, then, we are measuring the true kinetic rate constant, but if mass transfer resistance is very high where  $K_{og}$  is almost equal to  $K_g$ , the mass transfer rate, what we will be observing is the mass transfer coefficient rather than the kinetic rate constant. So, this also implies the following.

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So, we are looking at the relative value of  $K_g$  and  $K_r$ . For example, when it comes to temperature effect, you will recall that  $K_r$  varies as  $1/T$  in a linear manner if you are plotting  $\ln K_r$ , let us say because Arrhenius rate relationship.

Now, this is temperature low. This is temperature high. Now, what happens when we increase the temperature from low value to high value? The  $K_r$  value or the kinetic rate constant increases; that means, the probability that  $K_g$  will be less than  $K_r$  is much higher towards this end rather than this particular end or in other words, if this is what happens, then, what reaction rate we will measure? So, if you are now saying that we are looking at observed rate constant, then, what will happen at low temperatures? It is likely that  $K_g$  is higher than  $K_r$ . So, I will measure the same **reaction** rate, but as I am increasing the temperature, the mass transfer will start becoming limiting and reaction rate measured will deviate from the true constant. So, this is my  $K_r$ . This is my  $K_{naught}$ . Mass transfer coefficients are typically very weak functions of temperature unlike reaction rate constant which is an exponential function.

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The image shows a whiteboard with handwritten equations. On the left, there is a diagram of a boundary layer of thickness  $\delta$  with a mass transfer coefficient  $K_g = \frac{D_{AB}}{\delta}$ . The main equations are:

$$Re = \frac{d_p G}{\mu}$$

$$Sh = \frac{K_g d_p}{D_{AB}}$$

$$Sc = \frac{\mu}{\rho D_{AB}}$$

$$j = \frac{K_g \rho}{G} \left( \frac{\mu}{\rho D_{AB}} \right)^{1/3} = f(Re)$$

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$$

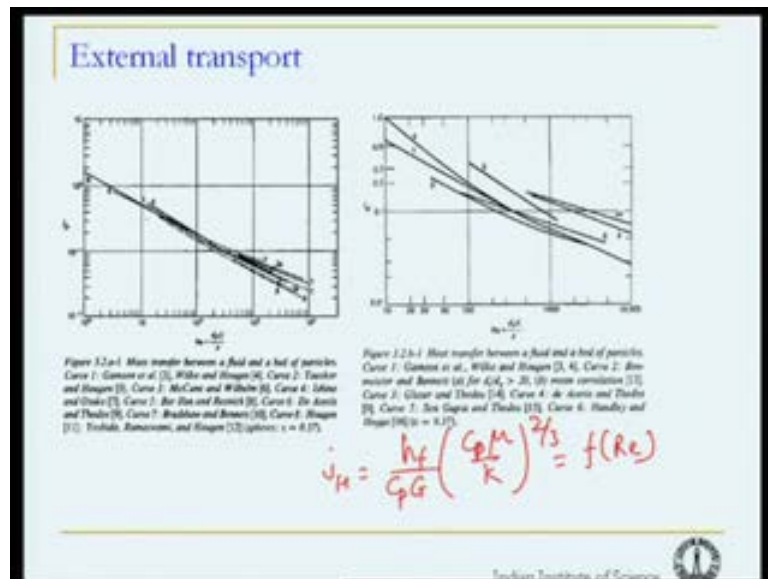
Now, how do we get this mass transfer coefficient? Recall that we said that, this is a surface, this is boundary, thickness delta. So, we can find the mass transfer coefficient, that is, if you actually write the diffusion equation, we can show that it is nothing but diffusion coefficient of A in the mixture A B divided by the thickness of the boundary layer.

Mass transfer coefficient is something which is not a property like density or mass which you can actually measure. It is there. This is a concept. So, we have to estimate it. How

do we estimate this, we typically use various kinds of correlations. For example, Reynolds number particle diameter superficial gas velocity viscosity Sherwood number  $K_g d_p$  by  $D_A B$ .  $d_p$  is the diameter of the particle.  $K_g$  is the **uh** mass transfer coefficient.  $D_A B$  is the diffusivity and the Schmidt number  $\mu$  by  $\rho_e f$  into  $D_A B$  viscosity divided by the density of the fluid  $D_A B$ . So, for example, Frossling correlation is Sherwood number is 2 plus 0.6 Reynolds number raised to 1 half Sherwood number raised to 1 third.

If the gas flow is very low; that means, almost a stationary flow. Reynolds number will go to 0. So, Sherwood number equal to 2, that is correlation you might have **already** seen or we use the correlation such as  $j_d$  factor which is  $K_g \rho_e f$  by  $G$  into  $\mu$  by  $\rho_e f$  into  $D_A B$  raised to 1 2 thirds and this  $j_d$  factor is a function of Reynolds number.

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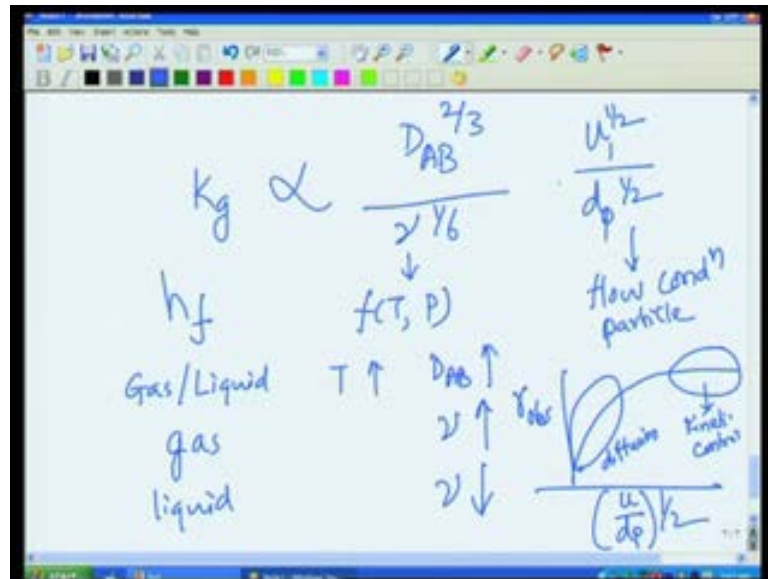


For example, what we see here is Reynolds number on the x axis and  $j_d$  factor on the right hand side over here and it is a fairly straight line correlation between  $j_d$  and Reynolds number and these are efforts by **different** **ah** researchers showing that the relationship is fairly a straight line.

When it comes to heat transfer, we could have the similar argument except  $j_h$  now,  $j_h$  for heat transfer is defined as  $h_c$  by  $C_p$  into  $G$  into  $C_p \mu$  by  $K$ . What is that? That is

Prandtl number raised to two third which is also a function of Reynolds number and you can see once again different relationships which different researchers have found between these two factors. So, what these correlations tell us is that mass transfer coefficient depends on various properties of the reacting mixture.

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For example, if we take all these Frossling correlation or even this  $j_d$  factor correlation, we find that the mass transfer coefficient is proportional to diffusivity raised to power two third and kinematic viscosity  $\nu$  raised to power one sixth multiplied by  $u$  that is the velocity raised to power half by  $d_p$  raised to power half.

Now, mass transfer coefficient  $K_g$  kinematic viscosity  $\mu$  by  $\rho$ . So, this is a function of temperature and pressure whereas, these are the property of flow conditions, the velocity as well as the particle or particle size we have. For example, what happens for gases and liquids as we increase the temperature? As temperature increases,  $D_{AB}$  increases. So, the mass transfer coefficient will increase in the value.

However, what happens to kinematic viscosity for gases as we increase the temperature, kinematic viscosity also increases, whereas, for liquids as we increase the temperature, kinematic viscosity decreases. So, depending upon whether we are looking at gas-solid system or liquid-solid system, temperature will have different effect on mass transfer

coefficient, but whatever it is, **it is it is it is** it is weak compared to the effect of temperature on the reaction rate kinetics.

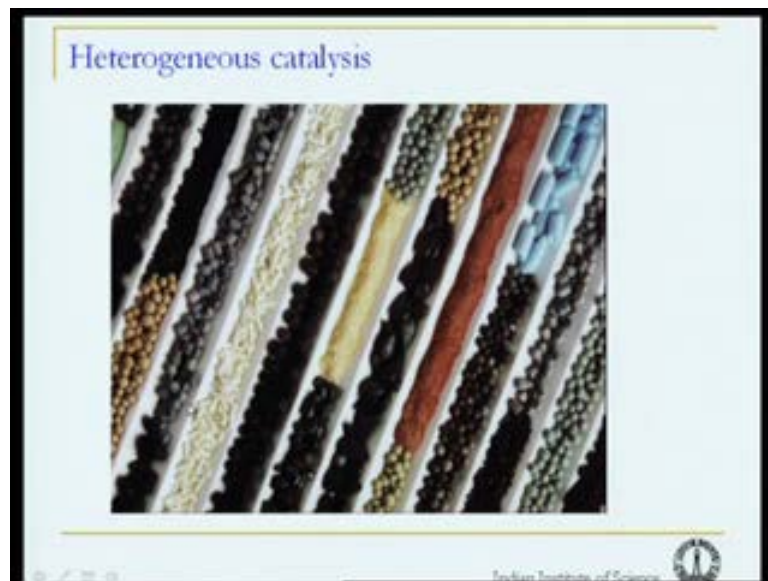
For example this  $u$  by  $d_p$ ,  $u$  is the velocity and  $d_p$  is the particle size. So, this clearly says that higher the velocity, higher is the value of mass transfer coefficient. Lower the size of the particle, higher is the mass transfer coefficient. In fact, we can put these results together and say that if you try to look at the observed rate against  $u$  by  $d_p$  raised to half, we typically see a behavior like this. **what** does this behavior mean?

Now, if our reaction is controlled by kinetics; that means, mass transfer is very fast. So, if mass transfer is very fast whether you increase  $u$  by  $d_p$  even more, the mass transfer rate is going to be even more, but that is not controlling. What is controlling is the reaction rate. So,  $u$  by  $d_p$  has no influence on the observed rate if reaction is kinetically controlled and not by mass transfer control. So, this is the region of our kinetic control.

Whereas, if  $u$  by  $d_p$  is very small, then  $K_g$  values are small; that means, mass transfer resistances are large. So, we are in a diffusion controlled region. So, this is **diffusion** control region. We can actually find out by doing experiments, same concentrations, same temperature pressures, everything is same except, we change the velocity or the diameter of the particle and then, if we get results something like this, we can identify the regimes under which reactions are kinetically controlled, that is the rate is independent of variation in  $u$  or  $d_p$ , then this is that region. If it is diffusion region, then, rate will increase as we increase  $u$  by  $d_p$  and then of course, there is a **transition** region. So, knowing  $K_g$  and when it comes to mass transfer  $K_g$ , heat transfer coefficient  $h_f$ , we can keep the same arguments for temperature as what we did for energy.

The only difference is instead of rate of reaction, we will now equate rate of heat generation to rate of heat energy generation because of **chemical** reaction.

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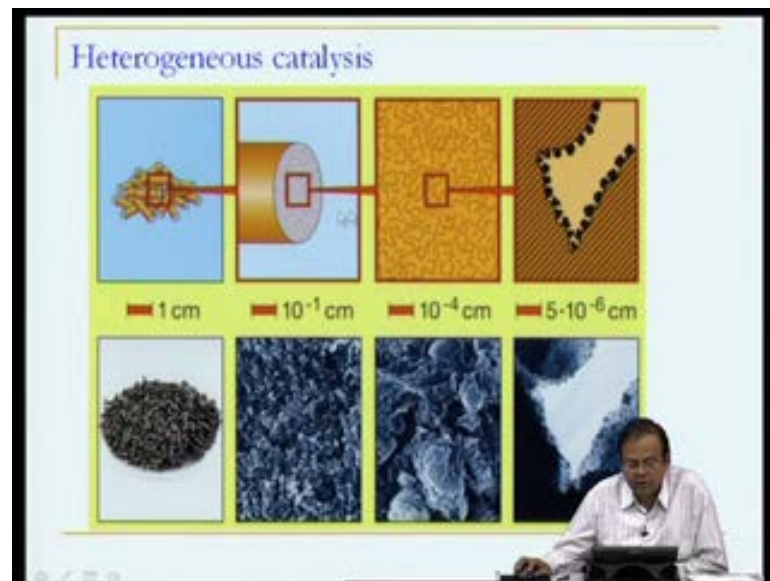
Now, let us start looking at what happens when we have these gas-solid reactions and let us take a closer look at the catalyst. What we discussed today so far is; what happens when we are looking at the external transport, but that is not the only thing that is happening. What we learnt from this discussion is that depending upon whether mass transfer rates is low compared to the reaction rate, the overall observed rate could be determined by the mass transfer rate. If the kinetic rate is smaller compared to the **mass** transfer rate, then the overall rate will be determined by the kinetic rate. We call that as kinetically controlled region.

Now, let us look at what happens when we have these gas-solid reactions, but, before we go there, this is just a slide showing the catalyst. This was given to me by professor Davidagar. So, I must **thank** him for this. Just showing, the catalyst does not come always in the same shape and size.

In fact, what we see here is that, this can be a hollow cylinder as seen over here or small cylinders, granular spherical tablets or cylinders with high  $l$  to  $d$  ratio or very fine powders. So, catalysts are of different types and not only of different sizes, they are of different colors also which you can clearly see over here. They come in all sizes, shapes and colors like green, blue, yellow, red. You name it and we have it.



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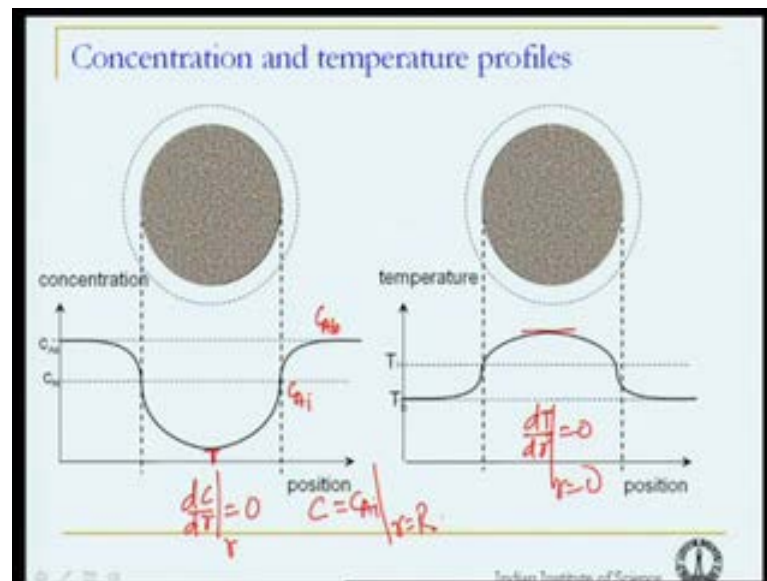


This is a cartoon illustration of what actually is happening. let us say that this is **cylindrical** catalyst. If you enlarge it, you see small pores on a micron level size, you will see the catalyst material deposited and these are in fact the real a c m photographs and micrograph of course, of the same material. This is a **cartoon** representation.

Our reactor is of the type of meters. So, this material is going to be sitting in a column which is of the length meter or so. So, when we talk about diffusion, we have to talk about diffusion at various different length scales from meso to micro, from meters and centimeters to millimeters to microns and may be these days, even to nano level.



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So, this figure over here illustrates what happens as a function of position to both the concentration and the temperature. Let us focus on concentration. What we said just now is that this is **catalyst** pellet which is porous. So, material has to diffuse inside. This is Bulk and this is boundary layer in which the entire resistance to mass transfer is located. So, what happens here is the concentration far away from the surface of the catalyst is the bulk concentration. It reduces to surface concentration  $C_{A i}$  because of resistance to the mass transfer outside the catalyst and then, the concentration decreases gradually as we move from the surface to the center of the catalyst and being symmetrical, the same thing can be seen from the other side as well.

So, what we have is actually the concentration decrease. Why is this concentration decreasing inside the catalyst pellet? Outside the catalyst pellet, the concentration decreases only due to mass transfer, but inside the catalyst pellet, the concentration decrease is not only because of mass transfer, but simultaneous chemical reaction because the reaction is taking place inside the catalytic pellet. So, we have to worry about reaction and diffusion taking place simultaneously.

Same thing can be said about temperature. Far away from the surface of this catalyst, the temperature is some bulk temperature  $T_b$ . Closer at the surface, temperature is  $T_i$ . We are assuming that this reaction as exothermic. So, temperature from the bulk is lower

than the temperature at the surface. Reaction is taking place inside. So, heat generation source is there inside. So, temperature is even further uh increased and then the symmetry from the other side. So, this cartoon which we will be using time and again to set up our mass balances or similar cartoons.

Once again, before we move forward the center of the catalyst pellet, this location over here, the surface of the catalyst pellet and the outer layer of the boundary, typically, we will say that catalyst, there is no preferred direction. The material can diffuse in and out from any direction. So, there is symmetry and whenever there is symmetry, you will see the slope of the line is 0 at the center point. So, if I call position as radius r and C as concentration, we can easily write  $dC/dr$  equal to 0 at the center point.

Concentration here is C A I, concentration here is C A b. Same thing can be written for temperature  $dT/dr$  is 0 at r equal to 0 and C is equal to C A i at r equal to capital R. If you are talking about a spherical catalyst, before we go to the actual reaction and diffusion simultaneously, let us look at the diffusion aspect.

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**Bulk/Molecular diffusion**

**Binary**

$$D_{12} = \frac{186 \cdot 10^{-9} T^{1.75} \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{0.75}}{P \sigma_{12}^2 \Omega} \quad [\text{gases: } 10^{-4}, \text{liquids: } 10^{-5} \text{ cm}^2/\text{s}]$$

$$N_1 = -D_{12} C_T \nabla y_1 + y_1 (N_1 + N_2)$$

*Handwritten notes:*  $D_{12} = D_{21} = D$   
 $D_{jm} = D$

**Multi-component**

$$N_j = -D_{jm} C_T \nabla y_j + y_j \sum_{k=1}^N N_k$$

$$D_{jm} = \frac{\sum_{k=1}^N \frac{1}{D_{jk}} \left( y_k - y_j \frac{N_k}{N_j} \right)}{1 - y_j \sum_{k=1}^N N_k / N_j}$$

Now, in case of Binary diffusion, the diffusion between a and b is given by correlations such as what we see over here. Correlations such as D 1 2 for example, which involves

temperature, which involves these fuller Giddings correlations and there are similar correlations for other researchers also, but by enlarge, they are more or same.

So, diffusion coefficient  $D_{12}$  depends on temperature, it depends on temperature molecular weight of two species and distance between the two species or their molecular diameter and so on. For example, for gases, the diffusion coefficients order of ten raised to minus 1 centimeter square per second. For liquids, diffusion coefficients are much slower about ten raised to minus five centimeter square per second and we all know that diffusion is a result of the total mass transfer is both because of diffusion which we write using Fick's law diffusion coefficient times the concentration gradient and due to bulk motion of the species. So,  $y_1 v_1 + N_1$  plus  $N_2$ , this is flux. So, what it says is that the diffusion is a result of interaction or the moment of these two molecules as well as the moment of the entire flux.

Now, when it comes to Multi component in a reacting species, you will have Multi component system and for Multi component system, these Stefan Maxwell equations are available, but those are not very convenient to work with. So, what we have is effective diffusion coefficient  $D_{jm}$  which is  $N_j$ . So, equivalent to Binary system, we have Multi component diffusion again  $D_{jm}$  where  $D_{jm}$  is actually not true binary coefficient because here, when you have more than one component a b c let us say or 1 2 3, we have diffusion coefficient Binary between 1 and 2, 1 and 3, 2 and 3 and so on.

All those things put together will determine what is called as effective diffusion coefficient. So, if you are looking at the  $j$  species, then the flux of the species  $N_j$  is given by the effective diffusion coefficient of  $j$  in the mixture and that is why we call it as  $D_{jm}$ . Of course, the Fick's diffusion Molecular diffusion equation concentration ingredient Multiplied by diffusion coefficient plus the flux due to the bulk motion of the fluid. What is this effective diffusion coefficient  $D_{jm}$  in the mixture? One can show that it is related to the composition of the mixture. So,  $y$  mole fraction and this formulas  $N_K$  by  $N_j$  and and and so on.

This equation may look little uh complicated at the moment, but let us consider few simplifications. For example, if I say that for all pairs  $D_{jK}$ , that is let us say  $D_{12}$   $D_{13}$   $D_{23}$  if you have ternary system, if all of them are equal, then as you would expect  $D_j$

m, let us say this is some value d will reduce to. So, if you put that all are D values are more or less equal. So, this comes out and D j m becomes simply. This should be 1 over D j m. So, that is one simplification. The other simplification that is possible is, let us say that we have a mixture where one of the components is dominant.

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**Bulk/Molecular diffusion**

**Binary**

$$D_{12} = \frac{186 \cdot 10^{-3} T^{1.75} \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{-0.75}}{P \sigma_{12}^2 \Omega} \quad [\text{gases: } 10^{-4}, \text{liquids: } 10^{-7} \text{ cm}^2/\text{s}]$$

$$N_1 = -D_{12} C_T \nabla y_1 + y_1 (N_1 + N_2)$$

*Handwritten notes:  $y_1 \gg y_2, y_3, \dots$ ,  $N_j \approx 0$*

**Multi-component**

$$N_j = -D_{jm} C_T \nabla y_j + y_j \sum_{k=1}^N N_k$$

$$D_{jm} = \frac{\sum_{k=1}^N \frac{1}{D_{jk}} \left( y_k - y_j \frac{N_k}{N_j} \right)}{1 - y_j \sum_{k=1}^N N_k / N_j}$$

*Handwritten notes:  $\perp$ ,  $D_{jm} = D_{j1}$*

Let us say that y 1 is far greater than y 2, y 3, y 4. All other components are present in the dilute quantity. Then if we therefore assume that N j flux of all other quantities is more or less similar, then, if we simplify these equations, we get D j m equivalent to D 1 or rather D j 1. That is, the mixture behaves as if it is a single component mixture. Another simplification possible; let us say that all the species are reacting with a certain stoichiometry.

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**Bulk/Molecular diffusion**

**Binary**

$$D_{12} = \frac{186 \cdot 10^{-3} T^{1.75} \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{-0.75}}{P \sigma_{12}^2 \Omega} \quad [\text{gases: } 10^{-5}, \text{liquids: } 10^{-7} \text{ cm}^2/\text{s}]$$

$$N_1 = -D_{12} C_T \nabla y_1 + y_1 (N_1 + N_2)$$

**Multi-component**

$$N_j = -D_{jm} C_T \nabla y_j + y_j \sum_{k=1}^N N_k$$

$$D_{jm} = \frac{\sum_{k \neq j} \frac{1}{D_{jk}} \left( y_k - y_j \frac{N_k}{N_j} \right)}{1 - y_j \sum_{k=1}^N N_k / N_j}$$

Handwritten notes:

$$\sum y_j A_j = 0$$

$$\frac{N_j}{N_i} = \frac{\nu_j}{\nu_i}$$

So, let us say that our reaction is  $\nu_j A_j = 0$ . Then, we know from our earlier discussion that the fluxes of two species  $N_j$  and  $N_i$  must be related by the stoichiometric coefficient. So, we can further further simplify **this** diffusion coefficient.

We will stop here. What we actually saw in this class is about diffusion, both external and we started little bit of diffusion coefficient discussion for inside the catalyst pellet. Now comes the real test, what actually happens when these gases try to diffuse inside the catalyst pore whose dimensions are of micron sizes. What happens to the diffusion phenomena? This is where we will start our next session. **Thank you.**