Heterogonous Catalysis and Catalytic Processes
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Lecture – 23

Good morning and in my last lecture I was talking about heterogeneous catalytic reaction kinetics. And, I discuss Langmuir Hinshelwood type of kinetic model; where the reactant species adsorbs on the surface of the catalyst and transform into a product.

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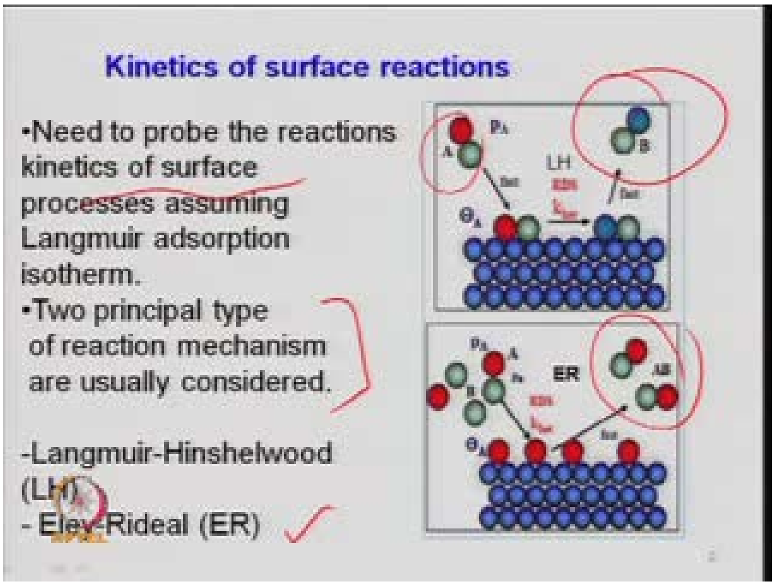

Kinetics of surface reactions

- Need to probe the reactions kinetics of surface processes assuming Langmuir adsorption isotherm.
- Two principal type of reaction mechanism are usually considered.

-Langmuir-Hinshelwood (LH)

- Eley-Rideal (ER) ✓

So, if you look at the rate kinetics here the reactant species A it adsorbs on the surface. Then, it transform into some surface reaction which is based on your adsorption, surface reaction and desorption; and then finally the product comes out. And, this is based on the Langmuir Hinshelwood approach; and the Langmuir isotherm which we have already discussed the rate of adsorption is equal to rate of desorption which is at equilibrium. So, one can the rate determining step; which is not at equilibrium will be used for calculating the rate.

And, other steps of the reaction will be considered as an elementary step and they will be very fast and at equilibrium. So, the basic principle of micro reversibility if you look at that these adsorbed species; they remain only for a small period of time just like in the kinetics of homogenous reaction. And, they transform into some stable product, right.

So, and the reaction step which slowest of the total steps among the all steps; that is considered at the rate determining step.

And, other steps here will be fast and at equilibrium. And, we assume that these individual steps of the reaction mechanism they are behaving like an elementary reaction step. So, rate is directly given based on the stoichiometric coefficient or whatever the partial pressure as I discussed earlier and the fraction of the weakened site. So, you need to poke a reaction kinetics; which is basically a surface reaction you are talking at this time assuming a Langmuir adsorption isotherm. So, in general there are 2 type of mechanism. So, one is based on Langmuir adsorption isotherm which has been discussed and will continue. And, second one is the Eley Rideal type mechanism.

So, in Eley Rideal type mechanism one species is present in the gas phase; the second species adsorbs on the surface. And, this adsorb species reacts with species which is present in the gas phase. And, then transform into a product; something like if I say that here that this A is the species which is here the species which adsorbs on the surface. So, fractions are covered here like theta A and then B remains in the gas phase. And, then it reacts and transform into some product which is here A B. So, that is another type of mechanism and that is known as Eley Rideal type mechanism.

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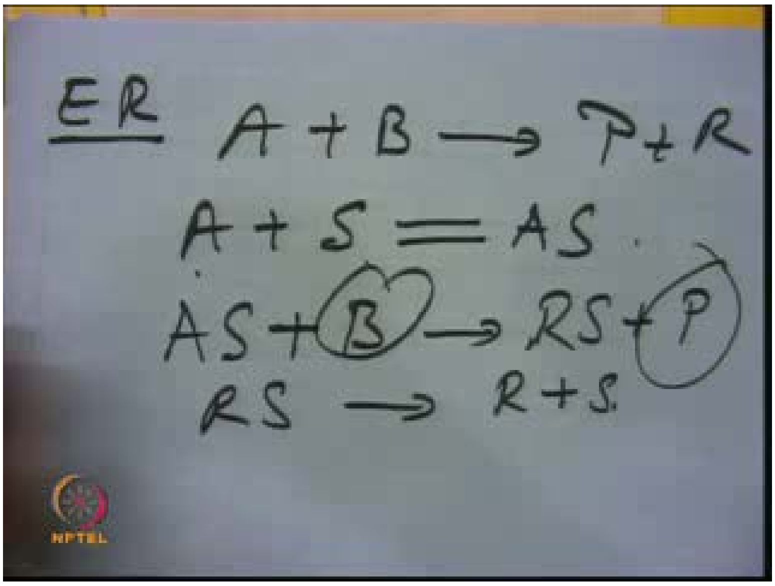

ER $A + B \rightarrow P + R$

$A + S = AS$

$AS + B \rightarrow RS + P$

$RS \rightarrow R + S$

So, here it will be something if you discuss some like reaction A plus B and gives a transform to a product P. So, A adsorbs on the site if I write S as the site then it gives some adsorbed species AS. And, then AS which is already adsorbed on the surface and the B will come; and it will react with that rather it is adsorbing separately on the another vacant site. And, then it may transform something like RS right and then plus may be where may be some other product something like P. And, then RS desorbs and gives you R plus whatever S vacant site. So, this is your product and this may be another or so I can write it P plus R also that depends.

So, this is a kind of Eley Rideal type mechanism where one species present in the gas phase and another is adsorbed on the surface. And, then reacting with this another can be several type of mechanism. And, based on the density function theory, based on the bondings, based on some surface factorization; one can identify the mechanism for a given reaction or one can postulate a mechanism and then confirm it from the experimental data.

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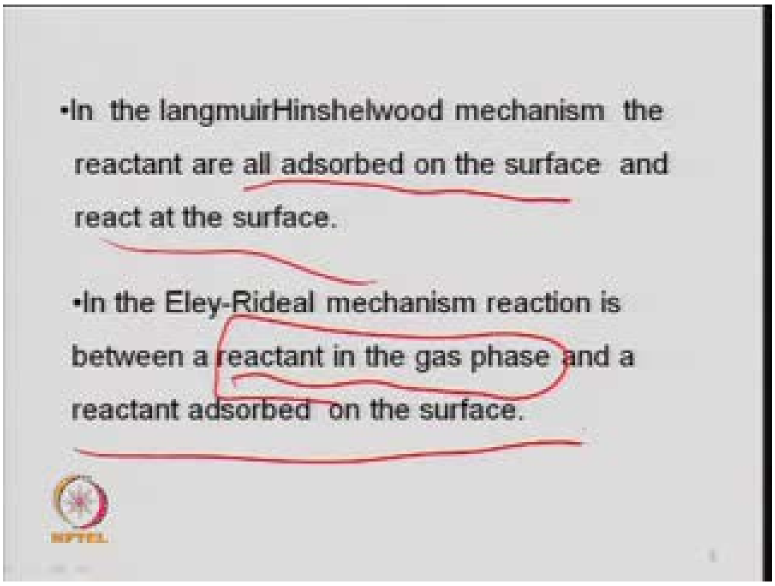

- In the langmuirHinshelwood mechanism the reactant are all adsorbed on the surface and react at the surface.
- In the Eley-Rideal mechanism reaction is between a reactant in the gas phase and a reactant adsorbed on the surface.

So, when the Langmuir Hinshelwood mechanisms just to distinguish between the 2 the reactants are all adsorbed on the surface and reacted the surface. So, this is a kind of the reaction throughout the on the at the surface of the solid or on the surface of the solid. And, in the case of Eley Rideal type mechanism the reaction is between a reactant which is in gas phase here and the second one which is adsorbed on the surface. So, it is a something like what AS you say or a star; and reacting with the gas phase molecule right and both kind of mechanism or both kind of postulations may be given for a given surface reaction. But finally the rate equation which has been obtained by assuming a particular step as a rate controlling step, rate determining step; the overall rate react of reaction has to be determine and confirm from the experimental data.

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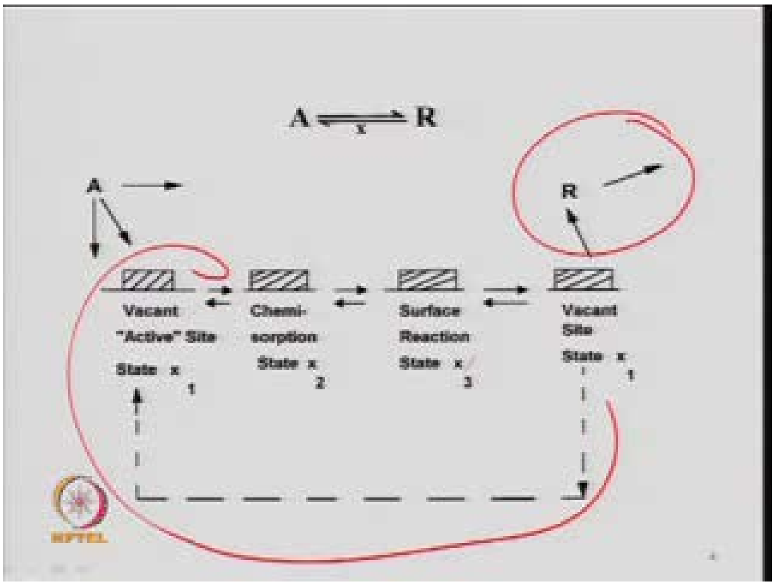

$A \rightleftharpoons R$ (x)

A

R

Vacant "Active" Site State x_1

Chemi-sorption State x_2

Surface Reaction State x_3

Vacant Site State x_1

So, overall any reaction which may be a reversible type say A gives you R. So, the reactant species they adsorb on a vacant site; and then there is kind of chemisorption right whether it is a Langmuir or a Eley Rideal kind of chemisorption. And, these steps are reversible and then it transform into surface reaction. And, then there is a kind of desorption of the product so finally you get a product, right. So, adsorption step which is here; then surface reaction where the product is forming. And, then the product species are desorbing from the surface and then you have a vacant site. And, this cycle continues, the catalyst is always free from the reactant species or active sites are available for further reaction. So, cycle continues.

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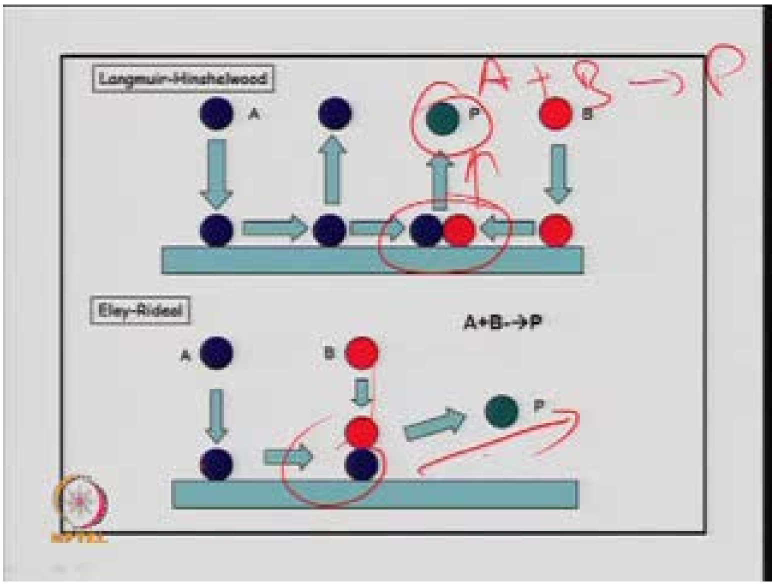

So, again there is a pictorial diagram for this Langmuir Hinshelwood; so species A adsorbs on the surface right then there is kind of chemisorption. And, then there is a surface reaction; the product transfer then there is another reactant. So, it is a kind of A plus B which is shown here transforms to P. So, this is your product P. So, A is adsorbed, B is adsorbed and then they are there is a kind of surface reaction here. And, then this species desorbs transforms into a product; if you look at here in the Eley Rideal type of mechanism adsorbs on the surface but B is already on the gas surface. So, it is a kind of the reaction between the adsorbed species of A and the B; A star plus B and that transforms into a product. So, this is just a distinction between the Langmuir Hinshelwood or Eley Rideal type of mechanism.

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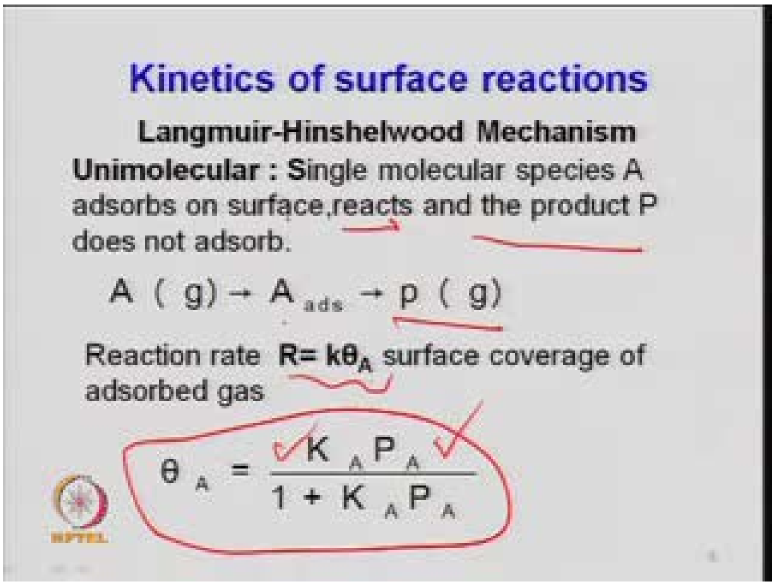

Kinetics of surface reactions

Langmuir-Hinshelwood Mechanism

Unimolecular : Single molecular species A adsorbs on surface,reacts and the product P does not adsorb.

$$A\ (g) \rightarrow A_{ads} \rightarrow p\ (g)$$

Reaction rate **$R = k\theta_A$** surface coverage of adsorbed gas

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A}$$

So, how to find the rate expression that is again important; and then determination of rate law parameter which is generally done by regression technique. And, different methods can be used for that purpose. So, Langmuir Hinshelwood mechanism is unimolecular. So, unimolecular as you have seen in the homogenous reaction kinetics or Langmuir that a single molecules takes part during the reaction.

So, unimolecular, bimolecular, multimolecular right and same kind of the species or different kind of the species may have a chemical reaction. So, unimolecular means when a single reaction molecule takes part during the reaction just like A goes to B, right. So, here it is shown here the single molecular species which adsorbs on the surface; then there is a surface reaction. So, it reacts and the product is disrobed, right. So, P is not adsorbed desorbs from the surface, right.

So, A which is adsorb like this and then product P forms; sometime it may happen that the product species may further adsorb. So, sometime the poison precursor the poison or the when the coke formation during the hydro carbon reactions the product forms. And, this may be a kind of the aromatic hydro carbon; and then further goes to the poly condensation reaction over the surface of the solid. So, these kind of reaction mechanism or understanding of these kind of reaction mechanism can give you some idea about the reactor design. So, that one can look at that which step is rate controlling by which step the undesired product may form. And, depending upon the activation energies or rate constant calculation; one can optimize the experimental reaction condition; and get them or maximize the product distribution especially when you have a multiple reaction right.

So, for this kind of reaction all of you know now that; suppose if I am saying that this rate of adsorption R is equal to K time the concentration of this covered right surface area that is the fraction of the sites of A which is covered here. So, it is just like the concentration of the species. So, basically there are you know that the when the system is at equilibrium then rate of adsorption is equal to rate of desorption. So, here you have to postulate the different mechanisms just like A adsorbs on one site A star.

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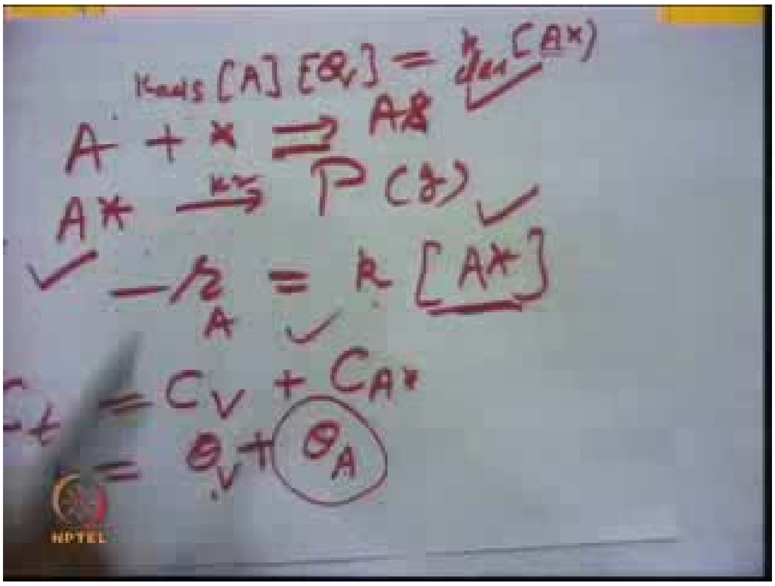

And, then A star and then A star which is written here in the first A adsorbed. So, that is basically you are A star and A star transform into a product P which is a gas phase and P is not adsorbed, right. So this term is may be a rate controlling or this term may be a rate controlling right. So, depending upon so this is basically your surface reaction and this is your adsorption of A. And, finally this will disrobe also you write it like this also right or write A star goes to a plus star which is a desorption of A. So, because the sites are vacant or A star transform into this. So, when I say that suppose this step is rate controlling; the rate will be direct you written based on this concentration. So, if so rate of reaction r A can be written simply some constant for this; suppose if I write it this is K 2. So, K 2 time the concentration of A star.

So, this is the general representation just like an elementary reaction. So, this is A star which is the concentration of the adsorbed species but not known. So, you have to write down a site balance what I discussed earlier that the sites; total sites balance C t is equal to vacant site plus sites which are covered by A. So, I will write it A star or something in terms of the fraction of the sites; so 1 is equal to theta v plus theta A. So, this is the fraction of the sites covered vacant site and this is the fraction of the sites which are covered by A.

So, one can very easily find either this you write rate of reaction in this form or you write in the form of K time theta A and apply the site balance. So, by knowing this and this step is now fast and at equilibrium. So, for this one can very easily write the rate of adsorption of this is equal to rate of desorption. So, rate of adsorption of A either you write it in terms of this is partial pressure of A or concentration of A, time the concentration of the vacant site right.

So, you can very easily write here say suppose if I write K adsorption time the concentration of vacant A right or in terms of partial pressure either way one can write is equal to or time the concentration of the star here. So, this is a vacant site; this is rate of adsorption and so is equal to rate of desorption. So, that is K desorption time the concentration of A star. So, that is so this is one can very easily write the expression. So, this is basically A star when I am writing it is something like this fraction of the sites covered by A. So, one and I am saying that this is not rate controlling.

So, this means this system is very fast right and so this will always be at equilibrium. So, one can very easily find out the lesensive for between theta v and theta star right. And, then use this equation and one can find out this A star or theta A; and substitute it here and this is your overall rate of reaction. So, this is what I am going to discuss it here right. So, basically when you are writing a rate of reaction; so just like in an homogenous catalytic the writing rate is proportional to the concentrations.

So, this is concentration of the active sites and the concentration of the reactant species and depending upon the stoichiometry, right. So, there can be several postulations; depending upon the mechanism or postulated mechanism the rate expression will be different. And, because we do not know as a priory that which step is rate controlling. So, in a model development one has to write or assume; each step as a rate determining step and then calculate. So, you can have 1, 2, 3, 4 models right; based on some literature review or based on some experimental information or based on some theory or bond energy theory; one can postulate that which is which may be the slowest step. So, we one can short list the number of reaction which are involved during the mechanism.

So, this is what this I this is nothing but simply Langmuir adsorption isotherm which had been shown here right the rate of adsorption is equal to rate of desorption at equilibrium; and that is what I discussed here. So, from it; it is calculated. So, this K adsorption divide by K desorption is your adsorption equilibrium constant K a which is shown here. And, this other things are simply the theta; this theta A is something like A star which is written here right. So, theta A which is the fraction of the sites covered by a is equal to this divide by this. So, K adsorption, K desorption is adsorption equilibrium constant time the concentration of A which can written in terms of P a partial pressure right and that term is here right.

And, the third term theta V that is nothing but what you have calculated from the site balance, right. So, this is the fraction of the sites which I am writing here theta v plus theta A. So, theta v is calculating theta this theta A can be substitute from here in this expression right and then substitute back in this. So, you have the expression which is something like one upon 1 plus K A. And, this is what the adsorption is just controlling; so this is just like what the R is equal to K time theta v.

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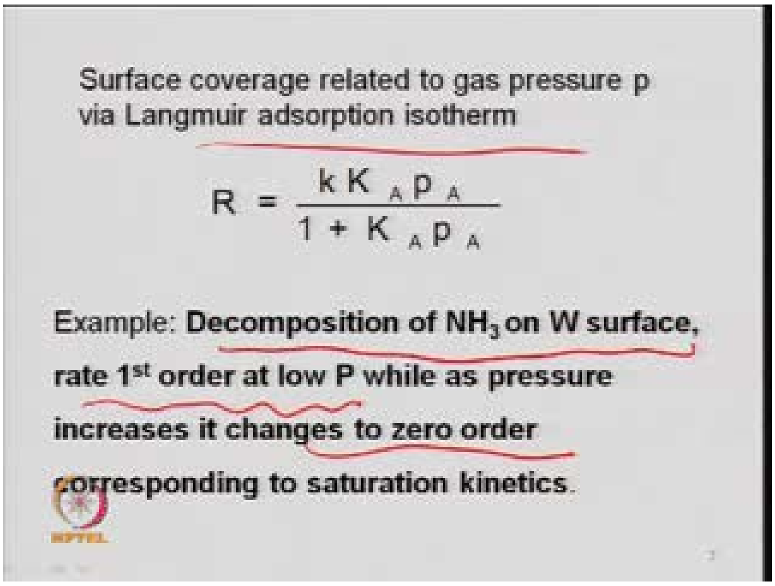

Surface coverage related to gas pressure p
via Langmuir adsorption isotherm

$$R = \frac{k K_A p_A}{1 + K_A p_A}$$

Example: **Decomposition of NH_3 on W surface, rate 1st order at low P while as pressure increases it changes to zero order corresponding to saturation kinetics**.

So, surface coverage which is related to gas pressure where Langmuir adsorption isotherm; that is the this expression which I was talking the this is based on the surface coverage. So, one can very easily write the rate expression by solving this equation; and you can have the expression in terms of rate. Then, the surface reaction is rate controlling; so either adsorption rate controlling. So, K time theta A and this surface reaction rate controlling the expression will come something like this. So, one can very easily write down these expression what I have shown here or derive the expression for different step as the rate controlling.

Because when the surface reaction is rate controlling minus r A is equal to this is my surface reaction here, right. So, minus r A is equal to K time the concentration of A star. So, concentrations of A star you will calculate form this expression which Ii have just talked right. And, that theta v is the concentration of vacant site which is calculated from here site balance. So, basically if I just show you the further calculation.

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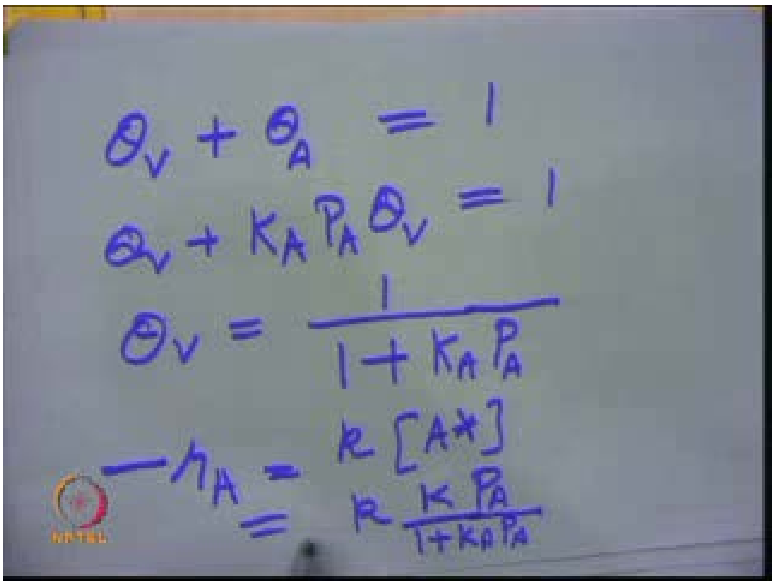

$$\theta_V + \theta_A = 1$$

$$\theta_V + K_A P_A \theta_V = 1$$

$$\theta_V = \frac{1}{1 + K_A P_A}$$

$$-r_A = k[A*]$$

$$= k \frac{K P_A}{1 + K_A P_A}$$

So, theta v plus theta A fraction of the site which is 1. So, theta v plus theta A which is calculated from the first expression; that will be simply here if you calculate theta A is simply K; K adsorption divide by K desorption time the partial pressure. Now, I am writing just to show you the result the concentration and time this is theta v from this expression.

So, k adsorption divide by K desorption this is your K A sometime you write like this. And, this is your P A partial pressure data and this is the concentration of vacant site. So, one can very easily substitute the value of theta A here. So, your expression becomes like this K A time P A time theta v and that is equal to 1. So, you can calculate theta v from here now that is simply your 1 divide by 1 plus K A P A, right. So, this one that is your surface reaction is rate control; so you write your minus r A is equal to K time A star. So, for surface reaction rate controlling minus r A which is rate constant for this surface reaction; time your concentration of A star adsorbed species. So, theta A which is already calculated this what I said here right.

So, you can very easily substitute it now K time this is your 1 over 1 plus K A P A, right. So, this rate which is given here r A time K time A star. So, A star is calculated form here that is K adsorption divide by this; so times your K times P A. So, this expression is you are A star. So, A star is calculated form here again which is simply K A which I have shown here already K A times A times theta v; and theta v is calculated from this expression right. So, r A is equal to K adsorption times A times theta v for adsorption rate control I will write it r A is equal to for adsorption; so let me write for adsorption first.

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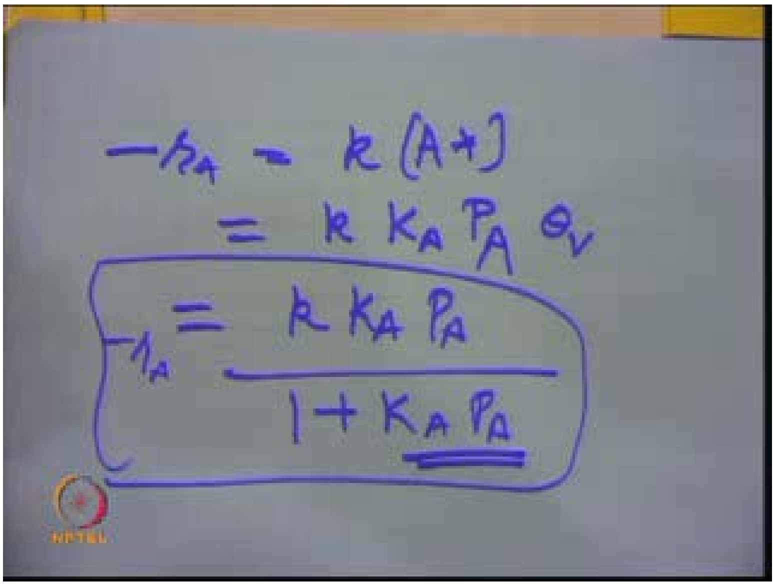

$$-r_A = k(A^*)$$

$$= k\,K_A P_A \theta_V$$

$$\boxed{-r_A = \frac{k\,K_A P_A}{1 + \underline{\underline{K_A P_A}}}}$$

So, your surface reaction let me write for surface reaction. So, minus r A which is your surface reaction rate controlling here. So, k times A star or theta A right and A star which we have already calculated form this expression is your now k times K A right times P A times theta v; this one this is from this expression because you are calculating A star. So, A star is k adsorption times A times theta v divide by k desorption and theta v we have already calculated here. So, instead of that I will write it now k times capital K A P A divide by that v 1 over 1 plus K A P A.

So, this is for a surface reaction rate control. If this step is the rate controlling which we have discussed here is this step is the rate controlling. Then, r A is equal to k times A star and A star is calculated form this expression; that is substitute here and then the value has been reported here. So, the this this is just a simple monomolecular reaction; there may be a bimolecular, multi molecular right or with different species A plus B gives you P plus R. And, the product species may also adsorb on the surface right.

So, different cases may come or case to case you have to look the overall mechanism of the reaction. So, this is the rate expression of Langmuir type or Langmuir Hinshelwood type when surface reaction is rate controlling. So, one thing is clear the species which adsorbed it appears in the denominator. So, it means the adsorbed species the for that you need more and more number of active sites.

Because if there is suppose poison precursor is there and it adsorbs on the surface it will come in the denominator of the reaction, right. And, if it is in the denominator and that product species does not disorb. Suppose the poison is there it has chemisorbed there and does not disrobe. So, those sites are already poison. So, this is used for deactivation also the same expression. So, there can be different expression for this and details of deactivation will study later.

So, just as an example here the ammonia decomposition has been taken over tungsten surface right twice N H 3 and gives you nitrogen plus hydrogen, right. So, that is what the decomposition of ammonia on tungsten surface. And, rate is generally first order at low pressure this has been observed experimentally; while as the pressure increase it changes to zero order right. So, sometimes based on experimental data you can postulate a rate mechanism.

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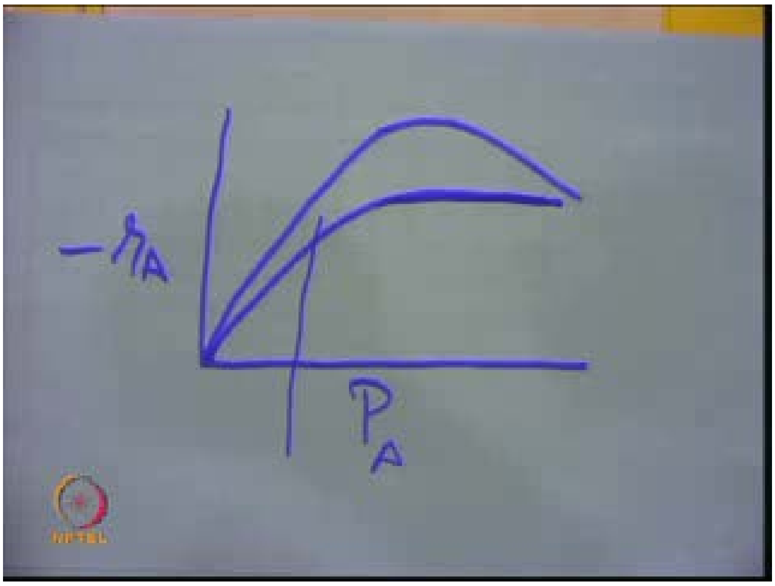

So, sometimes based on experimental data you can postulate a rate mechanism the meaning is something like that if you have minus r A rate of reaction of ammonia as a function of partial pressure of ammonia; one can check this strength by measuring this right. So, any type of this the train may be like this, it can be like this also. So, depending upon the experimental information you can see here in this case at low pressure rate is linear, right.

And, at a high pressure if this is the case; the rate is almost constant independent of pressure whereas it in this case it decrease with pressure. And, the drop may be a linear drop right, it may be some kind of polynomial drop also. So, by understanding this rate because you have the some micro kinetic reaction you mean data where you have the differential reactor. And, you have taken the data in terms of conversion and the space times support right and that can be at different temperature.

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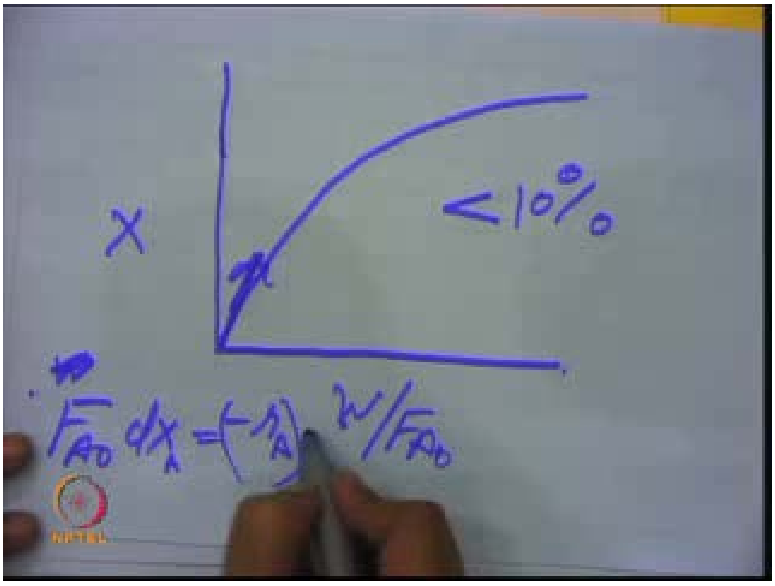

So, that is homogenous kinetics or heterogeneous catalytic reaction kinetics which you must be knowing now. So, conversion verses something like a space time data which is W is the mass of the catalyst, F A naught is the feed rate of the limiting component. So, these trends generally will go like this right; the conversion will increase as you increase the space time inside the reactor right or in other way F A naught by W you say that can be your space velocity right, gas hourly, space velocity, liquid hourly, space velocity.

And, the knowing this information generally for differential reactor we use the conversion data less than 10 percent or 15 percent. So, by having a slope or tangent here because you know your differential reaction design equation W by that is F A naught d x A I will write. So, F A naught d x A is equal to minus r A or if you have something like in the case of per unit mass of the catalyst. So, r A into d w.

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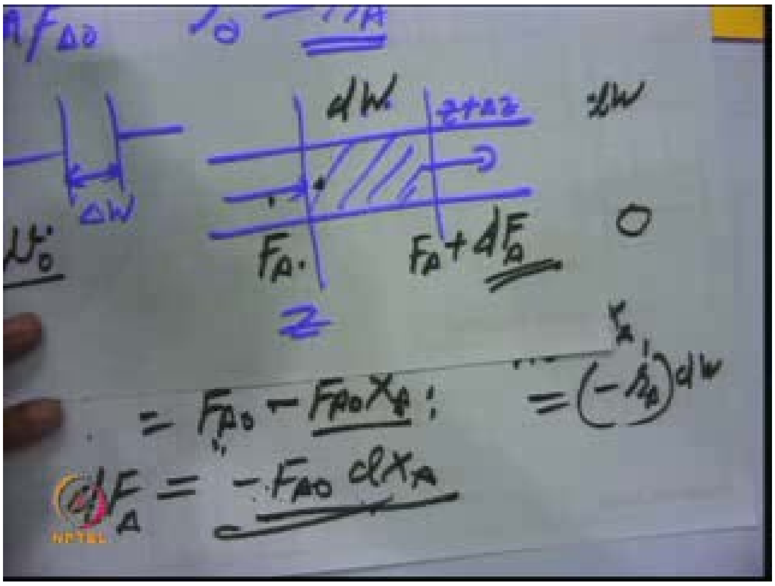

So, I can write it basically the equation which you write that W by F A naught for the integral reactor; generally you write it like this flux flow reactor suppose. So, 0 to x d x over minus r A right this is your flux flow. So, generally integral approach when you are taking the complete bed length. So, but generally this minus r A data minus r A data is taken from the slope of that right the conversion verses W by F A naught. So, in general what we say that for a differential reactor if you write a mass balance here in a pad bed reactor. So, this is your delta w mass what I discussed last time also for a flux flow reactor design equation.

So, something like this. So, something is in, something is out here right and this is your mass of the catalyst in the bed. So, if you have here suppose this mass is d W delta W this is input, right. So, F A here something; and here it is F A plus d F A change in the molar flow rate of species A, right. So, you write you can have a differential by or this F A can be dispersive term also or a convective term. But for a flux flow we just write it F A something like C A naught into v naught if you look at that concentration multiplied by the volumetric flow rate, right.

So, either you write in this form that is you know the volumetric flow rate of the field; you know the concentration of the limiting component in the field. So, this is your F A right input molar flow rate like that F A naught if I write here. So, at any point in a differential section if you are selecting a differential reactor or micro reactor then you can find out how many moles in? How many moles are out right and what are the number of moles which is reacted here?

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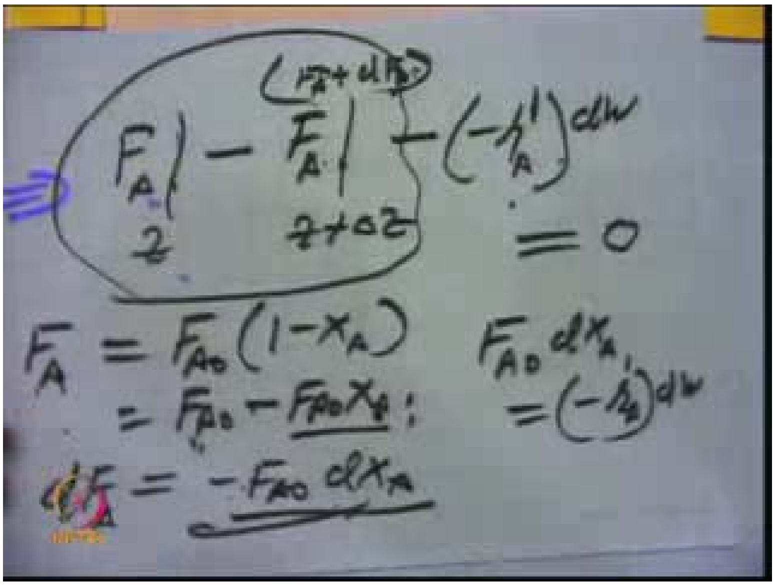

$$\overset{(F_A + dF_A)}{F_A\Big|_{z} - F_A\Big|_{z+\Delta z}} - (-r'_A)\,dw = 0$$

$$F_A = F_{A0}(1-x_A)$$

$$= F_{A0} - F_{A0}x_A;$$

$$dF_A = -F_{A0}\,dx_A$$

$$F_{A0}\,dx_A = (-r'_A)\,dw$$

So, your material balance equation is simply F A suppose at z minus F A at z plus delta z input minus output; material balance equation minus disappearance because of chemical reaction. So, that is minus r A dash I am writing here because rate of reaction is per unit mass of the catalyst, right. Since, this is per unit mass of the catalyst; so into delta w or d w whatever. So, input minus output minus disappearance because of chemical reaction and that is equal to accumulation but at steady state there is no accumulation.

So, within this differential section of the reactor what are the moles of A in and what are the moles of A out and that has been calculated. Now, you know that F A if input is known; F A is basically moles of a at any differential section z right. And, that is simply related to F A naught 1 minus x A moles in minus moles reacted. So, basically this how did you get this thing moles of A left right that is the concentration of reactant species present at that point z. So, this is basically input F A naught minus the moles reacted. So, that is simply F A naught into x A because F A naught is the molar flow rate and x is the fractional conversion. So, moles in minus out divide by in right if this is your F A naught minus F A naught x A and that is your F A at any point. And, if you are doing F A plus d F A that is what we have said in the differential section this is d F A, right.

So, basically this equation which is written F A at z plus delta z that is nothing but what is the moles in at F right. And, what is in the differential section change in that moles right that is F A plus what I wrote d F A. So, basically this equation which is F A here is F A plus d F A here; change in that in the differential section and which one can directly write from tailor expression also differentiation of that.

So, what is this ultimately it is simply d F A, right. So, F A is this, F A naught 1 minus x A. So, just d F A of this will be simply minus of F A naught d x A differentiation of this right derivative of this. So, either you write in terms of d x A by d w; d F A by d w also one can write directly right F A plus F A times divide F A that is d F A by d w into delta w; in differential section. And, what is the differential mass in that section?

So, what I mean to say this is F A at z which one can write in terms of F A naught minus F A naught x at this is at F A at plus F A d F A so same number right. So, only the differential term d F A is left here F A naught d x A. So, this whole term is basically now your F A naught d x A in negative right sign. So, what do we get from this? This is same expression which you are done for homogenous kinetic right. So, what is the information you get here in terms of F A naught d x A is equal to. So, I have the expression left F A naught d x A is equal to minus r A which is representing just disappearance of A into delta w or d w.

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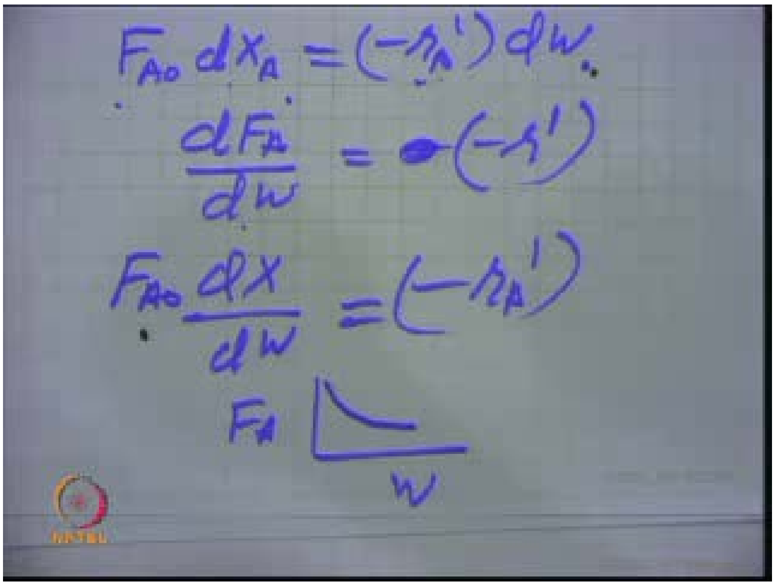

$$F_{A0}\, dX_A = (-r_A')\, dW$$

$$\frac{dF_A}{dW} = (-r')$$

$$F_{A0} \frac{dX}{dW} = (-r_A')$$

So, let me write it here. So, F A naught d x A is equal to minus r A dash times d w. So, this information which has been obtained from this mass balance in a reactor F A at z minus F A at z plus delta z. So, this is my z here and this is the z plus delta z between 2 differential section right.

And, this so either you write it in terms of delta w, d w or you write in terms of z right. So, that time if you write in term of z multiplied by area of cross section into the density; that is volume of catalyst multiplied by density of catalyst that is your mass of the catalyst. And, you can include the wide fraction if there are wide also right that wide fraction. So, one can very easily co relate this F A naught d x A is equal to minus r A dash into d w.

So, this equation is what I told the differential equation right. So, basically what you are getting here F A naught d x A by d w or d F A by d w. So, this is also my d F A by d w that is equal to minus r A dash here. So, this F A naught d x A I have already defined here right. So, this is your d F A. So, this is d F A by d w you say or F A naught d x A by d w. So, another the same definition is F A naught d x by d w and that is equal to minus r A dash; this is the expression for defining the rate in the case of a heterogeneous catalytic reaction right.

So, it means d F A by d w; if you have the data on this F A as a function of w or either you say like this F A. So, one can have a expression like this also F A verses w right and take the slope. So, F A is basically decreasing right down the length of the reactor. So, in a commercial reactor you have large reactor right, large mass of the catalyst. So, from inlet the conversion is 0 right and exit it is conversion some value say 90 percent, 80 percent whatever x value right. So, your F A which is basically F A naught 1 minus x A. So, x is increasing, x is your conversion. So, if you have this data it will go like this; and if you have x verses w which I was talking earlier that will increase.

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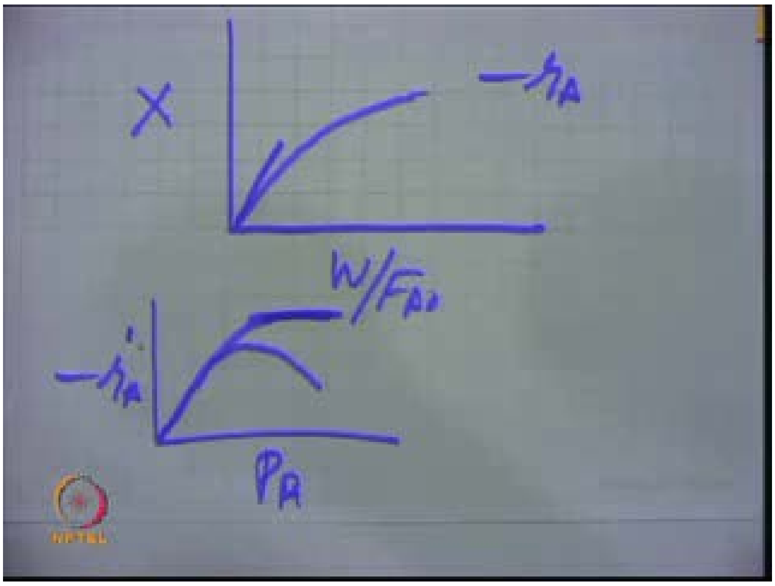

So, that information you get now you get this w by F A naught which I was talking is your space time. So, conversion verses w by F A naught delta; one can have and which will go like this right. And, this if you have different temperature you know at higher temperature the kinetics will dominate. So, you will have more data parts right more the slope of this line will increase; the rate will be higher in one way. So, the tangent here is simply your this rate.

So, one can very easily calculate minus r A by taking this slope of this line right. And, this is what information you get when you have the different kind of expression. Now, so one can get this rate and then you have the expression at different partial pressure or the concentration of the reactor ant species. So, you can look at the trend in terms of minus r A that is overall rate as a F of partial pressure right. And, this may be like this as we are talking; it may be like this also. So, that is what the experimental observation of the data right.

So, once you have this information one can postulate the mechanism; that you know that at low pressure, low relative partial pressure the rate is increasing linearly right. So, it means that time something here; this term is dominating compared to this denominator term right or when you see at high pressure the rate becomes something like here; suppose this constant. It means, the denominator is now dominating somewhere here right. And, when denominator is dominating compared one this is almost a constant line rate is constant independent of partial pressure. So, it means by looking at your experimental data for any unknown reaction one can look at what kind of mechanism has been developed or to be developed.

So, these are certain fundamentals of the reaction to find out the rate. And, co relate the rate as a function of temperature, partial pressure or other say factor of inert can be studied right other parameter; some effect of poison precursor can be studied. And, one can look at these effects and then can develop a mechanism. And, that mechanism is important for reactor design or commercialization of the process right. So, this is what for ammonia decomposition has been observed that the rate is first order at low partial pressure or when the pressure is high it shows a zero order kinetics.

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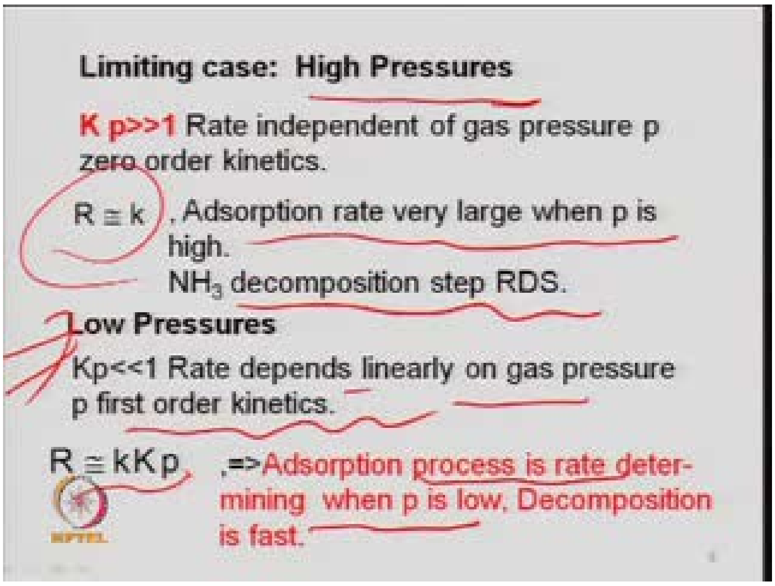

Limiting case: High Pressures

K p>>1 Rate independent of gas pressure p zero order kinetics.

$R \cong k$, Adsorption rate very large when p is high.

NH_3 decomposition step RDS.

Low Pressures

Kp<<1 Rate depends linearly on gas pressure p first order kinetics.

$R \cong kKp$,=>Adsorption process is rate determining when p is low. Decomposition is fast.

So, this is what we have discussed now that when the pressure is very high right. At high pressure; then your K into p denominator right this term; at high pressure this K p is very high compared 1. So, the denominator approximates to something like this just K p in the denominator. And, so your rate will just become like this right K with K cancels; so almost constant. So, that meaning is that adsorption rate is very large when pressure is high. Because I told you the species which adsorb on the surface; that is the rate that is that will come in the denominator of the rate expression right.

So, when you see that at higher pressure there is no adsorption of that species observed. That means, that time this adsorption rate has become very large compared to second parts of this reaction. So, that time surface reaction may be a rate controlling. So that is the ammonia decomposition step is the rate determining. So, ammonia decomposition means when ammonia decomposing it comes and adsorbs on surface of the tungsten. And, then there is a surface reaction by which it splits to nitrogen and hydrogen and that desorbs form the surface. And, when the pressure is very high then your adsorption of a is very high. And, that step is not rate controlling the second case when the pressure is very low right. So, low pressure; so this term which is here in the denominator because pressure is low. So, this term one will be dominating compared to the second term of that right.

So, in this case your K p; K into p basically much more less than 1. So, rate will go as a straight line linearly on gas pressure and it is showing the first order kinetics right. So, when that time where rate is simply K times K that is adsorption equilibrium constant times of partial pressure right. So, it means that time the adsorption process is the rate determining step when the pressure is very low. It means that the controlling factor is the adsorption of ammonia on to the surface. But the as soon as it adsorbs immediately it transfers to the product. So, decomposition is very fast that is not controlling or the time taken for decomposition step is very low.

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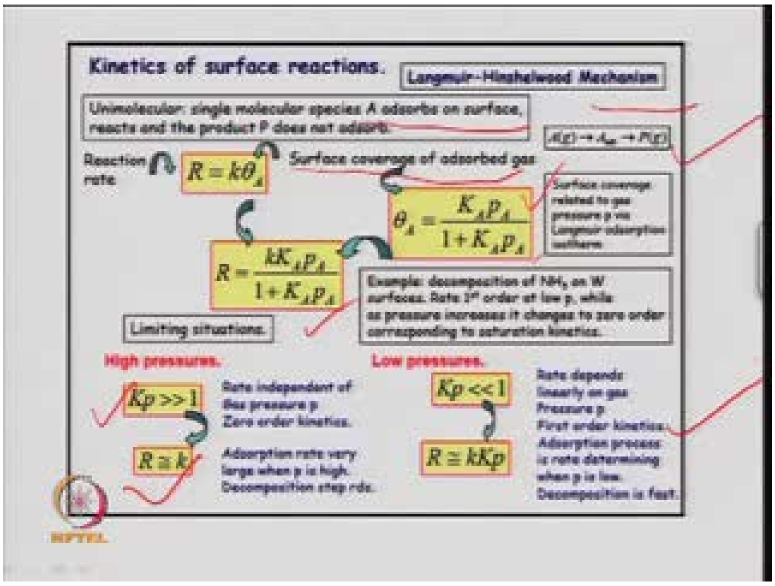

Kinetics of surface reactions.

Langmuir-Hinshelwood Mechanism

Unimolecular: single molecular species A adsorbs on surface, reacts and the product P does not adsorb.

$A(g) \rightarrow A_{ad} \rightarrow P(g)$

Reaction rate

$R = k\theta_A$

Surface coverage of adsorbed gas

$\theta_A = \frac{K_A p_A}{1 + K_A p_A}$

Surface coverage related to gas pressure p via Langmuir adsorption isotherm.

$R = \frac{kK_A p_A}{1 + K_A p_A}$

Example: decomposition of NH_3 on W surfaces. Rate 1st order at low p, while as pressure increases it changes to zero order corresponding to saturation kinetics.

Limiting situations.

High pressures.

$Kp >> 1$

Rate independent of Gas pressure p Zero order kinetics.

$R \cong k$

Adsorption rate very large when p is high. Decomposition step rds.

Low pressures.

$Kp << 1$

$R \cong kKp$

Rate depends linearly on gas Pressure p First order kinetics. Adsorption process is rate determining when p is low. Decomposition is fast.

And, this same thing has been just shown in summary as a summary. So, unimolecular reaction meaning that single molecule a species adsorbs on surface. And, reacts right the product does not disrobe adsorb on the surface. So, this is what the Langmuir Hinshelwood type mechanism. So, A gas adsorb on the surface and transform into a product which disrobes right. So, your rate of reaction for adsorption is simply R is equal to K times that theta A right here; the surface coverage of the adsorbed gas.

So, you substitute theta A value which is K A P A over 1 plus K A. So, your rate becomes k K A times p A times 1 plus K P A which we have already seen right. So, decomposition of ammonia on the surface which is a first order low at low pressure. And, as the pressure increase it changes to the zero order and just showing saturation kinetics. So surface coverage related to the gas pressure p by your Langmuir adsorption isotherm that has been discussed in this.

So, surface which is covered is your theta A proportional to the pressure of the gas and denominator will have the adsorption species. So, there can be different limiting species situation which we have already discussed. So, K p is much more greater than 1 right which will show that rate is independent of the gas pressure. So, zero order kinetics and that time your rate will is a just constant right. And, the second case when the pressure is very low the rate will depend linearly on the pressure and showing a first order kinetics right. So, that time adsorption is the rate limiting. So, one can have the analysis based on the mechanism and comprising with the experimental data can be done.

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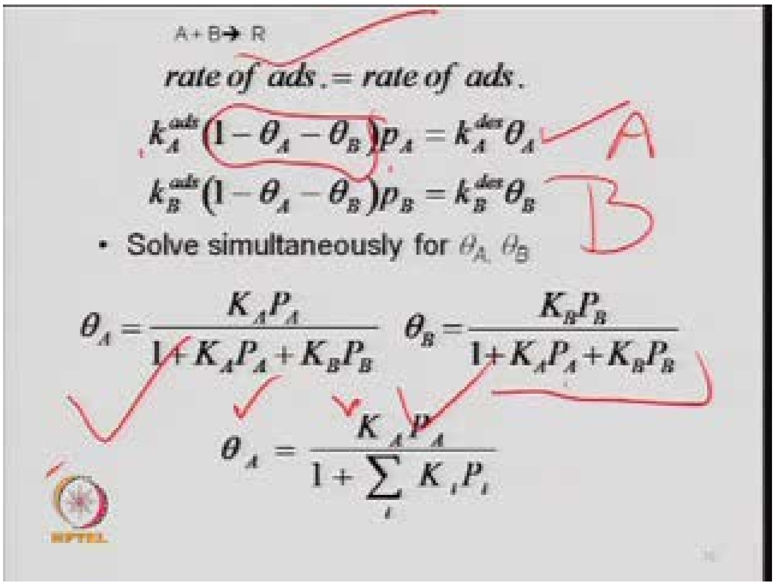

$A + B \rightarrow R$

rate of ads. = rate of ads.

$$k_A^{ads}(1-\theta_A-\theta_B)p_A = k_A^{des}\theta_A$$ A

$$k_B^{ads}(1-\theta_A-\theta_B)p_B = k_B^{des}\theta_B$$ B

- Solve simultaneously for θ_A, θ_B

$$\theta_A = \frac{K_A P_A}{1+K_A P_A + K_B P_B} \quad \theta_B = \frac{K_B P_B}{1+K_A P_A + K_B P_B}$$

$$\theta_A = \frac{K_A P_A}{1+\sum_i K_i P_i}$$

So, just a again a summarize form. Suppose the reaction A plus B gives you R. So, at that condition your rate of adsorption is equal to rate of desorption when you say the equilibrium. So, if you write two species now right so as I said earlier also.

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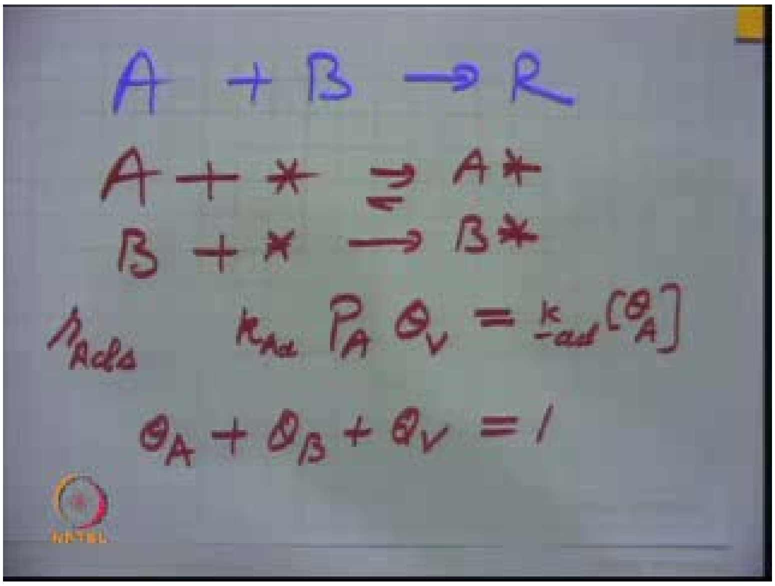

$$A + B \rightarrow R$$

$$A + * \rightleftharpoons A*$$

$$B + * \longrightarrow B*$$

$$r_{Ads} \quad k_{Ad} P_A \theta_V = k_{-ad} [\theta_A]$$

$$\theta_A + \theta_B + \theta_V = 1$$

So, A plus B transforms to R. So, both species here if you look at theta A is the fraction of the surface covered by A and theta B is the fraction of the surface covered by B right. So, A is adsorbing it means so A plus star some A star here right. And, then same thing for B plus star gives you B star. So, these 2 terms which have not been shown here rather right but have been written directly? So, you know that rate of adsorption of A; so r A is simply here r A adsorption I will write; I am not writing overall rate right I am saying rate of adsorption of A one can say it is a net rate of adsorption also. But when you are saying at equilibrium and Ii am assuming that these 2 adsorption steps are at equilibrium right or just you are reporting that the net rate of adsorption here.

So, it is simply the adsorption rate constant first term which you has written here capital k A adsorption for A times the concentration or partial pressure of A at P A times the concentration of the vacant sites. So, theta v right the site will be theta v and other site if it is a reversible because these are desorption also simultaneously there. So, your k minus adsorption of A right k minus A I can write here or k desorption you can write; and times the concentration of the site which is our covered by A. So, one can write it theta A right. So, this expression here is something like which is written here K A desorption times the fraction theta A and K A adsorption times the partial pressure of A. And, this theta v which is vacant site I told you the site balance. So, site balance is that site covered by A plus site covered by B plus the vacant site theta v and this will be 1 right. So, again we are talking here a Langmuir adsorption isotherm right.

So, it means the sites A is also covered B is also covering the site and then you are writing a site balance. So, this is just for adsorption of A right. Similarly, second step is adsorption of B. So, similar expression you get right here also that is partial pressure of B times the rate constant for adsorption and the vacant site; then the desorption and whatever the rate constant times the shell covered site B right. So, one can very easily solve these 2 equations right and find out theta A and theta B. Because now you have the expressions in terms of theta A and theta B and one equation you already you have written in terms of site balance right.

So, 2 equations two are known because only third one is known. So, you can find out theta A, you can find out theta B. So, theta A simply K A P A divide by 1 plus K A P A plus K B P B same thing for the theta B also one can see that the denominator has same. Because I said the species which adsorbs on the surface of the catalyst will appear in the denominator of the reaction. And, these are the species which adsorbed right. So, in general if you look at theta A is equal to K A P A divide by 1 plus sigma of K i P i as well K i P i or are the number of the species that is that may be adsorbing on the surface right.

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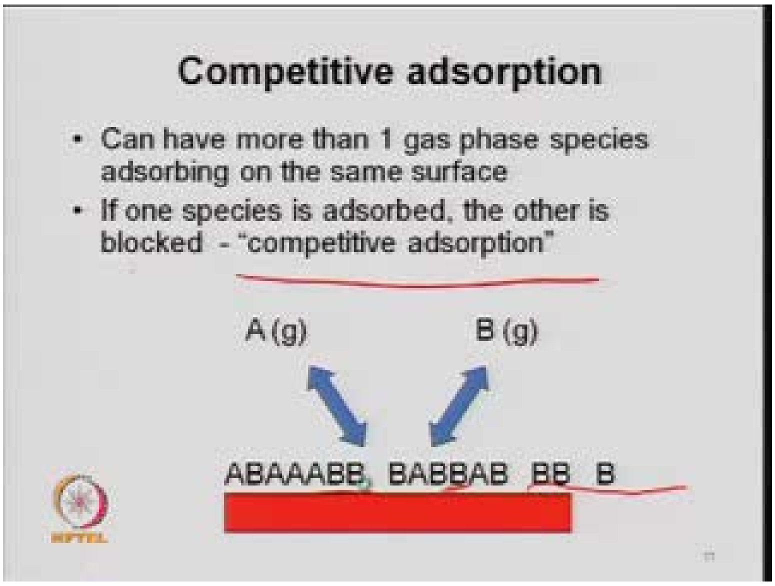

Competitive adsorption

- Can have more than 1 gas phase species adsorbing on the same surface
- If one species is adsorbed, the other is blocked - "competitive adsorption"

A (g)

B (g)

ABAAABB BABBAB BB B

There can be competitive type of adsorption. So, the just the same case what we have discussed earlier. So, A is adsorbing, B is adsorbing. So, this it can be like this a competition between the 2 because the sites available are limited and both species are adsorbing on the surface. So, it means where you can get a kind of maxima in your rate right; because the depending upon the partial pressure of A, partial pressure of B. And, the gas species reactant species in the reactant gas your rate may affect. So, effect of partial pressure becomes very important in this case. Because there is a competition right sometimes it may happen that A plus B and you have taken the large concentration of B. But B covers all the sites because it is adsorbing. So, A does not find A suppose concentration of A is low.

So, A will not have enough sites for adsorption on the surface. And, that will depend on the rate constant for adsorption right; that this is what the micro reaction kinetics which we are talking earlier or sticking probability right that will depend on the gas pressure and the kinetics. So, a fact that is the flux which we are talking earlier is related to these things that how fast is that adsorption on the surface of a catalyst. So, this can have more than one gas phase species adsorbing on the same surface. And, especially when you have bimetallic type of catalyst support right and you see that you have platinum, brenium on some alumina support. And, then on say the platinum the A species adsorb faster compared to the second species. Then, it may happen that these sites are covered by one species only and the you will not get any product right.

So, that time you have to look at the effect of partial pressure or optimize the process condition for the reaction. So, if one species adsorb the other is blocked and that is known as a competitive adsorption; and you have to look at the effect of this. So, A gas adsorbs on the surface gas adsorbs on the surface you can have B A B B like this and so on so on B B B same thing here and A A A. So, that is that is what the concentration of one species may be higher or lower on the surface right.

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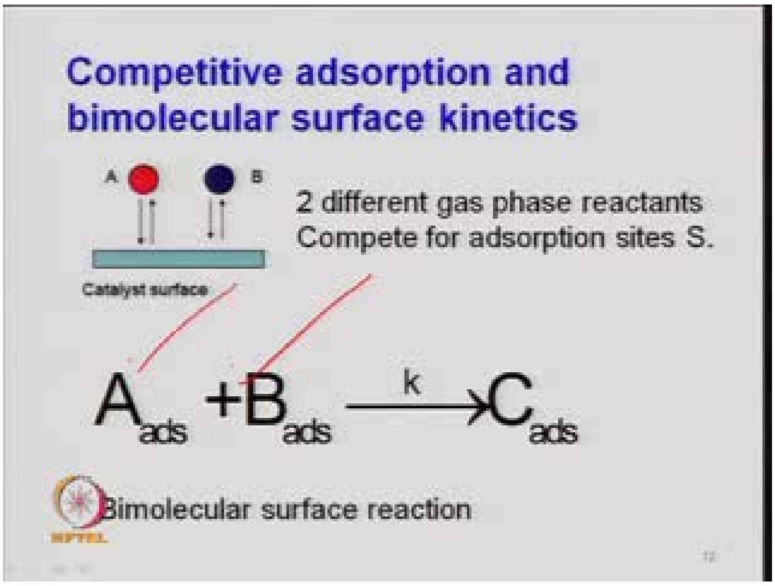

Competitive adsorption and bimolecular surface kinetics

2 different gas phase reactants
Compete for adsorption sites S.

$$A_{ads} + B_{ads} \xrightarrow{k} C_{ads}$$

Bimolecular surface reaction

So, this is what shown here that the catalyst surface A is adsorbing; 2 is B is adsorbing. So, two different gas phased reactants and they compete for adsorption sites. So, here the when these 2 have adsorbed on the surface now they are reacting together. Because reaction is between 2 adsorbed species. So, A is adsorbed, B is in gas phase no chemical reaction right. Because it is your reaction experimental data shows that you need the b also to, be adsorbed on the surface right. And, one can postulate these kind of mechanism. So, when A is adsorbed so in this case the reaction is something.

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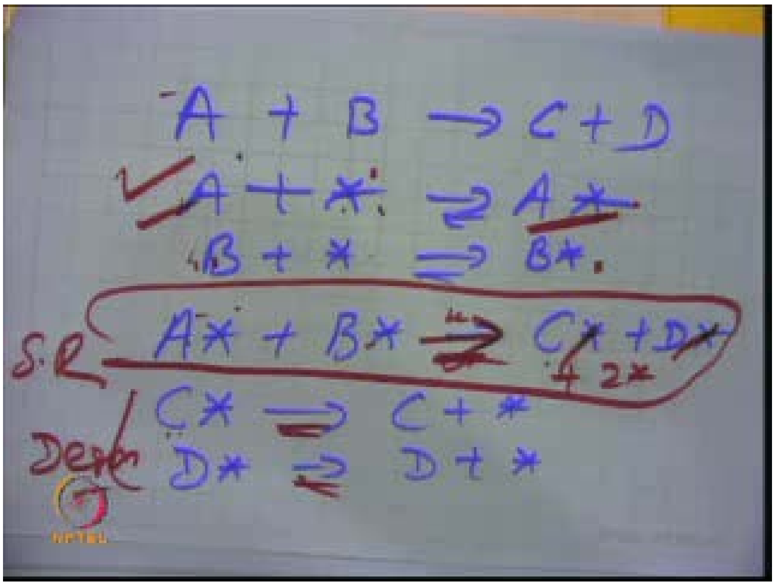

If you look at here that A plus B which is shown some product R say here C. So, A is adsorbing something like this A star, B is adsorbing. So, B plus star gives you B star these may be reversible step right adsorption desorption; and then these adsorbed species are reacting. So, A star plus B star gives you say some kind of C star plus D star like this or I can write it like this also right and then these product will disrobe. So, C star will give you C plus star and D star gives you D plus star which may be reversible, which may be irreversible. So, generally it depends on the rate so one can write like this also right. Now, so there can be several combination as I said this may be rate controlling, this step or this may be rate controlling. So, any one or there may be that 2, 3 steps of the rate reaction may also the rate controlling sometime it may also happen right.

So, you have to write that times pseudo steady state hypothesis that the net rate of formation of intermediate is 0; what you write in your homogenous reaction right pseudo steady state hypothesis. So, here this is the meaning that the competitive adsorption. And, this is here surface reaction they adsorption on of A, this is adsorption of B then there is a reaction between the adsorbs species at the surface. So, surface reaction and then finally, these 2 are the desorption steps; the product is disrobed from the surface. So, also known as bimolecular surface reaction.

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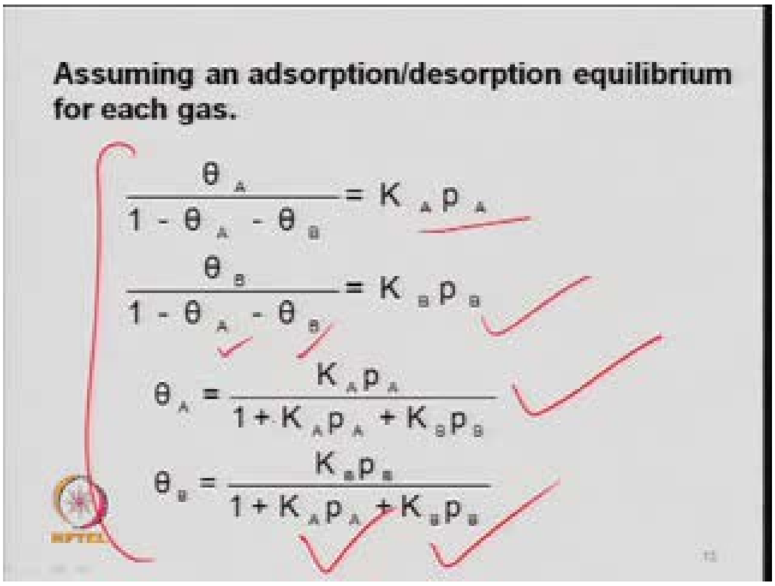

Assuming an adsorption/desorption equilibrium for each gas.

$$\frac{\theta_A}{1-\theta_A-\theta_B} = K_A p_A$$

$$\frac{\theta_B}{1-\theta_A-\theta_B} = K_B p_B$$

$$\theta_A = \frac{K_A p_A}{1+K_A p_A + K_B p_B}$$

$$\theta_B = \frac{K_B p_B}{1+K_A p_A + K_B p_B}$$

So, you can again solve these equation what I said earlier; again the expression for this will be same method, same approach. So, A plus star A star; so just you can write that expression K A times P A times the concentration of vacant site is equal to whatever K desorption types the sites covered by A right. A star means theta A right site covered by a same thing here site covered by B which is equal to here K B times the partial pressure of B times the concentration of vacant site right. Here, it is surface reaction you can consider as a rate controlling step or RDS. Because as I said most of reactions in heterogeneous catalytic reactions are controlled by surface reaction right; that is 80 percent more than 80 percent reaction are controlled.

So, first analysis can be done just based on this; if this is rate controlling this will not be at equilibrium right. So, you have to calculate net rate of reaction just like the K times A concentration of these adsorbed species times the concentration of these species minus the concentration of C adsorb min times the concentration of the B adsorb right just like an elementary reaction rate. So, same thing for desorption so this will a fast and at equilibrium; and this is also a fast and at equilibrium. So, adsorb sites are A B C D as it is shown in this case right.

So, you can have the fraction of the sites which is say total sites which is 1 is nothing but theta A plus theta B plus theta C plus theta D. So, one equation is there and other equation you can generate form the other steps assuming them they are fast and at equilibrium. So, calculate the again the unknown step like the theta A theta B theta C theta D can be calculated and submitted; and this is what here shown in this case right.

So, the first step of the reaction is simply K A P A which is written here right that is written here. And, here in this case it is shown that only A and B are adsorbing; I have made a more general statement here I said that C and D are product species are also disrobing. But here it is just mentioned that A plus B gives you the product species so these 2 steps are not there basically.

So, A star plus B star gives you C plus D and 2 stars something like this you can say right. So, that time these are not disrobed. So, you can have a step something just like this equation. So, this is the meaning here that theta A and theta B. So, only these 2 species are adsorbed. So, site balance is simply your theta A plus theta B plus theta v is equal to 1. So, this is simply representing your concentration of the 1 minus theta A minus theta B is the concentration of the vacant site right. So, theta a upon theta v that is the fraction of the sites covered by A divide by the vacant site and that is what written here in terms of K A P A. So, that is the first step of the reaction in this one right. Because this P A times theta v is equal right or if I write K A times P A times theta v is equal to whatever here is theta A right.

So, the A can be calculated here or you can write the relationship between these 2 this is theta A divide by theta v which is written here right; that is simply K A times P A same thing for B A also. So, K B times P B is defined by theta B upon 1 minus theta A minus theta v. So, that is here. So, one can very easily solve them and theta A is K A P A over 1 plus K A P A plus K B P B you can calculate from the site balance, overall site balance. And, apply this here by calculating the value of theta A and theta B form these 2 equations. So, just solve these two equations for theta A and theta B. So, you will have the theta A and theta B and this just indicates that these are only species which adsorb on the surface. So, they will appear in the denominator.

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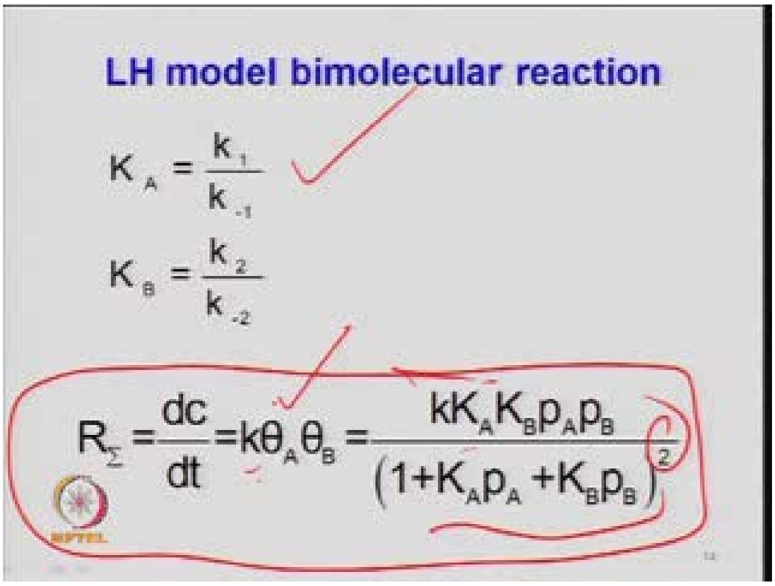

LH model bimolecular reaction

$$K_A = \frac{k_1}{k_{-1}}$$

$$K_B = \frac{k_2}{k_{-2}}$$

$$R_\Sigma = \frac{dc}{dt} = k\theta_A\theta_B = \frac{kK_AK_Bp_Ap_B}{(1+K_Ap_A+K_Bp_B)^2}$$

Equilibrium constant we have already defined K A k 1 upon k minus 1 or k adsorption divide by k desorption; same thing for K B right. So, net rate right of reaction which is here written in terms of the adsorbed rate of A; that is fraction of the sites covered by A times fraction of the times covered by B. Because you are writing a bimolecular surface reaction right which is here third step right.

So, R is equal to K times theta A theta B assuming that step is a reversible right. So, this is what written here right. So, rate of reaction is simply theta A times theta B times the arte constant for the surface reaction. So, it is simply you substitute the value of this theta A and theta B from this from these 2 equations. So, you have finally the expression which is in the form of this k K A P A P A P B divide by 1 plus K A P A plus K B P B whole square right. So, surface bimolecular reaction and surface reaction is rate controlling you get a square here. So, basically what we say here the rate is proportional to some kinetic term this is your kinetic term right k and this is your driving force.

Basically, if the reaction is reversible then it will depend on the concentration of the C and D also you will have P A P B minus P C P D something like that right. So, for reversible reaction. So, that so it is nothing but the how much how far it is the reaction is away from the equilibrium right or that is what you call driving force for reaction. And, same thing here also that in terms of partial pressure; so A and B. So, they are the deciding factor for the reaction right and divide by 1 plus K A P A right. So, these are the adsorption term right. So, in general one can write the rate is equal to the rate constant that the temperature dependent term basically right; kinetic constant times the driving force and divide by the adsorption term to the power n. So, this is one also you have seen in the first case and here it is square.

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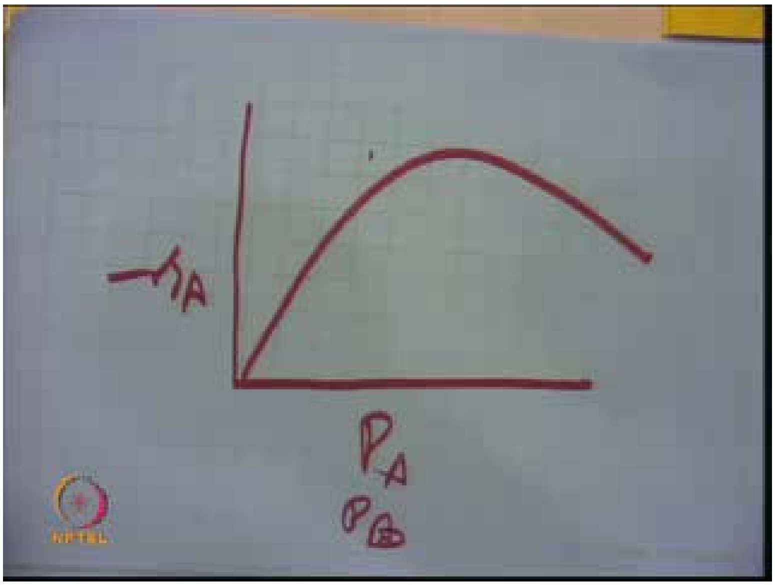

So, that can explain you rate if you get your minus r a as a function of partial pressure and it goes like this right. So, in this case you see here initially it is increasing either you can write in terms of partial pressure of A or it can be plotted separately as ammonia partial pressure of A and partial pressure of B. So, when you are studying partial pressure of A so partial pressure of B constant and vice versa right. So, these curves can be obtained as a function of partial pressure of A and partial pressure of B.

So, here this can just explain the term in the denominator. Because suppose you have a very high pressure right at very high pressure the denominator term if suppose I am just talking here K A P A term. So, denominator term K A P A is much larger compared to the other two term right at high pressure condition. So, that time this will become K A k A K A K B P A P B divide by p s square right. So, denominator it become P B upon P A at very high pressure of A. So, that time your rate will start decreasing right. So, it means you need to tune the partial pressure of A and B to find out the maximum in rate. Because same similar term you will get for effect of partial pressure of the B also right.

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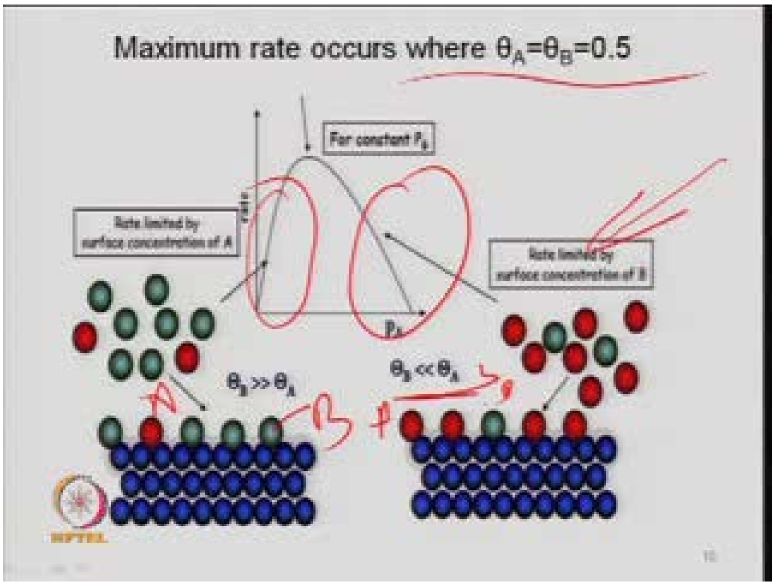

Maximum rate occurs where $\theta_A=\theta_B=0.5$

For constant P_B

Rate limited by surface concentration of A

Rate limited by surface concentration of B

So, this is what the expression shown here and if you just find out a maximization of rate. So, rate will be maximum when the partial pressure of A is equal to partial pressure B or theta A is equal to theta B and value is 0.5 right.

So, this is just the analogy you can very easily find out to find them maximize this slope will be 0 at that kind right or apply your maxima, minima conditions take the derivative. And, set it to 0 and find out the condition for that right. So, what I mean to say here is that this rate expression can be explained based on the whatever you get from experimental data. And, can be postulated based on the mechanism or mechanism can be postulated based on those rate expression data. So, here you can see the rate is limited by the surface concentration of A. So, rate verses partial pressure of a has been shown but very high partial pressure the rate has gone down right almost 0 here. So, this is what the because very high partial pressure means this all the surfaces covered by A right. And, now B is not able to find any activation site right for adsorption. And, when B is not able to adsorb; there will not be any chemical reaction.

So, though surface reaction which you are written A star plus B star and transform into a product that is not possible at this case. So, this is the or there are 2 postulations which have been shown that in this condition the rate is limited by surface concentration of A in this zone. Because the partial pressure of A is low right; when the partial pressure of A is low. Then, your rate of adsorption of B is larger right the more sites of B are covered compared to A. So, limiting component will become this and other site here when you are saying partial pressure of A is very high then B is low. So, that time this is rate is limited by surface concentration of B and this is the meaning here or surface theta B is much more less than theta A right. The fraction surface covered by A is much high. Here in this case if you see here the theta B is much more greater than A. So, this is your B and this is your A right here. So, accordingly your rate of reaction will change right. So, I will continue it next time unless it is mechanism.