Heterogeneous Catalysis and Catalytic Processes

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Lecture - 22

Good morning, last lecture I was talking about the zeolite, catalyst preparation, application in the process industry. In this lecture, I will talk on catalyst reaction mechanism and basically the Langmuir adsorption based isotherm; which we have discussed earlier and their application or application of Langmuir adsorption isotherm for chemical adsorption or a catalytic reaction, chemical reaction.

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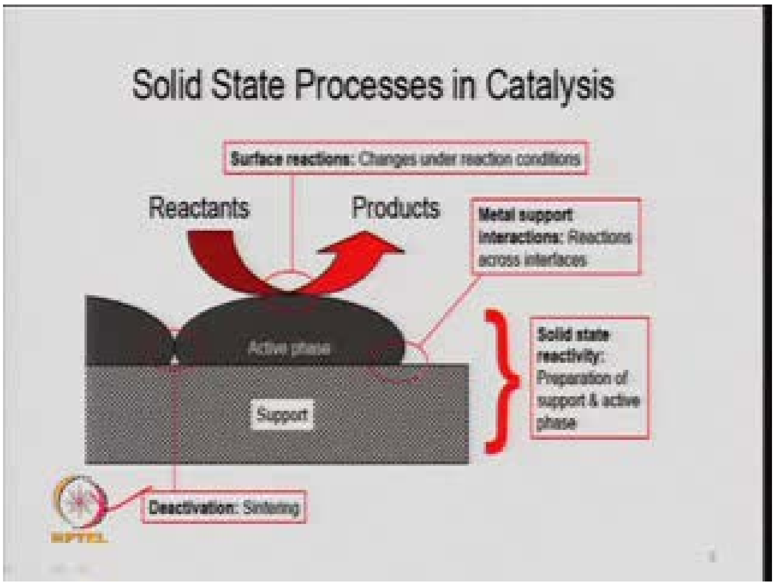

Solid State Processes in Catalysis

Surface reactions: Changes under reaction conditions

Metal support interactions: Reactions across interfaces

Solid state reactivity: Preparation of support & active phase

Deactivation: Sintering

So, we had discussed this slide before also; so, any reactant species that adsorbs on the active phase of the metal. So, during the catalyst preparation we have talked about this and we also said that dispersion of the metal is very important; so, how these metal during your calcination condition there may be a kind of sintering here and that may cause the deactivation of the catalyst. Then, this side it is the metal support interaction which just gives you the idea about the reaction across the interfaces. And, this may; that is the metal maybe just weakly adsorbed or strongly adsorbed so that is what the chemisorption of this metal and that can be studied from hydrogen chemisorption study. So, this is just a solid state reactivity and we just develop this kind of surface during the preparation of catalyst. So, reactant material comes to the surface adsorption some metal and then, transform into some product specie and then finally, the product desorbs. So, this is phenomenon is known as surface reaction; where the changes under reaction condition takes place.

So, these changes which have taken place during the reaction; that can be studied by understanding the mechanism of a reaction and that is what the catalytic reaction mechanism.

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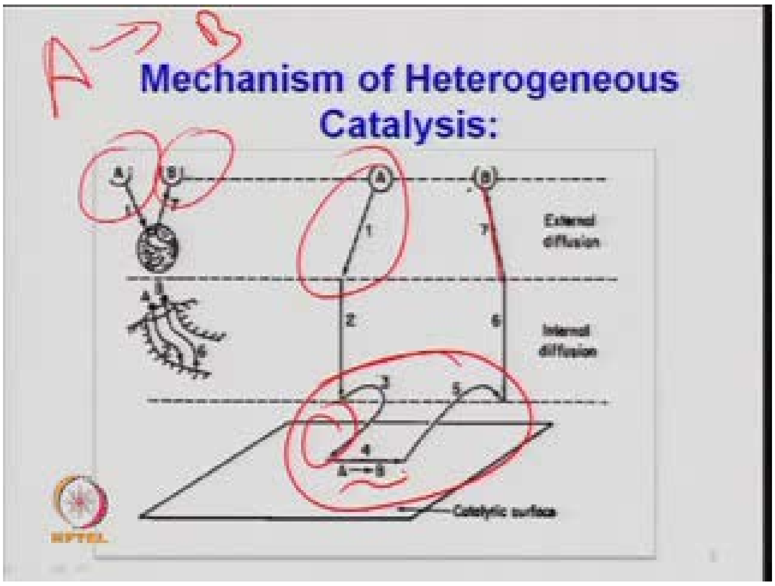

Mechanism of Heterogeneous Catalysis:

So, any gas A and B; suppose, there are two A goes to B is simple reactant which may; A may be a gas specie or vapor, it comes on to the surface of a solid, adsorbs there. So, now when I say adsorption; because the solid has a different kind of pore structure which I just show you like this.

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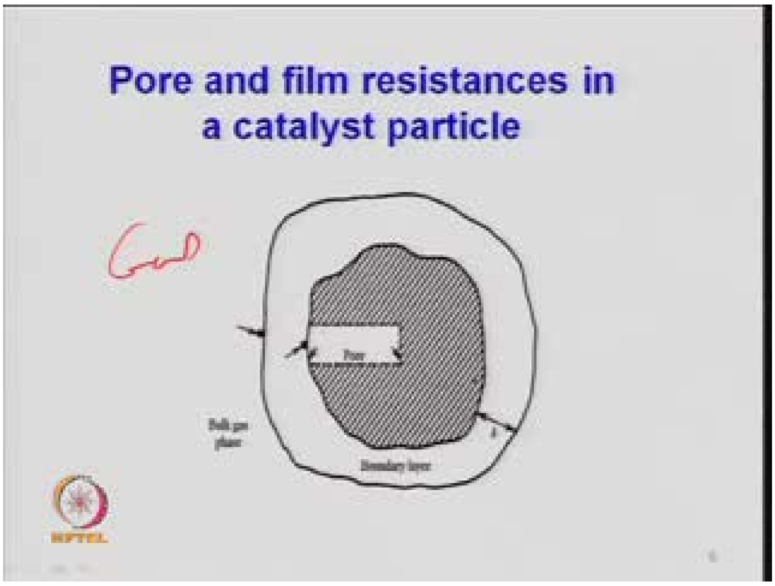

Pore and film resistances in a catalyst particle

So, the solid will have a pore like this. So, the; this is the gas phase here, something like a gas here and that goes to the surface; so, this is crossed barrier and comes to this pore mouth and then, diffuse inside. So, depending upon the pore geometry and pore size this will be; there will be kind of diffusion and then, it will adsorb on the surface; what I have shown here. So, I will come back to this but before discussing that point; as I discussed that the catalyst have, all the catalyst have the micro pores, macro pores and the mesho pore; if you are talking any porous catalyst. So, depending upon the porous structure of catalyst, this phenomenon will happen. So, some reactant species which has crossed the gas barrier or film of the gas; if I just show you the spherical pellet here and which has some kind of pore here.

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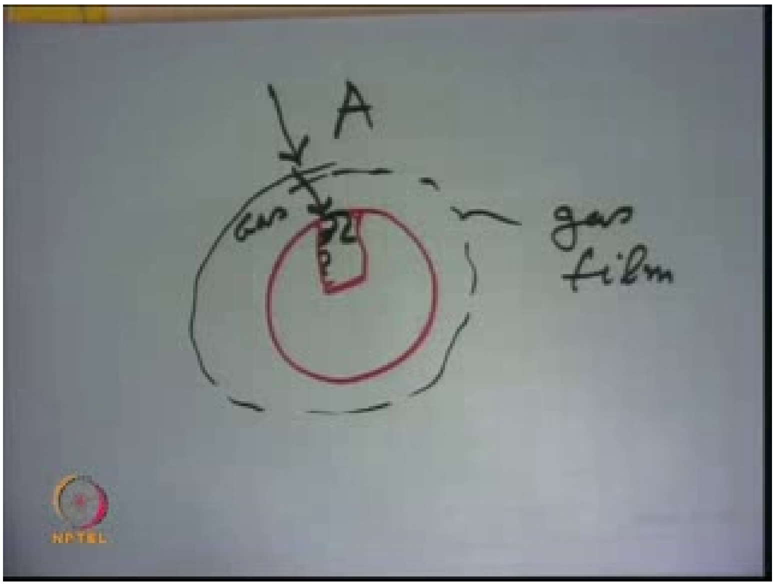

And then, there is a kind of film here, a gas film; this maybe a film of the gas that thickness will depend on your operating conditions and type of gas physicochemical property of the gas. And this, from the bulk; this gas which is in bulk comes to the surface of the solid which is surrounded by a film of the gas. So, this is a gas film; if it is a gas liquid reaction it can be another liquid film also. So, then, it has to cross this barrier and it comes to the surface of a solid and then, this gas has to diffuse inside; because your active metal is deposited here, inside these pores. So, in this pore the metal gas A will adsorb and then, it will transform into some product and that product will again go back.

So, there are the steps like the mass transfer then, diffusion and the chemical reaction and again then diffusion and mass transfer of the product species. So, these steps have been shown here, this is first one which is a mass transfer here; from bulk gas to the external surface of the solid. And, when this happens then, from external surface it comes to the pores of a solid, that is the kind of what you see here; the gas comes to the external surface and then, it is diffusing inside the pore and comes to the surface. So, this is, what the internal surface of a catalyst which is pore geometry; and that what I said it is a very high surface area. So, metal is dispersed there; so, here you have a kind of mechanism which needs to be demystified. So, this is external mass transfer; then, this is the internal mass transfer diffusion into the pore and then, this is adsorption on the surface of a metal. So, this is a kind of chemical adsorption, chemisorption; and because of chemisorptions, surface diffusion and several steps may take place here.

And then, this transform into a product D. So, and then, once the product forms then it has again; because of the concentration gradient it goes out of the pore. And, then; so, this is the from this it comes to out of the pore and then, it comes from this surface to the surface of the bulk gas that is main body of the gas. So, all these phenomenon will be involved or steps will be involved; when you have a catalytic reaction. So, each step will have its resistance; so, this step will have some resistance, this is step will have some resistance. And then, this is what we are talking the catalytic property; so, this is basically your crucial factor when you look at kinetics of a catalytic reaction. These two are the mass transfer steps and these can be controlled by selecting the pore geometry by selecting your operating condition like flow rate of the gas, particle size, reactive geometry. So, you can control this parameter. But here, when you look at kinetics; this is a function of temperature and definitely, the catalytic property that is material which has been selected.

So, if you look at these, what I have discussed the steps; so, first step is your bulk diffusion of reacting molecules to the surface of the catalyst. So, from the main body of the gas, it reached to the external surface of the solid; which has certain kind of thickness say delta. So, you know the mass transfer coefficient k g and you know the concentration in the main body, you know the concentration at the surface of the solid say C s. So, basically, the moles which are transporting it is simply mass transfer rate k g times C a G minus C s. So, one can very easily write the expression by understanding the mass transfer so k g times C a G minus C a S is the transport from the main body to the surface of the solid.

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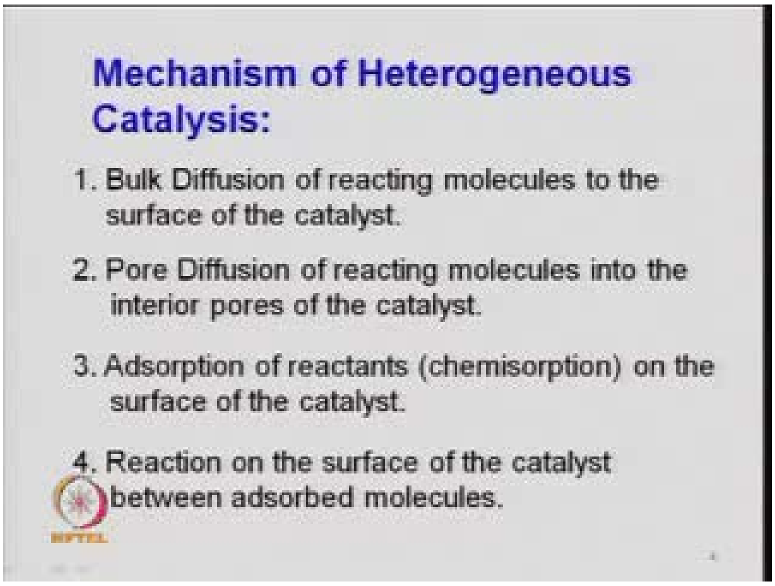

Mechanism of Heterogeneous Catalysis:

1. Bulk Diffusion of reacting molecules to the surface of the catalyst.
2. Pore Diffusion of reacting molecules into the interior pores of the catalyst.
3. Adsorption of reactants (chemisorption) on the surface of the catalyst.
4. Reaction on the surface of the catalyst between adsorbed molecules.

The second is the, pore diffusion of reacting molecule into the interior pore of the catalyst. So, this is now diffusion into the pore and that will be related to your again mass balance and based on fixed law of diffusion. So, you know that the flux J A is given based on minus d which is diffusion coefficient times d c by d x where x is the direction; if I just talk in terms of the pore.

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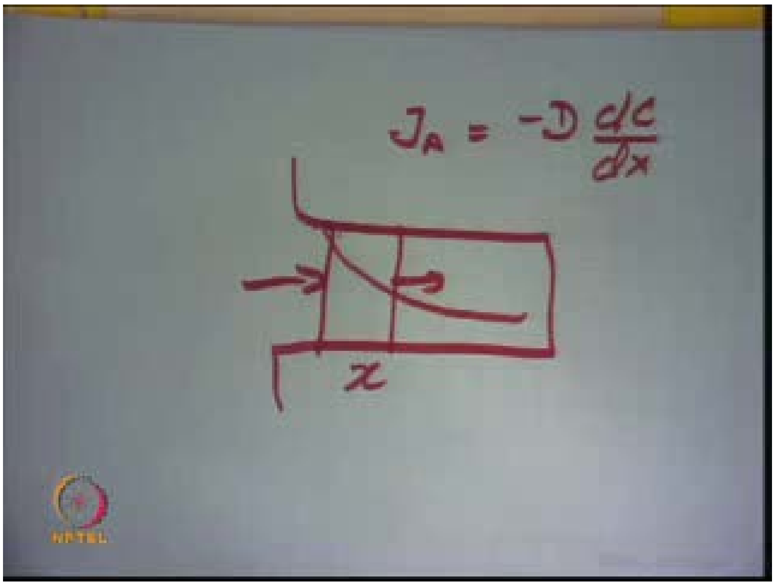

So, this can be calculated; we will talk on that later. But basically, we are talking this kind of phenomena diffusion into the pore. So, pi r squared times D d c by d x if I say diffusion in this direction axial diffusion kind of ((Refer Time: 08:16)); so, the simply your featured law diffusion where you say that, J A is equal to minus D d c by d x concentration gradient. So, you will have a kind of concentration profile in the pore depending upon the pore geometry or depending upon the resistance offered in the pore. And, that becomes a very crucial factor especially, when you have a micro porous, mesho porous materials and your molecules which are the reactant species have large kinetic diameters. So, that that becomes very crucial depending upon the size of the reactant species and the pore; the diffusion may be a phenomena in the pore of a catalyst. So, it will have some of its own resistance, which will affect your overall rate of a reaction of kinetics of the rate.

Once this happens, the molecule gas molecule has reached into the pore and now it is accessible to the active sites; say metals which I am saying platinum, nickel which is deposited or any P G M group metal. So, the adsorption will take place; so, reactant specie will adsorb and that is known as chemisorption, on the surface of the catalyst. So, basically this is a kinetic terminal ((Refer Time: 09:32)); adsorption because it will depend on the type of the metal; what you call depending upon that how many molecules have reacted, it will depend how many molecules have adsorbed on the surface a kind of micro kinetics reaction engineering. So, you are just looking in terms of the pressure of the gas that will decide the concentration of the active site. Because we have already discussed this phenomena that, rate of adsorption is proportional to the pressure of the gas partial pressure and the number of sites which are available for adsorption.

So, that is the crucial factor here and which has already been discussed the Langmuir adsorption and the b t isotherm physical adsorption. So, Langmuir is a kind of chemical adsorption here; so, we will discuss this phenomenon again in detail. And then, finally, when adsorption takes place then there will be a kind of chemical reaction; that is transformation of the reactant into a product species. So, reaction on the surface of the catalyst, between two adsorbed molecules. So, that is again important factor which transform the reactant into a some adsorbed product and that product may desorb from the surface here.

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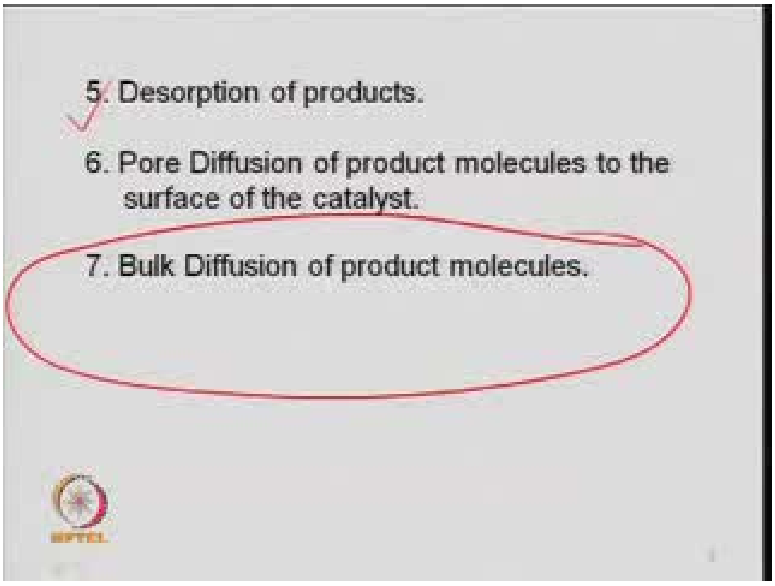

5. Desorption of products.
6. Pore Diffusion of product molecules to the surface of the catalyst.
7. Bulk Diffusion of product molecules.

So, the next step is that, it is a kind of adsorbed product; and, that has to be desorbed from the surface of the solid to make the catalytic site free. So, desorption of the product; and once, the product has formed and there will be a kind of concentration gradient; so, these will be the reverse of the steps which I had discussed in terms of diffusion and mass transfer. So, again, the product molecule will diffuse out of the pore of a catalyst and come to the surface of the solid. And, then, there is a gas film again so, it will go out of the product; from the surface of the solid to the main body of the gas. So, finally, you get a product at the outlet; so, from the catalyst surface something is; so, actually you have seen now that the catalyst take part in the reaction and it takes part or catalyst has some role in terms of the chemical reaction. So, the definition which says that catalyst does not take part is not right; so, actually the catalyst takes part in the reaction but at the end, it comes out as a free or specie.

So, this is what I was talking there is a kind of mass layer of the gas and so, depending upon the velocity you have the thickness. Because it is related to mass transfer coefficient; if you recall, your mass transfer study is proportional to some velocity to the power half; and also, inversely proportional to the diameter to the power half. That is very basic correlation between mass transfer and the size of the particle; so, larger particles means, the thickness will be more, larger size. So, you need some kind of particle size and same thing; larger gas velocity it means, your mass transfer coefficient will be high; so, the thickness will decrease. So, that is means, how to eliminate this external mass transfer resistance; you can control it during the experiment you can check how these mass transfer resistance is or diffusion mass transfer diffusion resistance it can be eliminated.

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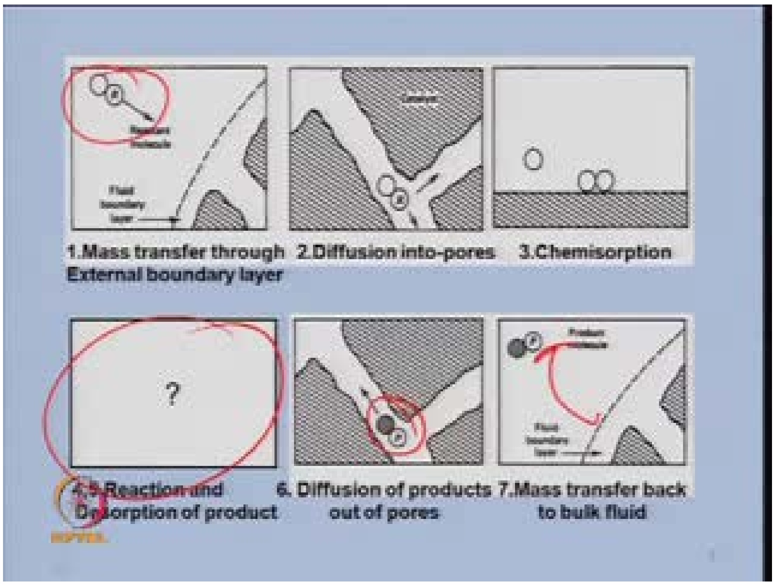

1.Mass transfer through External boundary layer

2.Diffusion into-pores

3.Chemisorption

4.5.Reaction and Desorption of product

6. Diffusion of products out of pores

7.Mass transfer back to bulk fluid

So, that the step which I have discussed that, this is your reactant molecule and that is a boundary of the gas film and, this is your catalyst which is a porous in nature. So, if the catalyst is non-porous it means, only there will be external mass transfer and then, the action of the surface. So, you will not have the internal diffusion into the pore for the non-porous type of solid. So, this is then, here the molecule comes and then, this is the adsorption of the reactant specie on the surface of the solid. So, this is the catalytic surface basically here, inside a pore and then, you need to demystify it that is; what kind of kinetics actually taking place because here is a kind of surface reaction A goes to product. So, how does this transform into a product, will depend on the active site of the catalyst, that is the role of catalyst or in depth the mechanism need to be learned in order to look at the catalytic reaction; especially, when you have multiple reactions. So, one need to demystify this point and then, once the product has formed; so, this is the step where you get a kind of product specie.

So, this product specie now will diffuse out; because of the concentration difference and finally, it will reach to the outer surface of the solid and from here, it will go out to the bulk gas.

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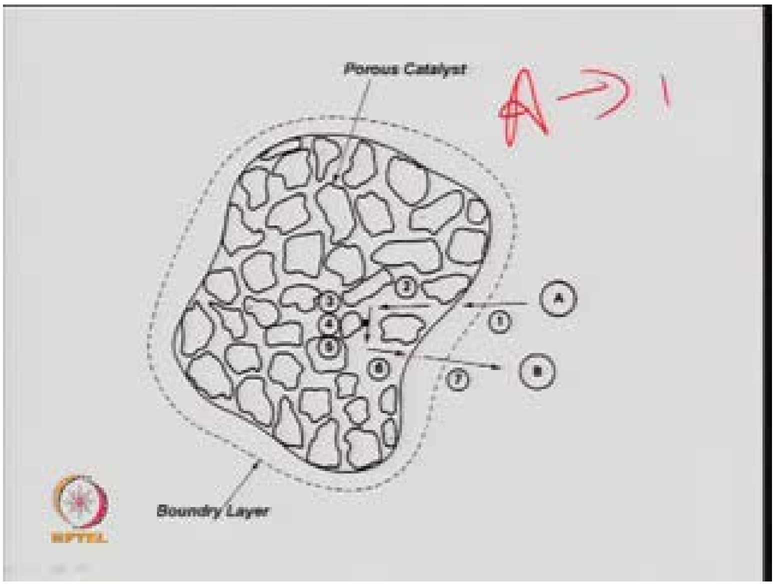

So, this is all the catalyst porous geometry they have already seen this part; so, these are the pores, that can be micro pore, macro pore, mesho pore all type of geometry may be that is structure porous structure may be available. And, this is what the diffusion which we have discussed bulk mass transfer then, diffusion pore or cavity and, then surface reaction, product formation, product diffuse out and out and finally, get the A goes to B. So, this is just a reaction that A converts into B.

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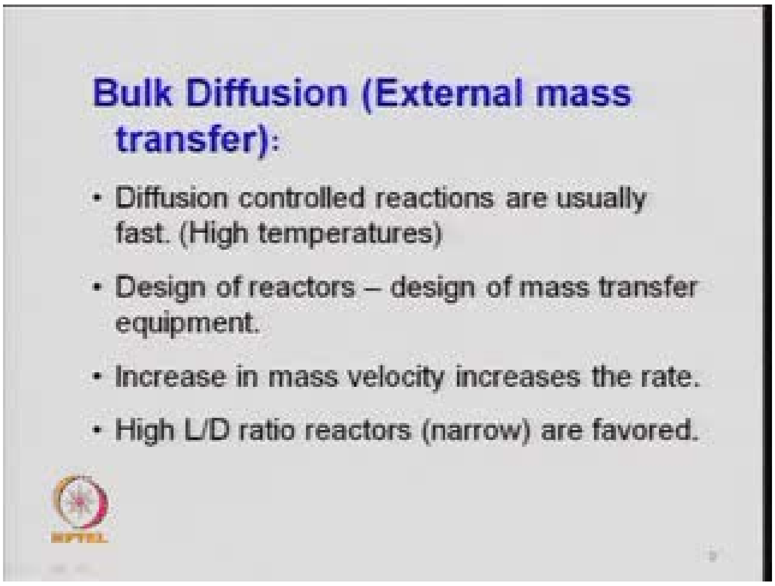

Bulk Diffusion (External mass transfer):

- Diffusion controlled reactions are usually fast. (High temperatures)
- Design of reactors – design of mass transfer equipment.
- Increase in mass velocity increases the rate.
- High L/D ratio reactors (narrow) are favored.

Now, as I said that, you have to control the step; because each step what is here the based on the diffusion, you have to calculate how many molecules have transported. So, basically, if I just look at some steady state all these rates should be equal because whatever the number of molecule; they because it is steady state, there is no change not change. So, whatever, the molecule which transferred from the main body; the same molecule will go inside by mass transfer, same molecule will diffuse inside and they will react chemically. Because there is no accumulation of the reactant specie in the pore, if you just talk steady state conditions. So, this is one where you can calculate because otherwise the concentration ((Refer Time: 15:32)); these are intermediate concentration what I was talking here.

So, it may be C aG here; so, main body in the gas concentration of A. And, when it reach to the surface it may be something like; so, C aG here and then, because it is main body so, same concentration uniform throughout. But when it reach here, it becomes C aS, concentration at the surface and when it diffuse inside; so, there will be a kind of concentration profile.

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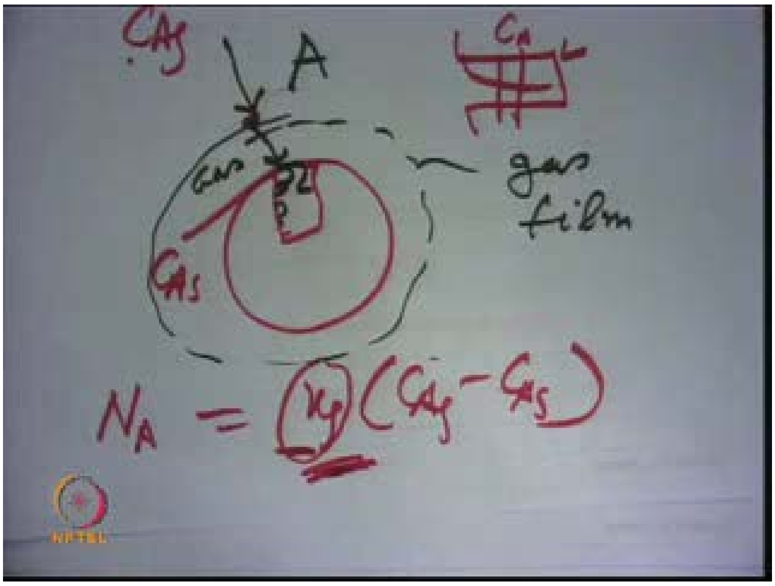

So, you have to find out at differential concentration at a given condition and based on that how many molecules reacted inside the pore and then intrigate. So, that will give you a kind of concentration profile in the pore but we have outside here like this. So, and then, at some react concentration average concentration just like in a differential reactor or intregal reactor you do; some average concentration and rate can be calculated minus R A is equal to say simple K C A; suppose, if I is a first order reaction. So, this is the C awhich is the surface concentration here, and that will change; so, you have to intrigate it from zero to length of the pore and then, you calculate the total number of molecules which have been reacted.

So, at a steady state, all the number of molecule which have been transported by mass transfer step; they are reacting chemically. So, one can very easily write the equation and eliminate these intermediate concentration and find out the overall rate in one way. So, overall rate basically, which will see later but overall rate will be a contribution of mass transfer resistance diffusion resistance and the kinetic resistance. So, the resistance is something like the delay in the process, delay in the reaction activity. So, it is something like the step which offers the highest obstacles in the path of the chemical reaction and one has to minimize that or eliminate that. So, we need to understand, the physical properties of the gases, we need to understand the catalytic behavior or catalytic property and then, look at how to control these steps.

So, this is the first step for external mass transfer control. So, as I said that mass transfer simply is given by any if I write moles transported which k g times C aG minus C aS something like that. Where C aG is the concentration in the main body and C aS is the concentration at the external surface of the solid and this k g is the mass transfer, mass transfer coefficient rather. So, the how many moles have been transported will depend on this or this C aG minus C aS; suppose, if I say there is no film of the gas, no mass transfer resistance; so, it means C aG will approach to C aS. So, that there is no gradient or the no concentration difference. So, that time; this concentration, this concentration will be same. So, it means you are eliminated that mass transfer resistor; in one way you are saying that the k g value will be very very high. The same thing when diffusion takes place you are writing a second law of diffusion something like say, pore if I am writing so D d C aby d x that is minus D d C aby d x at x.

And, same thing will be expressed delta x; so, input minus output minus dispersion because of chemical reaction is equal to accumulation your steady state mass balance equation if you write the accumulation term is zero. So, the basically a mass balance equation you are writing; where you are saying the; at differential section what we discussed here that for any differential section you have a differential section here x and x plus delta x.

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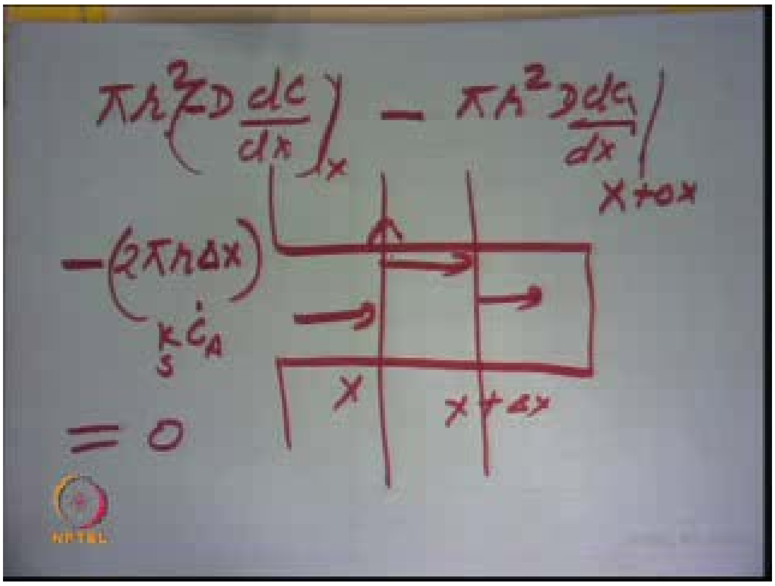

$$\pi r^2 \left(-D \frac{dc}{dx}\right)\Big|_x - \pi r^2 D \frac{dc}{dx}\Big|_{x+\Delta x} - (2\pi r \Delta x)\left(k_s C_A\right) = 0$$

So, one can very easily write down a mass balance equation for these two zones. So, simply say if I say here f a z which is only because of diffusion now which may be a contribution of convection and diffusion but in the pore we are assuming that the; it is mainly because of the diffusion phenomena. So, this will be simply here pi r square if I write area cross section r is the radius of the pore so pi r square and times D times d c by d x so this is the flux which we are written like this D d c by d x multiplied by area of that geometry normal area. So, pi r square D d c by d x with minus sign because this is because of the concentration gradient that the; it will move from higher concentration to lower concentration. So, this is at x and same thing will be at x plus delta x. So pi r square D d c by d x and this will be violated at x plus delta x. So, input minus output; now, there will be a kind of chemical reaction if you are saying a catalytic reaction; so, minus disappearance because of chemical reaction if I write a disappearance.

So, chemical reaction just if I assume minus r a is the chemical reaction rate for disappearance; so, and if I define it based on surface area then, this will be simply 2 pi r L area of that pore. So, this is the area of this geometry; because it is on the surface, it is a surface reaction basically. So, this is the surface area so, 2 pi r L which is the area of that. So, instead of L I will write it delta x here; because x and x plus delta x. So, that is the distance.

So, this is your surface multiplied by; suppose, if I write a first order reaction I will write k C aor just you write minus r a. So, this is now input, minus output, minus disappearance because of chemical reaction term; which is surface because k’s this is based on surface reaction constant. So, this will have a surface reaction rate constant; that is rate of reaction based on per unit surface area of the catalyst. So, there may be various stage of defining this rate; so, based on per unit mass of the catalyst per unit volume of the catalyst, got this. So, this is input, minus output, minus this term because of chemical reaction and when you write the steady state this is zero; because accumulation is zero. So, very easily you can have a expression in terms of the diffusion reaction and reaction in a pore of a catalyst.

So, this is simply pi r square is constant term so this will get cancelled; so, you have simply minus D d c by d x minus same thing at x plus delta x; minus simply here it will become 2 k s upon r C ais equal to zero. And, you know that limit delta x tends to zero; so, this will become D d c by d x minus same at x minus same thing at x plus delta x; so, that will give you the D d 2 c by d x square. So, you can have a very simple expression in terms of the differential equation; which can be solved for concentration profile. So, this is what; so, one can get the idea, because the diffusion resistance will depend on this D value, coefficient. Because its say, now, there is no diffusion resistance suppose the pores are very large; so, it means the concentration gradient inside the pore will be negligible. Then, it means, throughout the surface you have a same concentration. So, this is what so you need to understand whether mass transfer controlling or diffusion is dominating; diffusion resistance I mean, that is dominating or the kinetics is dominating. So, mass transfer controlled reactions, generally, when the temperature is high because k is equal to k zero into the power minus e by r t that is the Arrhenius rate.

So, at high temperature the kinetics will not control the rate of reaction. So, it means, if the reaction temperature is very high; so, your kinetics will be very high rate of reaction will be very high. Then, the remaining two may be controlled; the mass transfer or the diffusion may be the rate controlled. So, in that case your; this may be the important parameter one of that that k g value which I am talking mass transfer coefficient. So, you need to look at it then the design is just like a mass transfer equipment design. So, there is just like in the metal plate; when, nothing is diffusing just non-porous material. So, diffusion is not there and if you are saying temperature is also high kinetics will not controlled then the; this, mass transfer will be controlled in that case. So, just like in your automotive exhaust catalyst which were wire gauge type of catalyst platinum wire gauge; so, that has been just inserted. Now, quadrate structures are used, which are non-porous kind of materials and on that the platinum can be coated.

So, platinum, rhodium which are; which can be used for knox ((Refer Time: 24:31)) socks the carbon dioxide, nitrogen oxides, sulfur oxides these can be removed. Selective oxidation reduction process or three way catalyst nowadays have been used in a honeycomb structure; a monolith type of structure. So, in that case the mass transfer may be controlling; because the reaction temperature is high and the mass transfer controls reaction. So, that time, the velocity becomes important; because the hydrocarbon burned hydrocarbon that is unbind hydrocarbon and the gases which comes from the exhaust of the engine that will pass through the catalytic band. So, that time the mass transfer is the; may be a rate controlling step and then, you write your simply when the rate controlling step is mass transfer then, simply it k G times k G minus C S. So, one can find out what should be the length of that convertor required; monolith convertor required because that delta x, now, which I am talking that is nothing but the length of that reactor; in case of mono lengths. When you have the mass transfer, step not the diffusion.

So, then, it is a mass transfer control reaction; so, just like suppose you have a starrer and you fill that mass transfer rate control you increase the r p m. Because the higher r p m; there will not be any layer of the liquid which is surrounded by which may be surrounding the solid. So, these are the some basic principles of mass transfer by which you can minimize the mass transfer resistance or you can enhance the mass transfer resistance.

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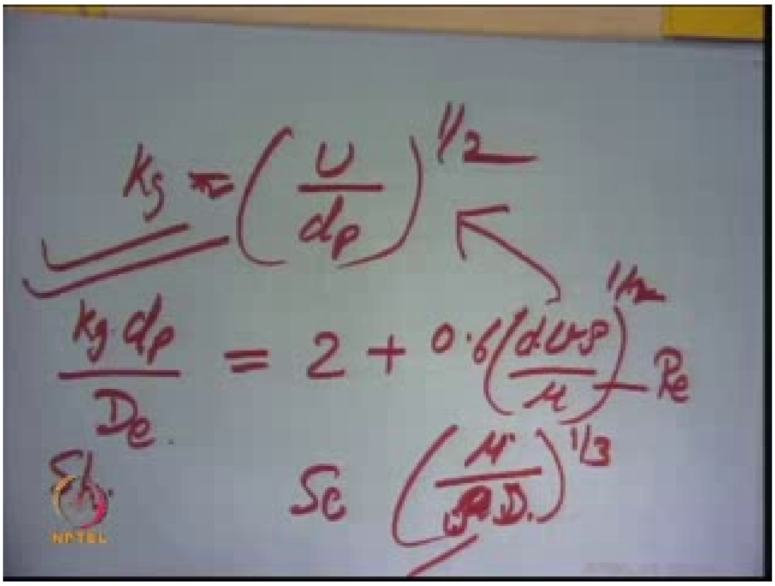

$$k_g \propto \left(\frac{U}{d_p}\right)^{1/2}$$

$$\frac{k_g d_p}{D_e} = 2 + 0.6\left(\frac{d v \rho}{\mu}\right)^{1/2} \; Re$$

Sh

$$Sc \; \left(\frac{\mu}{\rho D}\right)^{1/3}$$

So, in one way as I said that k G is roughly proportional to U by d p to the power half. Actually, a mass transfer coefficient depends on several factors; so, there is one relationship where the k g d p over D e you know that share wood number for mass transfer. And, that is given by 2 plus 0.6 times reynold number; so, reynold number so d v rho upon mu to the power half and sieve number which is defined by mu by rho d this is mu by rho D to the power 1 by 3. So, this is your share wood number, you know that; this is your reynold number d v rho upon mu; so, this is known as reynold number and this is known as mu upon rho D; rho is the density and D is the diffusion coefficient and mu is the viscosity of the gas. So, this is known as schmidt number; so, if this reynold number is low, at a very low reynold number this reynold number to the power half. So, you can neglect the second term and that time this is just like a constant k g d p upon D e is a 2 value. So, but on the other case, when your reynold number value is high, then, this k g d p by is simply proportional to this reynold number to the power half.

And, from there we have just gotten this, at high reynold number. Because generally, you use the high gas velocity and this is just like an a stokes region; so, that time k g is inversely proportional to the diameter; that is just like an a stoke region where the reynold of a particle reynold number is less than 0.1. So, these; so, generally this method can be used here, because we have a feed by reactor type and we pass the gas at high linear velocity. So, you can see here, that your mass transfer coefficient is increasing, if your velocity is high or your particles should be smaller in size. So, one can look at the combination or if the particles size is fixed; then, the just measure the superficial gas flow step of across the bed and report the value. So, these informations can be used with a mass transfer is dominating during the reaction or not. So, in this case if the mass transfer controls the rate then, your reactor is just like a mass transfer equipment design.

So, increasing the mass velocity; increase the rate. Otherwise, you say mass velocity superficial gas velocity across the bed; so, that can be factor which can check or which can let you know whether mass transfer is controlling or not or you can illuminate the mass transfer resistance during the experiment. High l by d ratio generally, a narrow type reactors are favored here; so, that is another important aspect of the design. So, especially, when you have the slurry type reactors or when you look at C st r type reactors you just try to maintain the diameters accordingly. So, here, in this case the L by D ratio that is; high is desired, height should be higher compared to the diameter of that reactor; especially, when the mass transfer controlled reactions. So, generally, to get the pluck flow condition to neglect the axial dispersion in the reactor.

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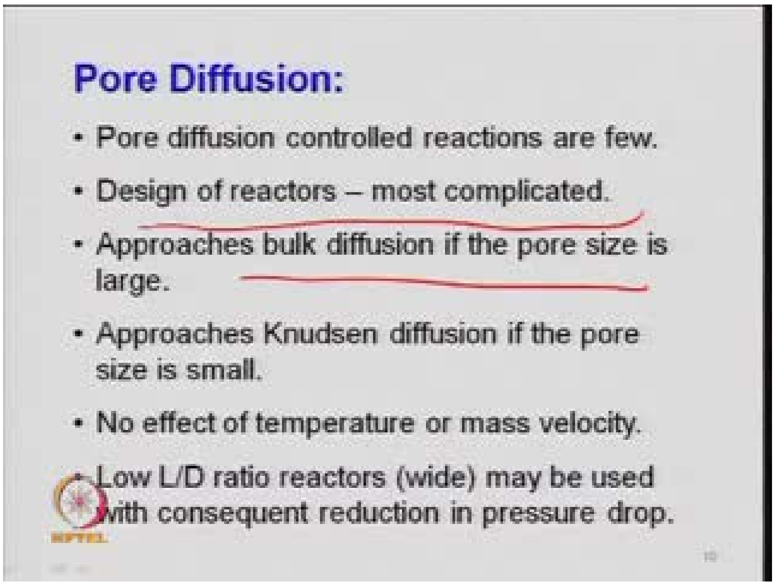

Pore Diffusion:

- Pore diffusion controlled reactions are few.
- Design of reactors – most complicated.
- Approaches bulk diffusion if the pore size is large.
- Approaches Knudsen diffusion if the pore size is small.
- No effect of temperature or mass velocity.
- Low L/D ratio reactors (wide) may be used with consequent reduction in pressure drop.

The second is the pore diffusion what I said; so, pore diffusion controlled reactions are very limited. Actually, the diffusion if you look at the bulk diffusion and knudsen diffusion; what I discussed earlier lecture and a the knudsen diffusion is generally, that that happens in the small pore. And, bulk diffusion when we say takes relatively in a larger pore. So, they actually these two depends on the mean free path of the gas molecules. So, that is one thing; and so, here in this case the reactor design which comes very very complicated; when the diffusion is the rate controlled reaction actually it will depend the porous structure of the catalyst; so, micro porous, mesho porous material. So, most of the time we select our experimental conditions of select our design conditions such a way that it should be in the kinetic controlled region. Because there, you have the option to get the selective products or selective region issue; so, the bulk diffusion depends on the pore size, as I said in the larger pores you will have the bulk diffusion where as knudsen diffusion will take place in the a small pore.

So, here the if you look at; when the main pre path of the molecule, main pre path molecule is greater. So, main pre path of the molecule; when I am saying, the molecules are colliding inside the pore and they are colliding with the wall also. So, if, the pores are narrow, the molecule will have the probability to collide with the wall; more they will collide with the wall in the small channel. So, that time in the small channel you will have a knudsen diffusion; so, because the molecules are colliding with the wall. And, in the case of bulk; the pores are wider so, molecules collide among themselves rather colliding with the mole. So, that will happen in a larger pore; so, that is the definition of bulk diffusion and knudsen diffusion. So, knudsen diffusion can be calculated because it is proportional to t is temperature to the power half and the; if you calculate the bulk diffusion, knudsen diffusion; the empirical correlation for bulk diffusion are available chapman-irskoff formula. So, lot of empirical formulas are available to calculate these bulk diffusion terms.

Same thing for knudsen diffusion which is proportional to square root of temperature and divide by the molecular weight. So, one can calculate the knudsen diffusion also; so, bulk diffusion, knudsen diffusion these two can be calculated and then, we define the average diffusion coefficient. So, that I will just talk little later. So, effect of temperature or mass velocity is negligible in this case. Because diffusion has less effect on the; compared to the kinetic term rate constant or the mass transfer coefficient terms. The effect of mass velocity is negligible in the case of diffusion controlled reaction and low L by D ratio means, wider reactors; when the reaction is diffusion controlled then wider reaction reactors are preferred like just as I said H by D ratio where the height to diameter ratio may be kept larger. So, it is a wider basically, in one way may be used with the consequent reaction, reduction in the pressure drop. Because that is again an important issue, the; when the particles you have, your particles are smaller in size then again, the pressure drop inside the reactor.

So, one has to look at the effect of particle size, linear velocity across the bed and while selecting the reactor I D and the length of the reactor. Pressure drop calculations are equally important when you fix the catalyst inside a reactor; especially, for the commercialized application. So, rate determining step; that is very crucial rather the mass transfer control that is one thing diffusion control; so, these two are other different aspects of the kinetics.

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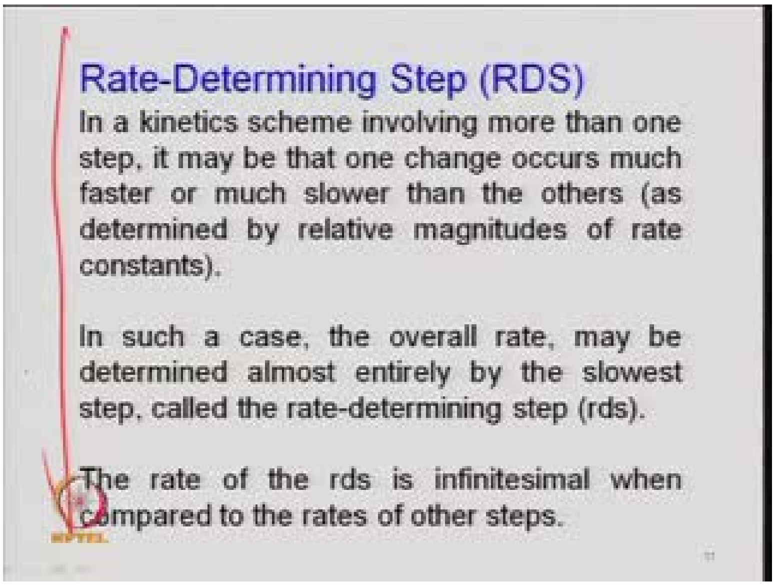

Rate-Determining Step (RDS)

In a kinetics scheme involving more than one step, it may be that one change occurs much faster or much slower than the others (as determined by relative magnitudes of rate constants).

In such a case, the overall rate, may be determined almost entirely by the slowest step, called the rate-determining step (rds).

The rate of the rds is infinitesimal when compared to the rates of other steps.

So, that I will cover later, but right now I am talking on this step when the diffusion has taken place and the molecules adsorb on the surface of a catalyst. And then, there is a adsorption, surface reaction and diffusion.

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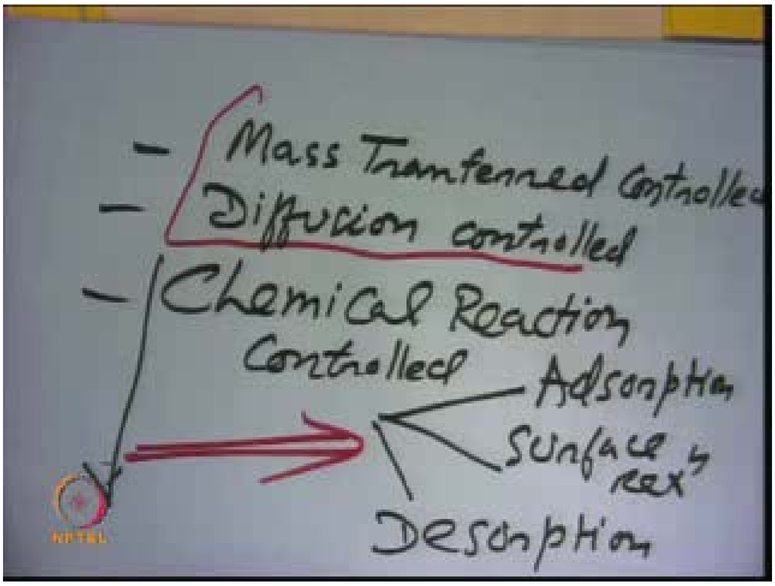

So, I am talking among these 3 steps; when this is chemical reaction control, so, the overall what you have seen now; that a reaction can be mass transferred, controlled diffusion controlled and third is, chemical reaction controlled. So, I am talking now, in chemical reaction controlled step also again there may be adsorption, surface reaction and desorption. So, these we are now we are discussing this part; that the mass transfer diffusion this is depending on the pellet geometry, your flow conditions which will be consider discuss in little later. So, now, I am talking this catalytic reaction part which is depending on the active site present in the catalyst.

So, here again, you have the adsorption controlled surface reaction may be controlling or desorption may be controlling. And, this is what the reaction mechanism the understanding the mechanism of a catalytic reaction because this decides what product will form. So, that is important for the catalytic from the catalytic view point. So, the kinetic schemes involving more than one step, it may be that one change occurs much faster or much slower than the other. So, rate determining step when you say that is the slowest step of the reaction. As I discussed, that when I say rate determining step so that will the slowest step of the reaction. So, that is what r d s infinite symbol when compared to rates of the other steps. So, other steps will be relatively very fast compared to this step. So, in general what I am saying suppose the time taken basically, we are just comparing it with respect to that time taken in a step.

So, suppose the reaction is taking place mass transfer takes 1 second diffusion takes 1 second chemical reaction step takes 10,000 seconds. So, it means, that step is more crucial; because it takes highest time during the reaction so, one has to control that factor while designing the commercial reactor. Because if, that time can be reduced your activity will be faster; so, same thing just like a the resistance you see in the wire resistance is R 1, R 2, R 3 connected in a series so, this becomes R 1 plus, R 2 plus, R 3. Similar thing is happening here, in the catalytic reaction that; if these all 3 resistances are added, then your rate will become slower. Because your current which you calculated is nothing but v voltage divide by the resistance. So, same thing here, the rate which we are correlating is depending on these; what about the resistance which takes this? So, that that a kinetic term which we are talking and then, the different adsorption which takes place. So, they may create a kind of resistance during the reaction, we have to look at; so, that is what we need to discuss.

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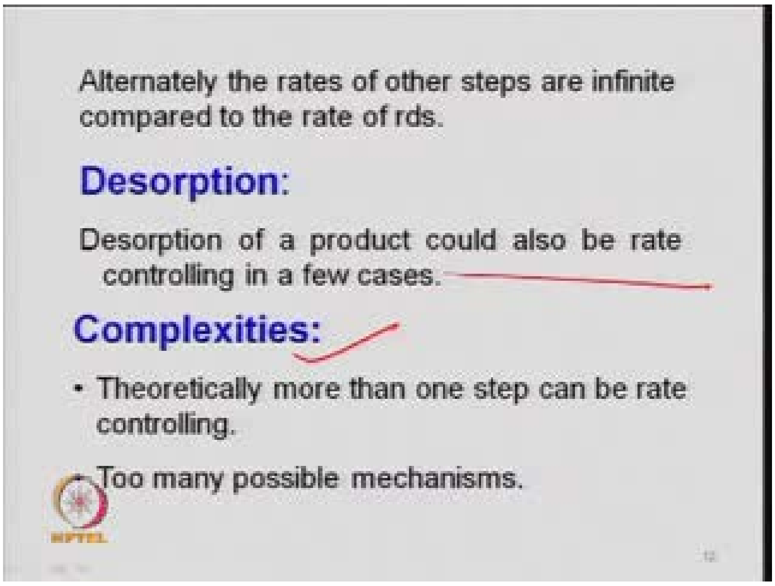

Alternately the rates of other steps are infinite compared to the rate of rds.

Desorption:

Desorption of a product could also be rate controlling in a few cases.

Complexities:

- Theoretically more than one step can be rate controlling.
- Too many possible mechanisms.

So, as I said the desorption; the product may be rate controlling. So, here the adsorption, desorption for the reactant we are talking and similar step may happen for the product specie also. The product may be desorbing it may be a rate controlling and same thing. So, the product which comes out from that after desorption again the mass transfer tool mass transfer diffusion of the product specie from the pore to the external surface.and from external surface to the bulk gas. So, these steps has similar to what the first two steps we have discussed that is mass transfer of the reactant and the diffusion of the reactant. So, these are reverse of these; the 6th and 7th step of that are the reverse of step 1 and 2. So, similar steps; so, the same rate expression will be written for the product specie in that case. So, the complexity is always there; because theoretically more than one step; can be rate controlling that may be another just as I said 1 second versus 1000 thousand second, but it may happen that 500 second versus 600 second.

So, one step takes 500 second another 600 so these are equally compatible. So, one need to control; needs to control the both steps simultaneously, so that becomes the complex type of rate expression or mechanism which need to be so looked into. So, there may be too many possible mechanisms, if you look at a combination of these permutations and combination. So, there can be several combinations and in terms of their reaction mechanism. So, that is that is what is a very complicated phenomena if you try demystify the reaction mechanism for unknown catalytic reaction.

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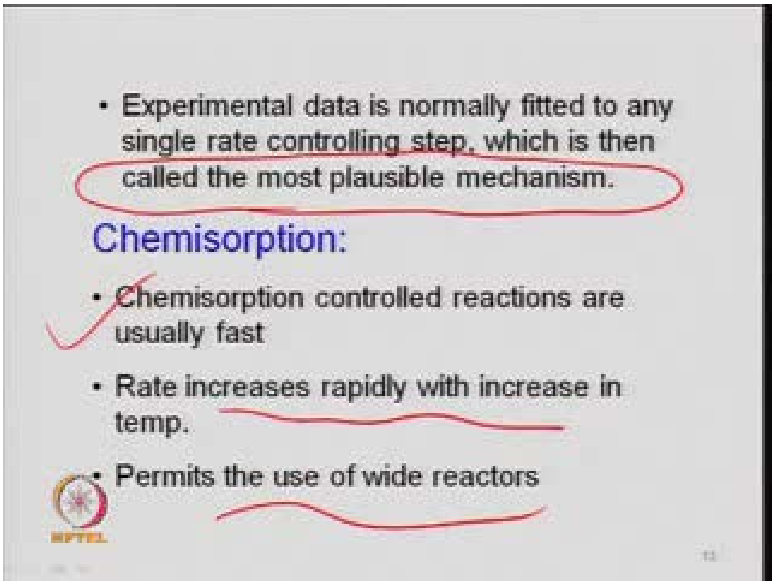

- Experimental data is normally fitted to any single rate controlling step, which is then called the most plausible mechanism.

Chemisorption:

- Chemisorption controlled reactions are usually fast
- Rate increases rapidly with increase in temp.
- Permits the use of wide reactors

So, generally, most of the time; the experimental data are fitted to any single rate controlling step. Because the actual; the mechanism is very difficult to predict there are some theories behind, there are some software tools are available density function theory like then, the chemical software; so, softwares are available nowadays you look which compare the binding energy. Suppose, you have a molecule methane and that is to be converted to benzene; so, there may be several possibilities of converting methane to benzene. So, depending upon the bond energy between carbon hydrogen bonding is benzene and what could be the several possible products; based on the bond energy as well as the thermodynamics of the reaction. So, one can write the mechanism, that is theoretical postulation of the kind of mechanism or the in order to confirm it one has to do the experiments also.

So, the experimental validation or the analysis of the mechanism based on experimental data is possible. So, you have; you provide some hypothesis and then, validate it through the experimental data and then, whatever the steps you have hypothesize justify it based on the physics or chemistry or the whatever the catalytic reaction theory. So, this can be done and then you identify the most suitable mechanism for the reaction. So, data are verified from the experimental data and then, you regress the data find out the error. And then, one can look at the compare this; the periti ((Refer Time: 40:15)) plots; the simulated data versus experimental data, in terms of rate selectivity and gives some tolerance limit. And then, optimization package can be used accordingly and you can find out the most suitable mechanism for the reaction. So, chemisorptions; the reactions are very fast, when the reactions are chemically controlled the chemical adsorption reaction though rate surface reaction term will be high that is the minimum adsorption; so, adsorption rate controlling in that case.

Same thing, the rate of reaction rapidly increase with temperature; because you are talking a kinetic term here, so rate increase and permits a use of wide reactor. So, there are series of reactors, have been tested or being used commercially in these type of reactions the slurry bubble column reactor, like that trickle bed reactor which is basically mass transfer controlled reaction pad bed reactor, fludised bed reactor, gasifier. So, there are plenty of reactors, where we look at the catalytic reaction or application all these kind of catalyst straight used in the commercial reactors. Hydro desulphization say most of the refined petrochemical reaction; so, they are used in this refined agent petrochemical industry.

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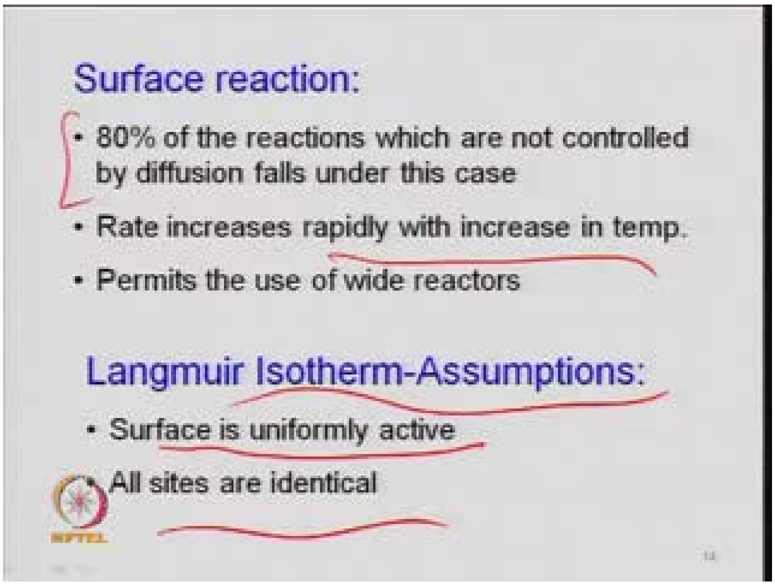

Surface reaction:

- 80% of the reactions which are not controlled by diffusion falls under this case
- Rate increases rapidly with increase in temp.
- Permits the use of wide reactors

Langmuir Isotherm-Assumptions:

- Surface is uniformly active
- All sites are identical

Surface reaction, so first is as I said adsorption. So, adsorption we call chemisorptions; because the chemically adsorption. And, second is surface reaction so the most of the time; when you start a mechanism or write a rate controlling step, so, most the reactions which are not controlled by diffusion they are controlled basically or generally by the surface reaction step. So, the surface reaction step means, where the reaction happens on the surface of a catalyst and reactant adsorb species is transferred into some product specie.

So, that is the transformation of the reactant specie into the product specie. A kind of, intermediate which is already on the surface of the solid transforms into a product; so, that is your surface reaction. So, more than 80 percent reactions are generally catalytic industry are controlled by the surface reaction mechanism. And this, again here because surface reaction; so, rate increase with the temperature and permits the use of wide reactors. So, again they ask series of reactors used and the Langmuir isotherm is generally used because as I discussed in the beginning the Langmuir adsorption isotherm talks on the chemisorption.

There have b t talks on the physical adsorption, multilayer adsorption. So, and isotherm assumptions as I have already seen the surface is uniform, energetically uniform; that is why it is not fit for b t that is not fit for the surface area physical adsorption determination of surface area of the catalyst it is not fit. And, all sites are identical; so, these are certain assumptions of Langmuir adsorption isotherm; which may not be correct if you look at the quantative or qualitative aspects of this isotherm.

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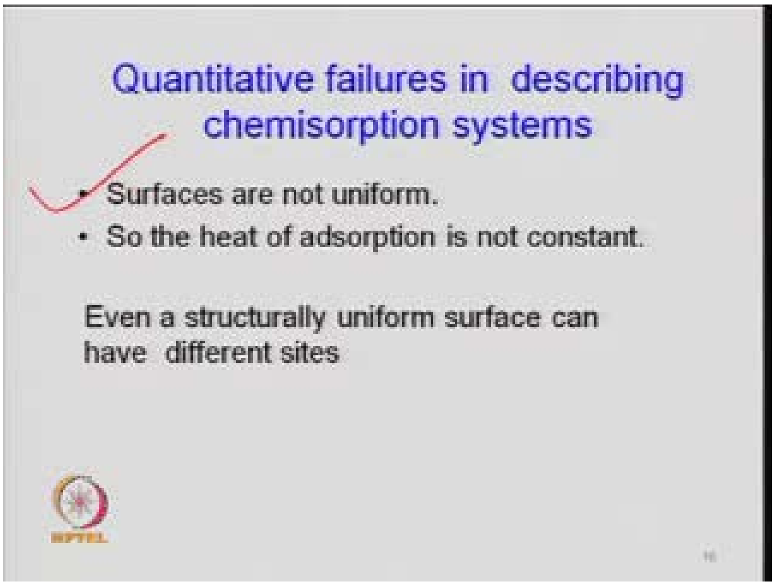

Quantitative failures in describing chemisorption systems

- Surfaces are not uniform.
- So the heat of adsorption is not constant.

Even a structurally uniform surface can have different sites

So, that is what the question raised here, that; is the Langmuir isotherm successful. So, in certain cases, it is yes but not in all cases. So, the adsorption isotherm is qualitatively correct; for adsorption system, where the molecule chemically bond to the surface. When you say chemisorption, because when the one molecule has already chemisorbed another molecule cannot come on to this site. So, that is why, the molecule Langmuir isotherm has been discussed based on monolayer coverage. So, once the monolayer forms; no multilayer adsorption is possible. So, qualitatively this is correct; when there is a chemical reaction. So, this is what shown here a molecule comes and adsorb and now these sites are blocked. The sites have; cannot be used for further reaction unless this chemisorbed species removes from the surface.

So, in this system the adsorption beyond a monolayer is not possible; so, that is what has been discussed. So, quantitatively it fails in certain aspects; as I discussed earlier also that heat of adsorption is not uniform. Generally, heat of adsorption decrease with surface coverage it may be exponential drop, it may be a linear drop; there are different isotherm what we have discussed before. But quantitative information from Langmuir isotherm if you look at in terms of the chemisorptions data it may fail in certain aspects because the surfaces are not uniform. And, heat of adsorption will change with the coverage fractional coverage and it says that, also it says that there are the there is no interaction between the chemisorbed specie.

But practically there will be the interaction; when there species adsorb, chemisorbed, it may have some interaction with the neighbor molecule. But the isotherms, assumptions says, that there is no interaction. So, that there are some drawbacks in this isotherm.

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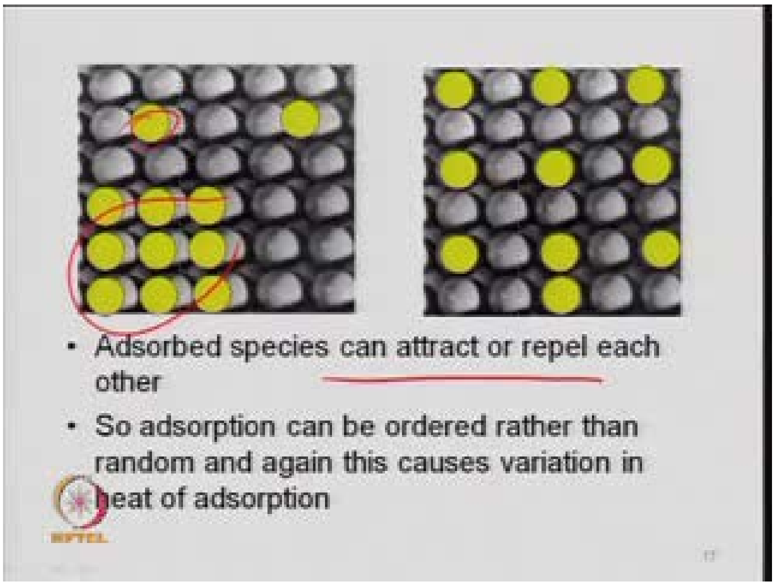

- Adsorbed species can attract or repel each other
- So adsorption can be ordered rather than random and again this causes variation in heat of adsorption

So, structurally uniformed surface can have a different sizes like this. So, the structure wise it seems to be okay, but if you look at they can attract or repel each other. The isotherm says that, there is no interaction but here, it can be a kind of some interaction or repel the isotherm which adsorbed species and there may be a kind of the species interaction either like this it can be like this also. It is not like that; if, this side the neighbor done so and so on. The molecule, gas molecule it will it depends on the chemical potential and it will it can adsorb throughout the surface anywhere. So, it cannot be just like that, there that there is no interaction between that adsorbed molecule.

So, there may be a kind of interaction during the adsorption. So, adsorption can be ordered rather than random and again, this cross variation in heat of adsorptions. So, heat of adsorption or heat of chemisorptions; which generally calculated from Langmuir isotherm and we assume it the uniform. But it may vary, with surface coverage because of these; whatever the irregularity in the surface.

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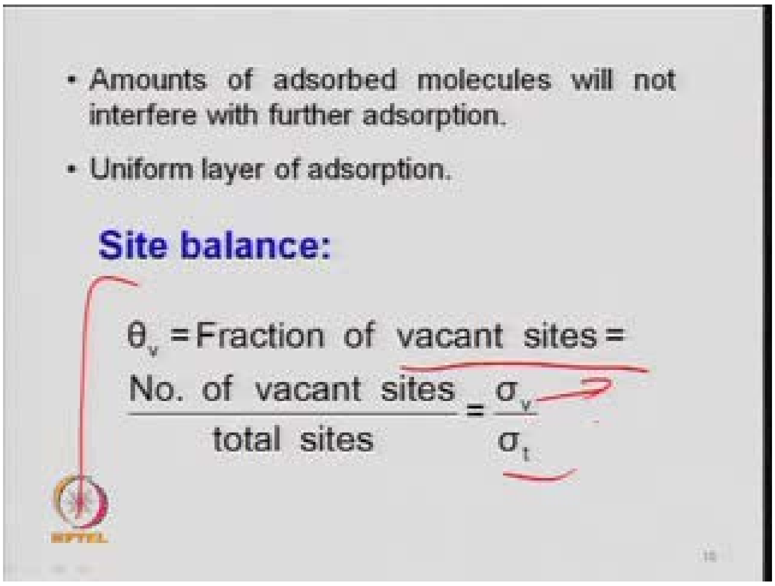

- Amounts of adsorbed molecules will not interfere with further adsorption.
- Uniform layer of adsorption.

Site balance:

$$\theta_v = \text{Fraction of vacant sites} = \frac{\text{No. of vacant sites}}{\text{total sites}} = \frac{\sigma_v}{\sigma_t}$$

So, amount of adsorbed molecule will not interfere with further adsorption this is what Langmuir said. So, that isotherm again assumes that, the rate of adsorption or amount of adsorbed molecule has no interference for further adsorption. But practically, it is not true, because it will change surface coverage; so, although the rate of adsorption is written in terms of professional to the fraction of the sites vacant. So, that is what the isotherm; but when you look at the structural array so, there is a kind of interaction and because of that heat of adsorption is different; so, this may also affect the rate if adsorption. And, uniform layer of adsorption has been assumed; so, this these are the isotherm lags but one can get the information from Langmuir isotherm in terms of chemisorption and to a large extent it is being used at present for the developing the mechanism.

Site balance we had seen before also, that a fraction of the vacant site because in the Langmuir adsorption isotherm, the rate of adsorption will be proportional to the fraction of the surface which is vacant. And now, how many sites are covered in a given reaction one cannot measure that actually; the only thing we are correlating it with some gas molecule which is adsorbed or the metal precursor which are adsorbed and at different rates or different temperatures. One can look at those rates or the surface covered and the molecule which are adsorbed on the surface. How many molecules are adsorbed; one can identify based on some analytical methods there available by which say dispersion can be measured or T P D studies can be carried out. So, one can have the idea or can get the idea in terms of the fractional surface coverage; but actually, how many molecules have covered that is not known. So, most of the time we report our rate in terms of turnover number; that is the turnover frequency turnover number; but the; identification of the surface sites which are vacant during a reaction is very difficult to report ((Refer Time: 48:42)).

So, but one can have the total site balance expression; so, theta v which you are writing here, fraction of the sites which are vacant; which is definition says the number of vacant sites divide by the total number of sites. So, sometime we write here the sigma v over sigma t; where sigma v is the number of vacant site and sigma t is the total number of sites. So, sites I am talking the concentration; which can be defined per a gram of catalyst or concentration of the sites and can be correlated with the Avogadro number also by writing it number of gram atoms of the metal species which are available on the surface per grams of the catalyst.

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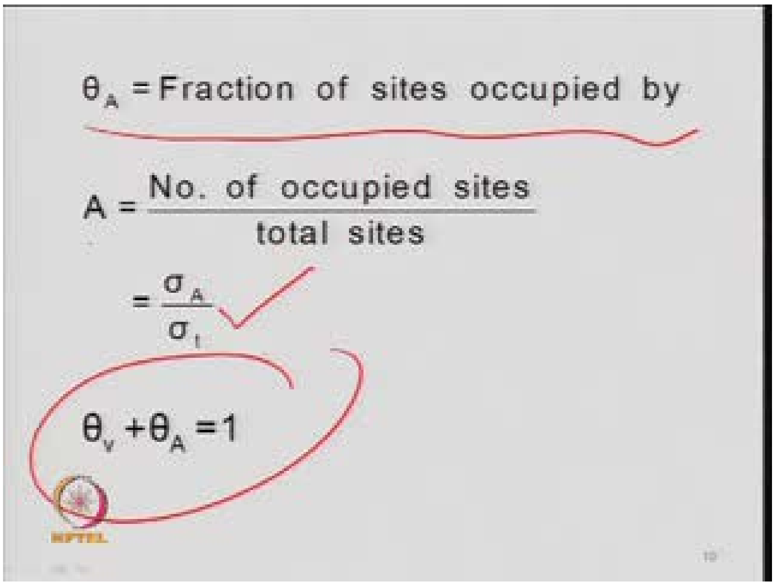

θ_A = Fraction of sites occupied by

$$A = \frac{\text{No. of occupied sites}}{\text{total sites}}$$

$$= \frac{\sigma_A}{\sigma_t}$$

$$\theta_v + \theta_A = 1$$

So, just one can write the site balance; if the theta is the fraction of the sites covered by A; so, fraction of the sites covered by A meaning; number of sites occupied by a divided by the total number of sites. Sigma A over sigma t; so, site balance that is because the total number of site initially you know; the fraction of the site which is total available is one, in one way. So, theta v plus theta A is equal to 1. That is a fraction some of all fractions vacant site plus site adsorbed by all species here it is just one specie. So, it will be 1.

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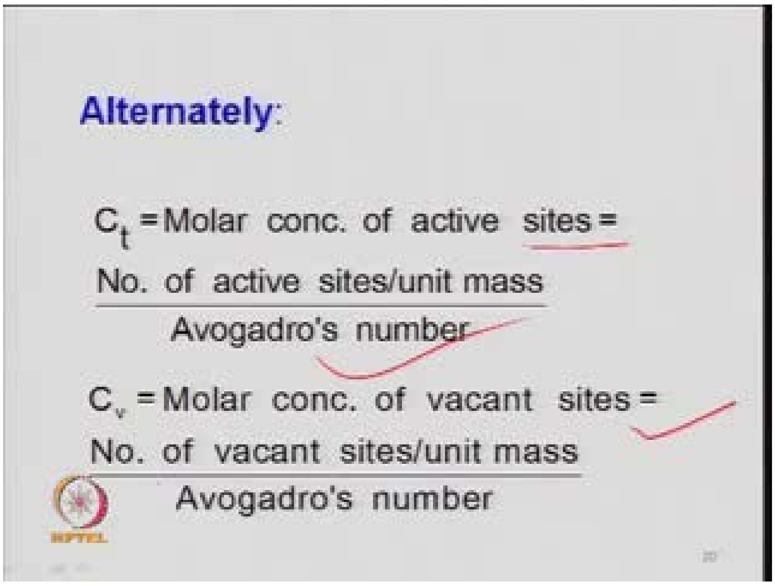

Alternately:

C_t = Molar conc. of active sites = $\frac{\text{No. of active sites/unit mass}}{\text{Avogadro's number}}$

C_v = Molar conc. of vacant sites = $\frac{\text{No. of vacant sites/unit mass}}{\text{Avogadro's number}}$

Alternately, as I said; one can write it in terms of the concentration of active site. So, either you write fraction of active site. So, fraction of the active site as I said the number of active site which is related to your dispersion metal dispersion you know the initial metal loading; say 10 percent of the catalyst means 100 gram there are 10 gram of the metal, active metal. So, you can calculate the number of gram atoms present in that; and one can calculate that in terms of the concentration of the active site. So, molar concentration of active site; which is written here is nothing but number of active sites per unit mass divide by its Avogadro number. So, one can very easily write this in terms of the concentration; so, in terms of moles of that active site.

So C v is the molar concentration of vacant site; that is defined number of vacant site per unit mass divide by the Avogadro number. So, one can write these concentration and then, again the same definition C v by C t. So, C t is the total concentration; so, C v upon C t is the fraction of the concentration of the vacant site the same thing what we discussed earlier. And, C aS upon C t will be written as fraction of the sites covered by A; so, one can very easily write here also site balance. Earlier, this was 1 because C t upon C t is the total and C supon C t that is the sites covered by A and C v upon C t is the fraction of the sites which are vacant.

So, fraction of the site vacant plus fraction of this sites covered by A and this will become that time 1. Then, this is; so, either way one can use the information for writing the rate expression.

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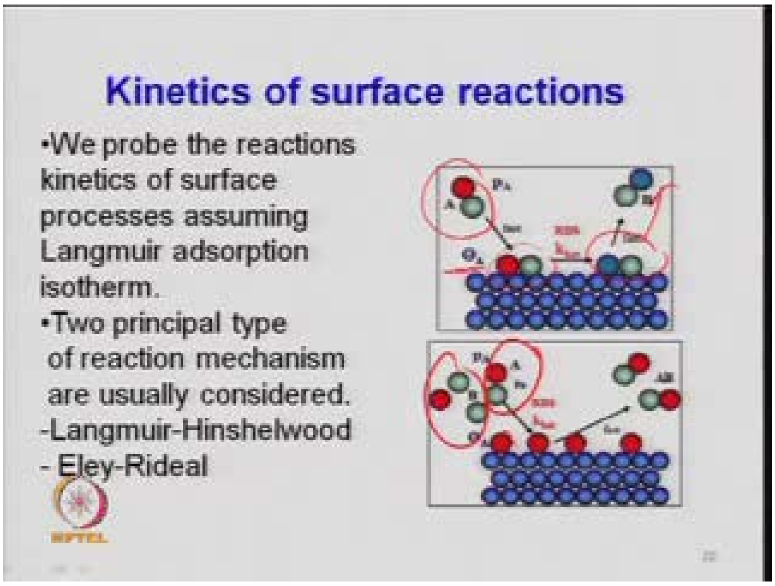

Kinetics of surface reactions

- We probe the reactions kinetics of surface processes assuming Langmuir adsorption isotherm.
- Two principal type of reaction mechanism are usually considered.
  - Langmuir-Hinshelwood
  - Eley-Rideal

So, kinetic reactions what we are talking; the kinetics of the surface reaction now I am discussing. So, any reactant species like say A, it depends on the pressure of the A what is the rate of adsorption so it is fast rate of adsorption generally depends on the pressure; you know the partial pressure of the gas. So, this adsorption on the surface; so, this is your theta a now reported here fraction of the sites which are covered by a and since this there is a kind of surface reaction, that is the hydrogenous catalytic reaction and transforms into a product and then it comes to a product B. So, this is on the surface of the solid I am talking; and after that there will be again diffusion and mass transform which are not rate controlling. So, out of question here; so, there can be different kind of mechanisms available.

So the kinetics of the surface process; if you look at the total catalytic reaction, different catalytic reaction which takes place on the surface of the catalyst, that we are assuming based on the Langmuir adsorption isotherm. So, Langmuir adsorption isotherm that is rate is proportional to the partial pressure and the surface covered.

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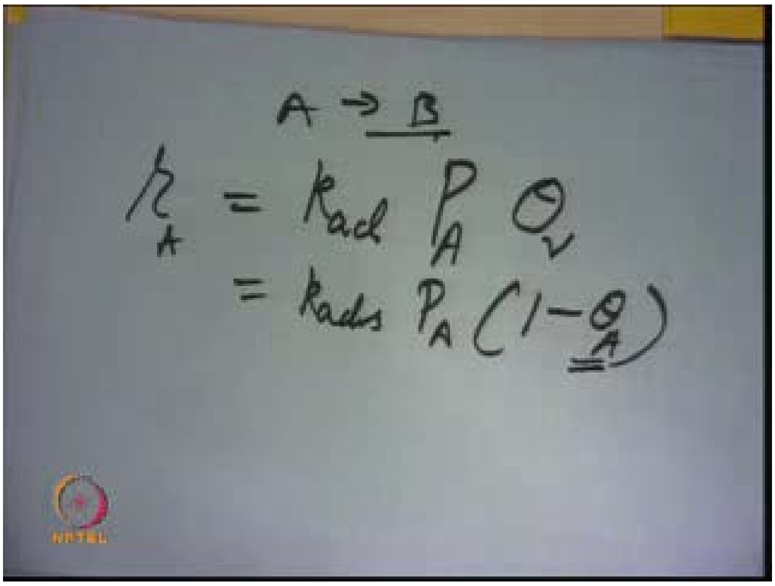

$$A \rightarrow \underline{B}$$

$$r_A = k_{ad} P_A \theta_v$$

$$= k_{ads} P_A (1 - \underline{\underline{\theta_A}})$$

So, this is your Langmuir adsorption isotherm k adsorption rate constant times the partial pressure of the gas times the fraction of the site which is vacant; rate of adsorption of A. So, sometimes vacant site; if I had just like this so I can write it k adsorption times partial pressure times 1 minus theta A also. Here theta A, is the fraction of the sites covered by A; so, this time I am just writing this expression; if B is also adsorbing then, this will become sigma of theta A and theta B. So, this may happen that, number of fraction of the sites which are available. So, I am writing here, just one only A is adsorbing on the surface; so, rate of adsorption will be on this.

So, this is what shown here in this case. Sometimes it may happen that, the two species suppose here in this second case; if you look at this is your A this is your B 2 reactant species. And A is adsorbed on the surface; the adsorption of A on the surface but B is on the gas species ((Refer Time: 54:19)) and so adsorbed species A and B interacts to this adsorb species rather adsorbing on the site, active site. And then, these two reactants; they transform into a product AB. That is means, one reactant species is present in the gas phase, another reactant is on the surface of the solid; this type of mechanism may also be possible and that is known as the Eley-Rideal mechanism, second mechanism. So, two principle type of mechanism now may be available, one is known as Langmuir-Hinshelwood which were based on the Langmuir principle and developed by this scientist Hinshelwood. And, the second one is the Eley-Rideal mechanism; so, we will just discuss this in the next time. So, I will stop here.