Heterogenous Catalysis and Catalytic Processes

Prof. K. K. Pant

Department of Chemical Engineering

Indian Institute of Technology, Delhi

Lecture – 24

Good morning. So, last I was talking about development of rate equation from a mechanism. So, the mechanism is to be hypothesized that is the first thing; and hypothesis is based on the experimental results. You have to do some experiments or some based on that fundamental of the bound theory that which surface or what are the type of surfaces, metal surfaces?

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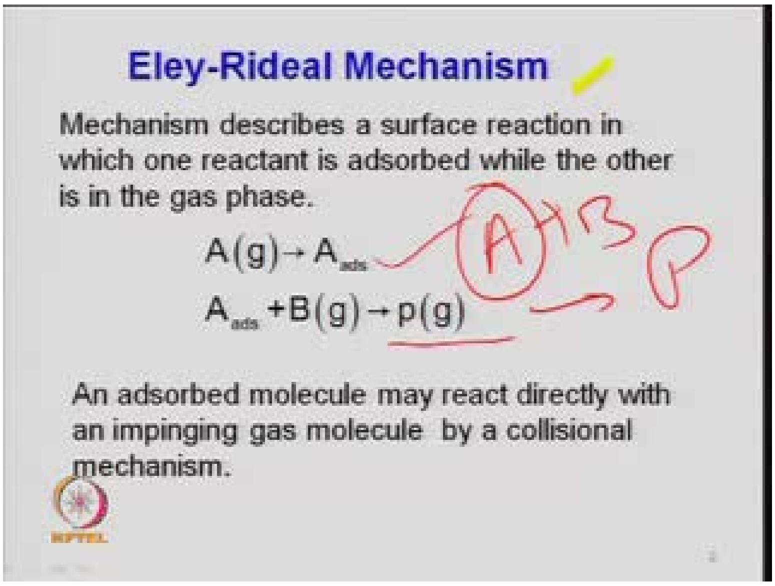

Eley-Rideal Mechanism

Mechanism describes a surface reaction in which one reactant is adsorbed while the other is in the gas phase.

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

$$A_{ads} + B(g) \rightarrow p(g)$$

$$A + B \rightarrow P$$

An adsorbed molecule may react directly with an impinging gas molecule by a collisional mechanism.

And, then how the molecule gas A or depending upon the molecular property of that reactant especially it will adsorb on the surface. So, rate of adsorption or just sticking probability or micro kinetics. So the at the micro or molecular level that is the molecular dynamics of these molecules or kinetics need to be understood first that is the first thing. And, once you know that then one can just suggest a mechanism which is based on certain hypothesis, based on the bound theory.

And, based on certain prispill of the reaction or metal type of the gases; especially though electronic configuration of the molecule what we were discussing during the catalytic, synthesis preparation categorization and the properties of the catalytic material; so all these depends.

And, based on those understanding you need to identify or devise a mechanism. So, we were talking about 2 kind of mechanism for developing a rate. And, there can be other also different researchers have provided some other kind of mechanism also. Basically these are what Ii told last time is a Langmuir Hinshelwood type approach in the second one I was talking a Eley Rideal type of mechanism.

So, in the Eley Rideal type mechanism I told you that one specie is present in the gas phase. So, that is a gas phase reactant. So, A which is a gas molecule reacts with the reactant that is the A reactant adsorbs on the surface of a catalyst which is active site of the catalyst. So, adsorbed A and then adsorbed A reacts with another gaseous phase which is your v and transform it into a product P. So, overall reaction is A plus B transforms to P. So, but A only adsorbs on the surface of the solid B does not adsorb right. So, that is depending upon their molecular theory or molecular kinetics or mechanism of the properties of the gas and the catalyst material.

So, that is to be understood based on a some mechanism that is the molecular reaction aspects. So, fundamentals of those based on bound theory as I said; energy related to the making a chemisorption rate. It should not be very strong, it should not be very week and there should be some optimum concentration of that species. And, then based on the adsorption prispill this will happen.

So, one can postulate both mechanism also that A adsorbs, B adsorbs and then react which will be a Langmuir type mechanism. And, then finally you have to just do some modeling. So, model discrimination and parameter estimation and that is what the overall purpose of this doing the kinetics. And, understanding the reaction mechanism that helps to commercialize the reactor or size a reactor, reactor designing right.

So, this adsorbed species reacts with the gas here in this case Eley Rideal mechanism and transform into a product. So, partial pressure of A, partial pressure of B both will be important when you look at the overall rate expression. So, basically the B is the collision between the molecules right; whether B is colliding with itself or B is colliding with A in the gas phase. And, then comes to the A adsorbed species and then transform into a product which is shown here something like that right here.

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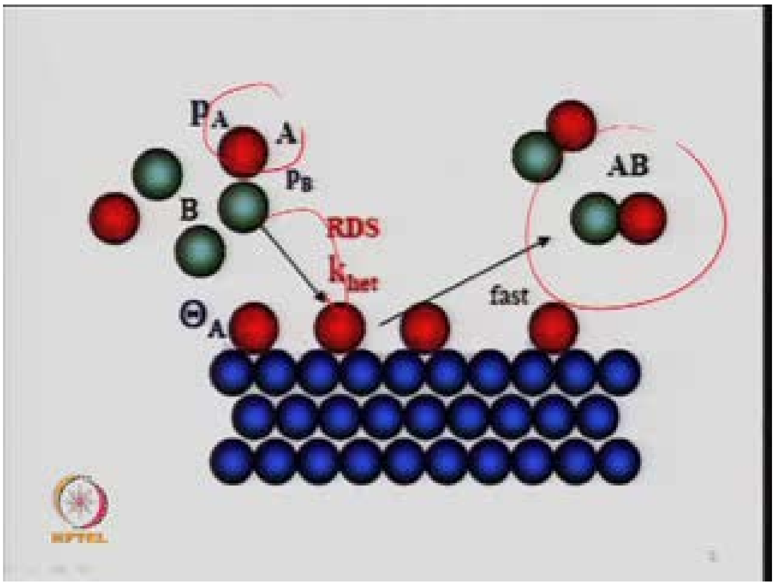

So, your A is this reactant molecule so this adsorbs on the surface B may also adsorb right. But it is a very weak adsorption or the chemisorption but mainly this B comes to the adsorbed A star right so on to this; and here it becomes a rate determining steps. So, this transforms it into a product and that desorbs.

So, here you can say it is not like A plus B A B star it could have been A P star also; right that is the product species may adsorb on the surface and then it detest from the surface. So, there can be a grievous kind of postulation when you device the mechanism. So, here it is directly that eight adsorbs here and immediately it release form the surface in the form of a product molecule.

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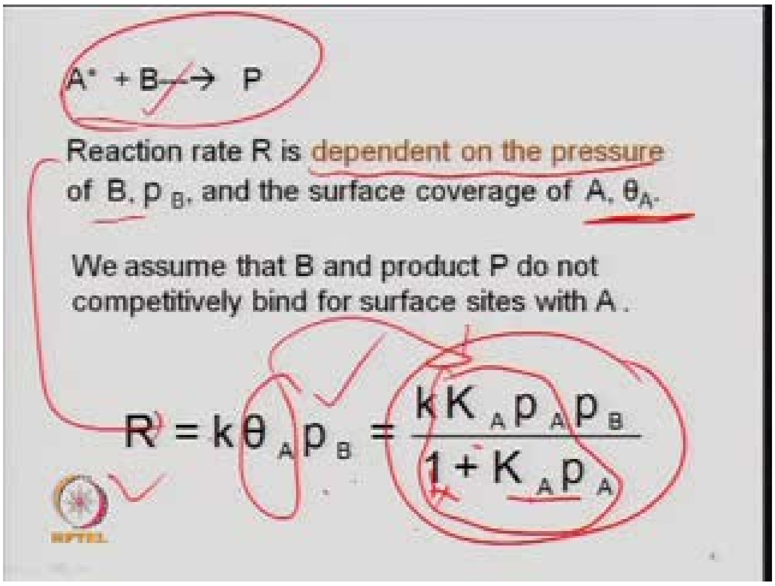

$A^* + B \rightarrow P$

Reaction rate R is dependent on the pressure of B, p_B, and the surface coverage of A, θ_A.

We assume that B and product P do not competitively bind for surface sites with A .

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

So, this is what shown here. So, reaction rate depends on the partial pressure of B as it is mentioned here right dependent on the pressure of B; P B and the surface coverage of A theta A right. So, but theta A will be depending on the partial pressure of A also. Because the you know that rate of adsorption is proportional to the partial pressure and the concentration of the vacant side; that is the concentration of the catalyst or metal species which is present on the surface of a solid. So, this is main in the case of adsorb because if if the more partial pressure of A. But if it is on the surface of the gas on the gas phase there would not be any chemical reaction; the reaction is only when this a adsorbs on the surface. And, then we can interact with that right.

So, we assume here that the B and the product do not competitively bind for the surface sites with A. So, another mechanism or the another mechanism can be devised based on this also that these also adsorbing but it is a weak adsorption. So, generally the species as I said last time also the species which does not adsorb on the surface will not appear in the denominator of that rate equation.

So, or in other words you can say it is weakly chemisorbed. So, weak chemisorbed especially which is strongly adsorbed it will appear in the denominator and that affects the rate right. Now, as you seen here for this kind of reaction your rate will be given by the concentration of the adsorbed species A which is this theta A and the partial pressure of B; just like in your homogenous elementary reaction kinetics the concentration of the reactant species right.

So, here the concentration of adsorbed species A right which is your theta A something like A star right. And, this is the partial pressure of the B which is mentioned here. Now, you have to find out theta A right. So, theta A we have already done this last time. So, you are writing that the step which is fast that will be at equilibrium right; that is adsorption equilibrium if the if you are writing this step something like here. Then, if I am saying that this is not rate controlling.

So, this at equilibrium rate of forward reaction is equal to rate of backward reaction. So, that is their this is simply your adsorption of A. So, one can very easily write down the expression for this which is proportional to the concentration of partial pressure of A times the fraction of the vacant site right. And, other site it is just the desorption because if it is a reversible that will be desorbing from the surface. Then, it is simply the fraction of the surface which is already covered which we have already seen last time.

So, one can very easily substitute this value of theta A and also you know the site balance. So, here there is no question of site balance because only A is adsorbing on the surface. So, just theta A plus theta v is 1 because other species are not adsorbing right. So, for this case this concentration of adsorbed species or fraction of the surface adsorbed A plus the vacant site is equal to 1. So, one can very easily write down the expression and I will just show that little later again.

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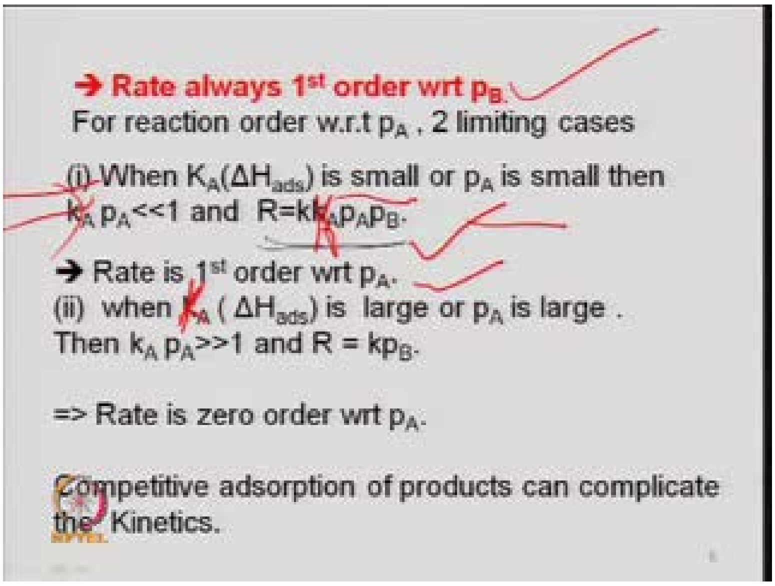

→ Rate always 1st order wrt p_B.

For reaction order w.r.t p_A , 2 limiting cases

(i) When $K_A(\Delta H_{ads})$ is small or p_A is small then $k_A p_A << 1$ and $R = k k_A p_A p_B$.

→ Rate is 1st order wrt p_A.

(ii) when K_A (ΔH_{ads}) is large or p_A is large . Then $k_A p_A >> 1$ and $R = k p_B$.

=> Rate is zero order wrt p_A.

Competitive adsorption of products can complicate the Kinetics.

So, what we have postulated from this? So, because this is K P B and theta A is this thing basically K P A over 1 plus K P A which we have done in the Langmuir adsorption isotherm also right; that is at equilibrium the rate of adsorption is equal to rate of desorption. So, a k adsorption times partial pressure of a right times 1 minus theta A is equal to simply k desorption times whatever the fraction of the A which is already adsorbed on the surface. So, that is desorption is proportional to the concentration of the species which is already adsorbed so theta A.

So, one can solve this and finally it is this expression which has been substituted. So, now if you look at this rate equation where we have said that this is the surface reaction; rate determining step and rate was determined by this. So, one can very easily postulate from here that this rate is always first order with respect to the partial pressure of B this right. So, as you increase the partial pressure the rate will increase from this expression.

So, it means if you have done experiments or if you want to verify the model which you have postulated is correct or not; you can do the experiment in such a way where the partial pressure of A is kept constant. And, you have varied the partial pressure of B right keeping all else constant. All else constant means say rate calculation will be from your convergent versus W by F A naught graph. So, when you do the kinetics or when you generate the data for your laboratory experiment.

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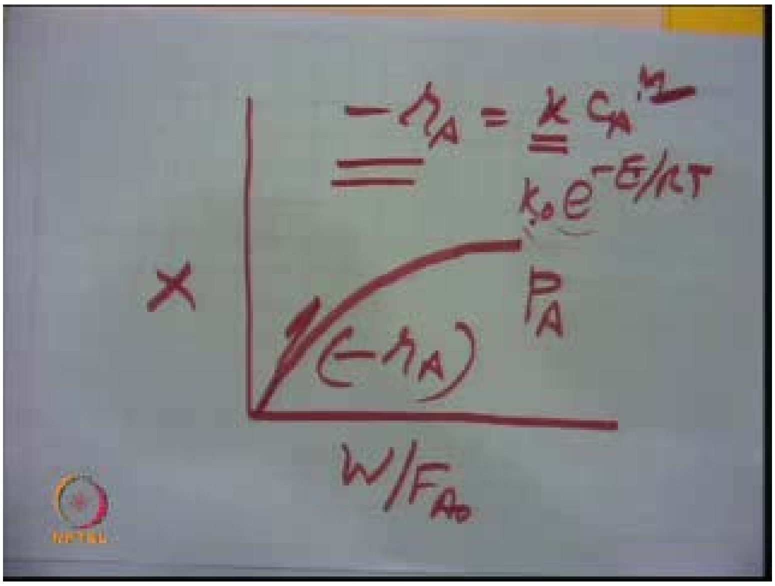

Then, their data will be generated like this right and you will have a data. And, as I advised last time also we should look at the low convergent data less than 15 percent not more than 20 percent something. But desirable within 10 percent because it is a differential reactor assumption right. And, you have to make certain assumption but the equation says like pro condition need to be maintained. So, you have to look at the height of the catalyst bed and that size of the particle also.

So, l by d p it should be more than 50 generally for a plat flow you should not have any axial dispersion right; same thing for you have to avoid the radial dispersion also right. So, radial dispersion again it means you have to look at that diameter of the reactor; and the size of the catalyst particle. So, there are several theories so generally rule of thumb says that a if diameter of the reactor divided by the diameter of catalyst is more than 20 you are safe right.

So, there will be negligible radial dispersion. So, it means you are closer to a plat flow model right. And, then isothermal condition you have to maintain if it varies the endothermic or exothermic reaction then temperature may vary. So, isothermal conditions also need to be maintained and there you can add enough quantities of the inert material right to dissipate the heat like silicon carbide right. So, some heat transferring material which can whatever the heat generates should be dissipated uniformly. So, these are certain experimental guidelines one can control and make the ideal condition for the kinetic study. So, here which is your convergent versus W by F A naught when you do. So, you can have the slope as I said and you get minus r A rate of reaction which is written here.

So, experimentally when you are doing this you need to find out the parameters k K P this is the meaning of model discrimination when you are selecting 4, 5 models. And, identifying the best model based on the regression technique some simulation package can be used for this purpose. And, you minimize the error between experimental and theoretical right that is called objective function. So, you square that because some time error may be positive, some time it may be negative.

So, you just square it. So, that all the time error is positive to minimize that error. And, then one can evaluate the models, parameter and see the error for each model. And, where you have minimum error you can say that that model is closer. So, under certain constraints again that constraints need to be defined. So, the optimization of these model parameters can be done right; because sometimes the different combination may come to the same result also. So, you need to look at the constraints of the parameters of this equation right and under those constraints you can just optimize the parameters. So, just like if you write k is equal to k 0 e to the power minus E upon R T or in this equation.

Then, the k is depending on e and k 0 if I put here minus r A is equal to k C A to the power n suppose the rate is written like this right. So, this k is a temperature dependent term which will be k 0 e to the power minus E by R T right. So, it means the rate dependent on temperature as well as on concentration. So, n if you are your n is also known; then this n k right or n k 0 E these need to be determined.

And, there may be a lot of strong interdependency between these parameters. So, it means if you get some value of n is equal to 10 that is not right; n is equal to 100 not possible order of reaction. So, it means you can define some parameter positioned for this n that n should not be more than 3 something like that right. And, same thing for activation energy if you are looking a kinetic controlled reaction the activation energy should be high. So, more than say 20 kilo joule per mole; so one can put that constant right. So, under these conditions one can regress the data and find out the error function and model.

So, those is the meaning of model discrimination and then select the best parameter. And, look at which does it match with the experimental results for rest of the set of the data. So, that is how this kinetic data is generated and model parameters are evaluated. So, here what the convergent versus W by F A naught is used these data. Then, make it clear that this is at one partial pressure if you are looking here this effect of P B. So, because you are saying that rate gain something like suppose here I am saying linear dependency.

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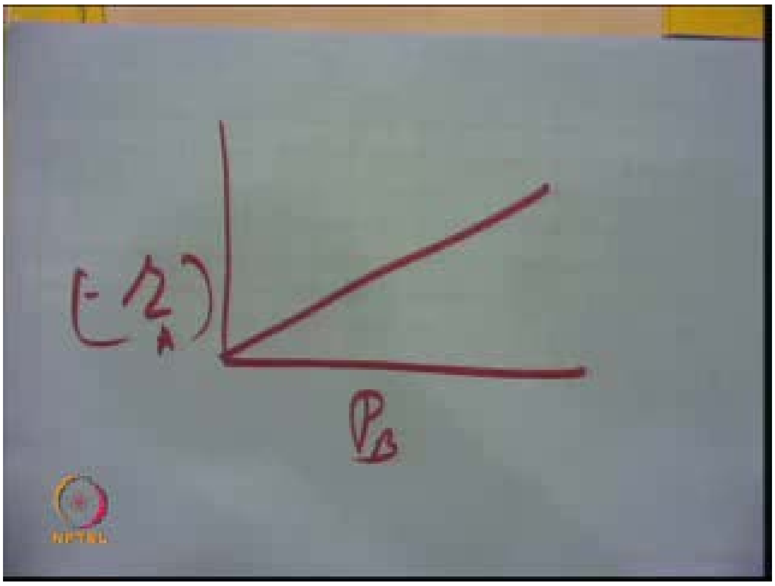

So, it means minus r A versus P B it is this right but under when the partial pressure of is constant. So, if you change the molar flow rate of a right then partial pressure is changing right. You have to adjust either by using some inert or you just make the total pressure of the system constant. And, then change the partial pressure of B and then add inert accordingly in such a way that the partial pressure of A does not affect the rate. And, since you change the flow rates W by F A naught may change if you have same mass of the catalyst inside the bed.

So, again you need to readjust your mass of the catalyst also. And, that is again under the constant as I said before that mass transfer should not control the rate; it should not affect. So, your velocity linear velocity of the bed should always be higher than whatever the minimum flow rate you have decided; superficial velocity. So, mass transfer has to be eliminated because these are the kinetic parameters right; no effect of mass transfer, no effect of internal diffusion into in a pore of a catalyst.

So, you need to identify. So, as it is mentioned here that the reaction rate is dependent on pressure of B, P B and the surface coverage of A. So, this is what your theta A right and we devised this thing. So, first order with respect to B that is keeping the partial pressure of A constant and one can postulate it experimentally. And, that is why one can say that B is not in the denominator because rate is always increasing with the partial pressure of B. So, it is not adsorbed on the surface. And, the meaning again is that K A adsorption equilibrium constant right which is again related to heat of adsorption right. If you have done some t p d studies right or temperature program study you can find out the heat of adsorption right delta H adsorption.

So, and then from the thermodynamics one can calculate this equilibrium constant k. So, amount of equations can be used here right d over d t of L n k is equal to minus delta H upon R T square. So, one can find out this equilibrium constant because delta H is known now right. So, this delta H adsorption or k either you say this or k heat of adsorption or equilibrium constant for A; if this is a small right either or P A is small.

So, I am talking these 2 terms here now right; this is your equilibrium constant for adsorption. And, that is related to your delta H heat of adsorption right because from heat of adsorption you can calculate that the K A. So, this either K A or P A so for small values of K A P A if you look at here than this one is larger compared to K A P A right.

So, in that case your K A P A is much more less than 1. So, K A P A much more less than 1 and in that case your rate becomes simply k times K A P A P B. So, this is basically K just a minute. So, for this case your rate here this denominator term because this value is much more less than 1 when your either K A is very small right or P A is very small or the combination of the these 2 is very small compared to 1. So, this is neglected.

So, your rate is simply k times K times P A P B and that is the term which is shown here. So, this is K adsorption equilibrium constant right capital K A P A P B right this will happen when low partial pressure of A or if heat of adsorption is very small. So, this is this K A is basically a thermodynamic parameter and will depend on the temperature right; as you know heat of adsorption changes. So, the rate is first order with respect to A in this case. So, at low partial pressure of A what I mean to say here right at low partial pressure of A also the rate is proportional to the first order; that what we have seen yesterday also for the Langmuir Hinshelwood case.

The second case when this value this K A which is your adsorption equilibrium constant here K A delta H adsorption is large or P A is large. Then, this denominator K A that will become much more larger than 1. So, you can neglect 1 in that case right and then this K A P A K A P A gets cancelled. And, your rate becomes something like K times P B right just it is depending only on the partial pressure of B independent of the partial pressure of AA that is at high pressure of A.

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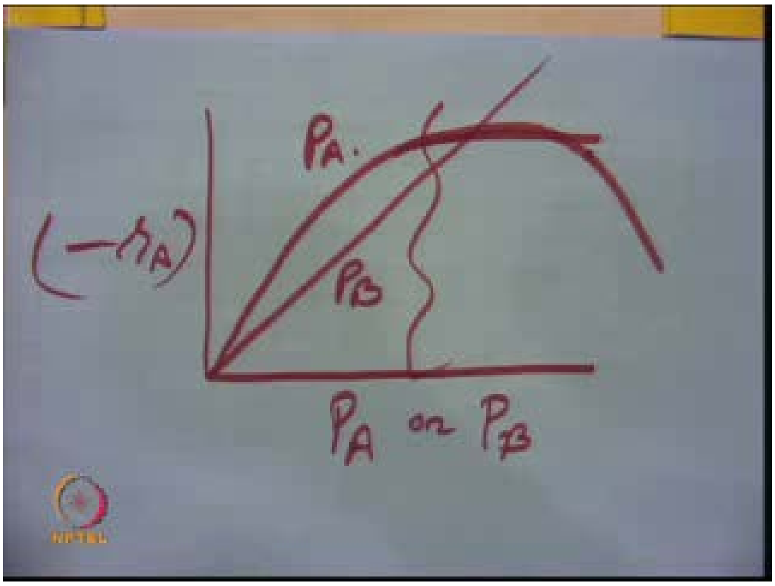

So, it means if I have the experimental data so one can very easily postulate the mechanism by doing the experiments right. So, your minus r A versus P A that is one set of data when P B is kept constant that data went like this. So, at high partial pressure of B it is independent of this right P A right. And, at low partial pressure it is changing linearly where as for P B if you plot so P A or P B if I look at here; then it will always be something like this.

So, effect of partial pressure of B is like this, effect of partial pressure of A is like this. So, one can postulate that with B so B is not appearing in the denominator. Because it is not decreasing the rate where A at high partial pressure of A the rate becomes a constant value. So, it means something is there that A is adsorbing on the surface. And, at when the pressure is very high or concentration is very high then this rate becomes independent of partial pressure of A. And, suppose I had a square term in the denominator it will go like this right; similar term what we have seen last time.

So, one the basic idea the question may arise that how do we postulate this mechanism? But we are postulating here how do we confirm that; you can confirm by carrying out the experiment right or you can confirm by doing some simulation molecular simulation right or these are software tools are available; nowadays to confirm them right born energy data are available which can talk yes when you have a gas molecule. And, this reactant molecule and this is the metal precursor platinum there will be the adsorption right. Say one can easily say hydrogen is strongly chemisorption platinum; right oxygen can chemisorb on silver like that right.

So, means these theories are already well established or can be the further experiments can be done like this characterization technique; by which one can identify that whether this kind of adsorption is possible or not. And, this is what the theory also behind how to select a best or most appropriate metal for a given reactant species right.

So, rate is here in this case if you look at it seems to be a zero order with respect to the partial pressure of A; independent of the partial pressure of B what you call zero order reaction right. So, it means the competitive adsorption or the product can complicate the kinetics. So, sometimes it may happen that A is adsorbing, B is adsorbing and the product may also adsorb right. Now, I have not talked anything about the adsorption of the product right.

But it may happen that the product which forms during the reaction; it adsorbs on the surface of the catalyst. And, then further it desorbs. So, when it desorbs it may just release the surface that may be one possibility that product is species itself desorbs. And, comes out as a product or it may react with some other reactant species. And, transform it into a second product different product that will be a kind of secondary reaction right. And, this may be an undesired reaction also like a multiple reaction happens right.

So, if you look at the mechanism so there may be more than 100 reactions possible; 100 possible reactions for one reaction just like in a cracking more than 200 reactions have been identified right; more than 200 products are identified; and still several are yet to be identified. So, mechanism becomes very complex for these kind of hydro carbon reaction and depending upon the surface of the solid. So, when you diagnose a mechanism whether it is Eley Rideal type or the Langmuir Hinshelwood type the approach is similar.

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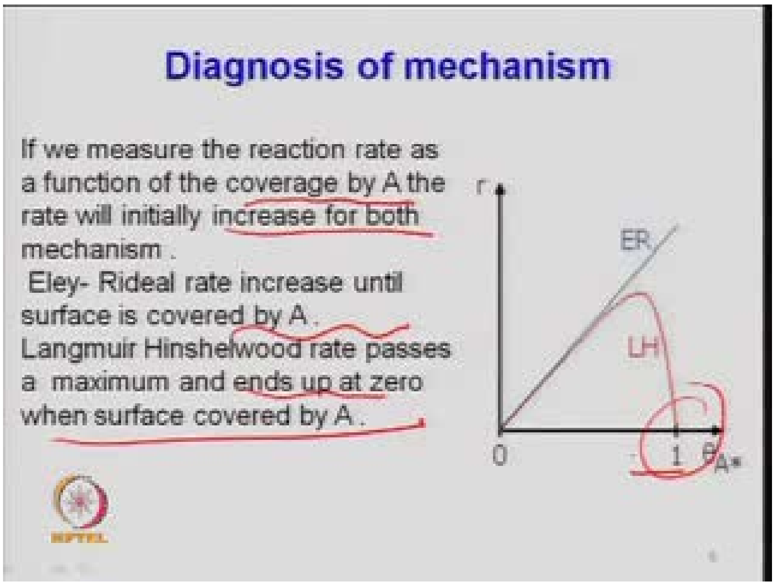

Diagnosis of mechanism

If we measure the reaction rate as a function of the coverage by A the rate will initially increase for both mechanism .

Eley- Rideal rate increase until surface is covered by A .

Langmuir Hinshelwood rate passes a maximum and ends up at zero when surface covered by A .

You have to postulate the mechanism right depending upon some basic fundamentals of the chemistry, surface science and molecular structure. And, then you have to just give certain hypothesis right. So, if we measure the reaction rate as a function of surface coverage the rate will initially increase for both the mechanism. So, whether it is Eley Rideal type mechanism or Langmuir.

So, you could have postulated a Langmuir Hinshelwood type mechanism also right where A adsorbs and B adsorbs. And, then these two desorbs right and transform to the product species. So, Eley Rideal mechanism it says that it is increasing with the partial pressure of A right and so it is increasing as the surfaces covered by A. So, when the surface is totally saturated than your rate will go like this right r A is equal to K times P A times theta A what we have written here right. So, when the surface is completely covered then effect of A is not there right.

So, Langmuir Hinshelwood rate passes a maximum and ends up to 0 when the surface is covered by A. So, in the Langmuir Hinshelwood hypothesis the adsorbed species will appear in the denominator right because A is adsorbing. So, this appears in the denominator. So, it will finally come to a value which is surface is totally covered right. So, in that case this the maxima rate passes and max rate passes to a maximum. And, finally it end up to a 0 when the surface is completely covered here right. So, theta A star it is written here so that is the fraction theta a covered by a plus the vacant side is 1 right. So, when the surface theta A itself is 1vacant sides are not there right.

So, this may happen when you have poison precursor. So, effect of poison precursor it will completely cover the surface but it will not desorb from the surface. So, that is the complete deactivation of the catalyst. So, the basic idea is that when you have a surface coverage something like this; what we have seen here the species which adsorb on the surface.

So, the partial pressure of A becomes important right. Because higher the partial pressure more will be the surface coverage; this is your theta A fraction of the A covered right. And, when the surface is totally covered but when I am saying this theta A becomes 1 it approaches to 1. And, this will approach to 1 when this number K A P A and the denominator number K A is larger. So, ultimately this becomes 1. So, R is simply K B what you have seen right partial pressure of B.

So, it means you can presume that the A has no role now right already the sites have been covered right at very high concentration or high partial pressure of A. So, that becomes important when you postulate a mechanism given mechanism. So, this Langmuir Hinshelwood rate will go some kind of maxima here in terms of the partial pressure of A when you look at that.

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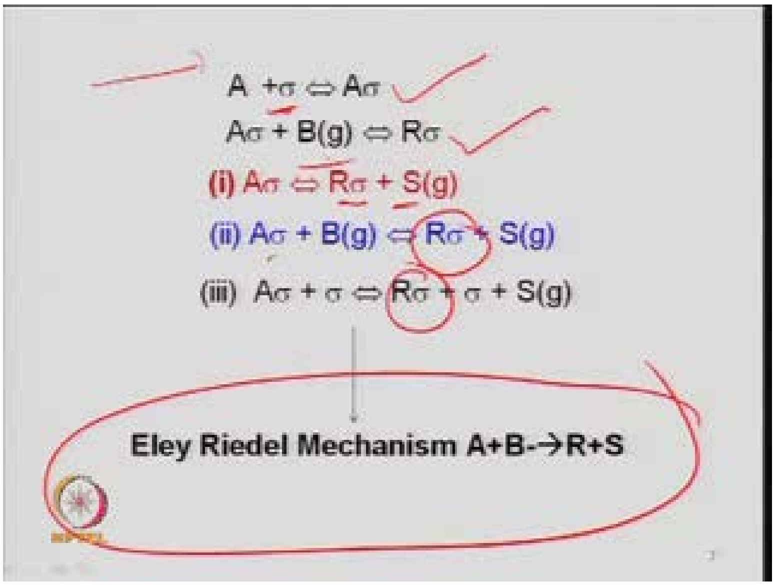

$A + \sigma \Leftrightarrow A\sigma$

$A\sigma + B(g) \Leftrightarrow R\sigma$

(i) $A\sigma \Leftrightarrow R\sigma + S(g)$

(ii) $A\sigma + B(g) \Leftrightarrow R\sigma + S(g)$

(iii) $A\sigma + \sigma \Leftrightarrow R\sigma + \sigma + S(g)$

Eley Riedel Mechanism A+B-→R+S

So, just again we have discussed the similar step but for exercise A is adsorbing on some sites sigma this is some A sigma. So, a reaction which is here and we are just assuming that the product also has some role on the surface generally here. So, far what I have said is that A adsorbs which is a reactant species B is also adsorbing reactant species. But when they react together they can directly transform into product species right. But what happens when these products also adsorbs on the surface? So, there can be a different kind of models of postulations of that for a given reaction on a surface of the solid.

So, A adsorbs on the surface this is a sigma B then A sigma reacts with gas molecule which is your and gives you R sigma. So, basically this is your Langmuir sorry Eley Rideal type mechanism because this is in gas adsorbed species. And, this is a gas phase and this gives you R sigma right not the R plus sigma. The another possibility can be that it gives directly you some product R and the site is vacated right. So, second the there can be the multiple option which have been written here a kind of models which may be possible and depending upon the theory right. So, A sigma it gives you the R sigma plus F. So, both are product and R sigma will desorbs A sigma will react with B in the gas phase. And, then again it gives you the R sigma and S another step. Then, it can also be A sigma reacts with another site on the surface right. So, the mechanism which you see here it can be a single side or dual side mechanism.

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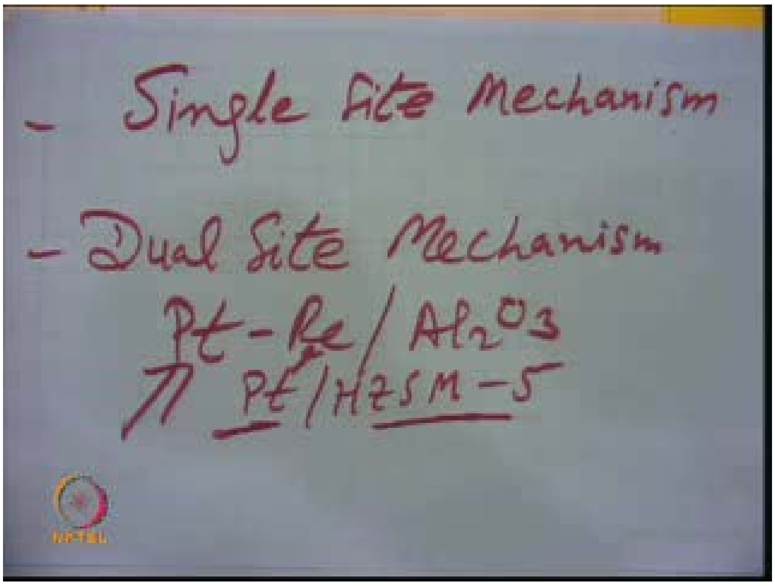

- Single Site Mechanism
- Dual Site Mechanism

$Pt-Re/Al_2O_3$

$Pt/HZSM-5$

So, single site mechanism; and second one is dual site mechanism with a single site adsorption site takes part for chemisorptions. It is known as single site mechanism right. And, when 2 types, 2 different kind of sites take part during the reaction it is known as dual site mechanism. So, it may happen sometimes suppose you take a bi metallic catalyst platinum rhenium on alumina or time you have just say some platinum on H Z S M 5. So, there some metal function and some acidity function right. So, certain reactions when you have bi functional some time we call it bi functional catalyst.

So, the catalyst metal part may have some role it may promote your hydrogenation activities or platinum here right or dehydrogenation activity. But the acidic site it may do the cracking job right the they promote a cracking reaction right or some isomerization, hydro isomerization is these case the platinum and the metal site and acid functions have too different. So, these are known as bi functional catalyst or similarly there can be multi functional catalyst also; where you have certain promoters which can remove the coke from the catalyst or which can reduce the coke on the catalyst.

So, this that so the active site in a catalyst we are talking in terms of these or whatever the acid sites of these supports. So, when I am saying that these adsorption is happening on some sites; it means those active sites right. Those active site means on the metal surface there is platinum which is dispersed, there is some kind of rhenium which is dispersed. So, some gas species may have the more chemisorption tendency towards the platinum site. The second kind of gas species may have chemisorption towards the alumina site it may happen.

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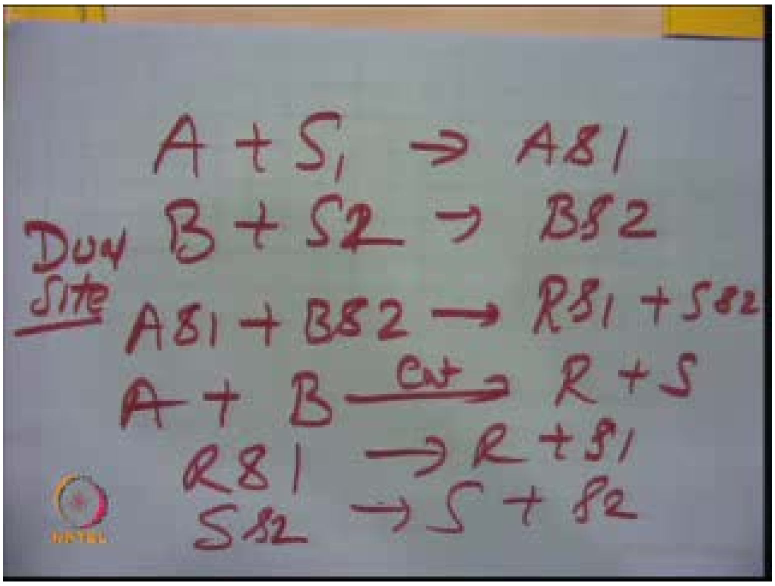

Dual Site

$$A + S_1 \rightarrow As_1$$

$$B + S_2 \rightarrow Bs_2$$

$$As_1 + Bs_2 \rightarrow Rs_1 + Ss_2$$

$$A + B \xrightarrow{Cat} R + S$$

$$Rs_1 \rightarrow R + s_1$$

$$Ss_2 \rightarrow S + s_2$$

So, these kind of when I write it something like this that A plus S 1 gives you A S 1 right. And, B plus S 2 gives you B S 2 something like this a dual kind of site 2 type; 2 different kind sites are available on the surface of the solid. And, then these two A S 1 plus B S 2 reacts and they give you R S 1 plus S S 2 something like this; where R and S are your products.

So, reaction is something like this A plus B over rate a catalyst transform to R plus S. So, this R S 1 now will disrobe and giving R plus S 1 site is free. So, I will write these small concentration here sites in terms of A S 1 if I write just to avoid the confusion bit between S and s. So, s is your some site right here. So, this R S 1 will give you R plus S 1 and S s 1 will give you S plus s 1 s 2; S s 2 S plus s 2. So, these finally these sites are vacant right.

So, 2 different kind of sites or a bifunctional catalyst which takes part during the with bifunctional catalyst on which the reaction takes place. So, in that case these kind of reaction mechanism is basically a dual kind of site; dual site mechanism 2 different kind of sites are available on the surface and then the reaction takes place. So, that is one important aspect when you have a bimetallic catalyst or bifunctional catalyst. But when you write a site balance you can write site balance for s 1 type of site, you can write the site balance for s 2 type of site; you know that what is the percentage of platinum is incorporated and what is its dispersion? What is the concentration of rhenium is added, what is its dispersion? So, concentrations of these active sites are known right.

So, the site balance for s 1 type, site balance for s 2 site. And, then you can write the same expression what you have derived before similar expressions not same. So, this kind of mechanism is a dual site mechanism. So, it means when A is adsorbing, B is also adsorbing on the site right then the or then also its kind of that A is adsorbing on one site A S 1; B is adsorbing on two second site. And, then there reaction takes place right and when the something like this also we are say said here that it is a sigma same site the A is adsorbing, B is adsorbing. So, two reaction are taking place on the similar site right and one can postulate the rate equation. So, what I have shown here these can be the possibilities during the reaction or mechanism postulation.

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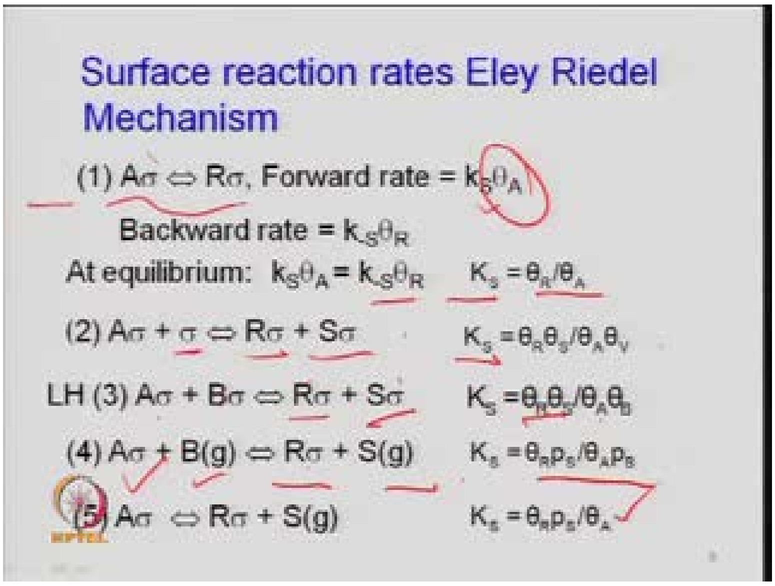

Surface reaction rates Eley Riedel Mechanism

(1) $A\sigma \Leftrightarrow R\sigma$, Forward rate = $k_S\theta_A$

Backward rate = $k_{-S}\theta_R$

At equilibrium: $k_S\theta_A = k_{-S}\theta_R$ $K_s = \theta_R/\theta_A$

(2) $A\sigma + \sigma \Leftrightarrow R\sigma + S\sigma$ $K_s = \theta_R\theta_S/\theta_A\theta_V$

LH (3) $A\sigma + B\sigma \Leftrightarrow R\sigma + S\sigma$ $K_s = \theta_R\theta_S/\theta_A\theta_B$

(4) $A\sigma + B(g) \Leftrightarrow R\sigma + S(g)$ $K_s = \theta_R p_S/\theta_A p_B$

(5) $A\sigma \Leftrightarrow R\sigma + S(g)$ $K_s = \theta_R p_S/\theta_A$

So, just to look at that how the what the species which is adsorb on the surface of the catalyst how does it affect the rate? So, as I have already told you that the species which adsorb will appear in the denominator; in one way you can say that the species which is strongly chemisorbed will appear in the denominator. So, this suppose you have the expression like this where A sigma gives you R sigma; some adsorbed species A plus sigma transforming into A sigma. And, then A sigma is transforming to R sigma.

So, again this is a kind of a surface reaction. Because this reaction is taking place on a surface of a catalyst right adsorbed species; that is why this is known as surface reaction.

So, rate of forward reaction now it is simply the surface reaction rate constant times the concentration of the sites which are covered by A here right; theta A rate of backward reaction desorption of R sigma can also be possible. So, backward reaction rate is K minus S times the concentration of the species adsorbed by R. So, then these two are at equilibrium just like as I said earlier the rate of forward reaction is equal to rate of backward reaction or what you say in the pseudo state also the net rate of formation of the intermediate is 0; that is in homogenous kinetics you say.

So, here this the meaning of equilibrium what I am saying that its rate divide by its adsorption coefficient is K; that is the rate adsorption is very fast. It is a very fast reaction not controlling the rate right. So, this K S into theta A is equal to K minus S into theta R. So, one can very easily find out because K S divide by K minus S is your equilibrium constant for surface reaction.

So, K S is theta R divide by theta A right but remember this will happen only when this is very fast, this is not controlling the rate. If this step rate controls then your net rate of reaction will be written K S times theta A minus K minus S theta R. So, when this is at equilibrium very fast; then your rate of forward reaction equal to rate of backward reaction. So, K S is equal to theta R divide by theta A that is the sides which are covered by R divide by the sides which are covered by A.

The second postulation if A sigma reacts with another site on the similar kind of site this can be a different site also; as I said s 1 and s 2 that will be dual kind of dual set mechanism. So, here it is on identical sites. So, A sigma plus sigma it transform into R sigma and S sigma right sigma plus S sigma. So, in that case again your if it fast and at equilibrium; so rate of forward reaction equal to rate of backward reaction. So, that is basically here if you say K S times theta A sites covered by A times and this is vacant site theta v right is equal to this whatever the minus of this K minus S times concentration of adsorbed species theta R times theta S.

So, if this is at equilibrium then your adsorption equilibrium constant for S is defined by theta R times theta S divide by theta A divide by theta B; just like you define your adsorption equilibrium constant in thermodynamics say concentration of these species. Same thing in the case of suppose it is Langmuir type of adsorption isotherm K sigma which adsorbs. And, then again B sigma which is again adsorbed and then these 2 reacts and transform into the R sigma and S sigma. So, here again you can define can K S which is theta R times theta S these 2 adsorbed concentration divide by theta A times theta B. So, this there can be different postulation and another one A sigma and this is your Eley Riedel reacting the gas phase transform into R sigma and S so K S again for this can be defined in terms of theta R.

So, P is in gas phase; so it will be partial pressure of the gas here right. So, P S and divide by theta adsorbed and P is in gas phase so partial pressure of D right. And, finally another one can be A sigma gives R sigma plus S. So, here K S is theta R times P S divide by theta A. So, it means one has to identify the reaction step and then define the rate. And, then also decide which step is the rate determining the others will be fast or at equilibrium. So, here just shown that if they are at equilibrium how the rate or equilibrium constant will be defined.

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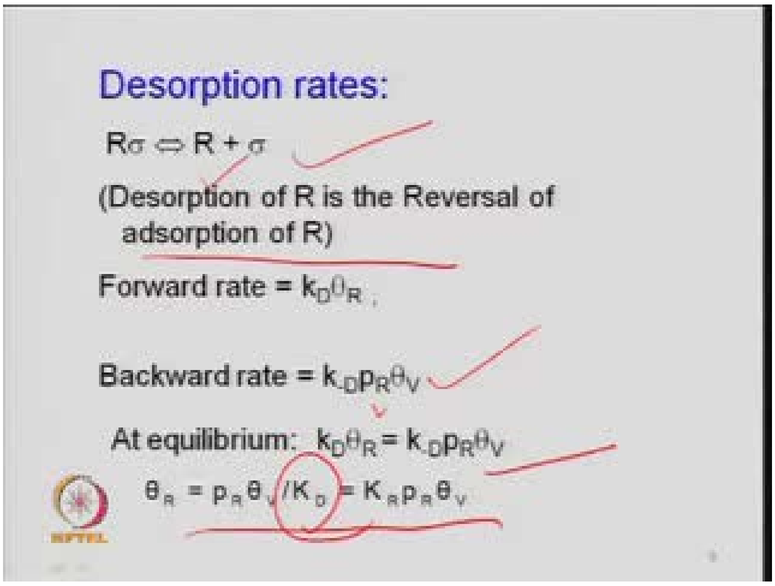

Desorption rates:

$R\sigma \Leftrightarrow R + \sigma$

(Desorption of R is the Reversal of adsorption of R)

Forward rate = $k_D\theta_R$,

Backward rate = $k_{-D}p_R\theta_V$

At equilibrium: $k_D\theta_R = k_{-D}p_R\theta_V$

$\theta_R = p_R\theta_V/K_D = K_R p_R \theta_V$

So, for the desorption because R is desorbing. So, your R sigma will give you R plus sigma. So, desorption of R is the reversible of the adsorption of R which we have already shown and discussed. So, forward rate K D times theta R, backward rate K minus D times partial pressure of R and the vacant site concentration. So, basically I have already talked this R plus sigma is R sigma. So, here just shown in the reversible but otherwise because it is a reversible. So, the what you got before same here. So, K D into theta R is equal to K minus D times partial pressure of R times the v right.

So, theta R can be calculated in terms of partial pressure of R times theta v which is vacant site concentration divide by K D. And, that rate of adsorption if you look at right that is equilibrium constant for adsorption will be one upon the equilibrium constant for the desorption that is another thing. So, what is written here in terms of K D right.

So, 1 upon K D is your what you have seen earlier for the forward reaction; so that is here right. So, that is adsorption and desorption both are identical in that way the that the R sigma which is written R plus sigma here right. And, I have not shown it here but basically what I am saying that if I write R plus sigma is equal to R sigma right that is adsorption of R. And, when I write R sigma is R plus sigma that is desorption of R. So, equilibrium constant for adsorption is reciprocal of the equilibrium constant for the desorption of the same step.

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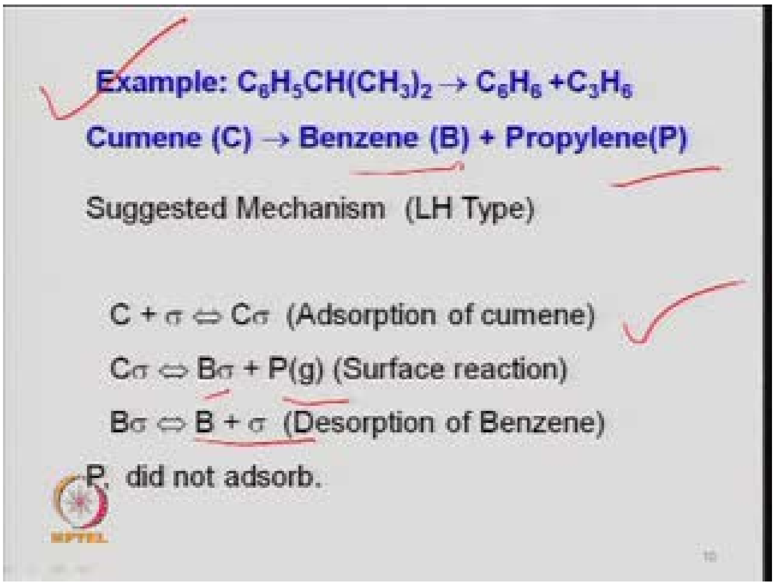

Example: $C_6H_5CH(CH_3)_2 \rightarrow C_6H_6 + C_3H_6$

Cumene (C) → Benzene (B) + Propylene(P)

Suggested Mechanism (LH Type)

$C + \sigma \Leftrightarrow C\sigma$ (Adsorption of cumene)

$C\sigma \Leftrightarrow B\sigma + P(g)$ (Surface reaction)

$B\sigma \Leftrightarrow B + \sigma$ (Desorption of Benzene)

P. did not adsorb.

So, just to explain the terms here an example has been taken for cumene right isopropyl benzene which is one of the important petrochemical rough material. And, can be used for producing benzene and propylene right. So, this is isopropyl benzene a aromatic ring compound right transforms to benzene and propylene right over some constant right. So, cumene C gives you benzene I have just given B benzene as B and propylene as P right. So, mechanism which can be suggested based on the experimental data some information's have been observed that propylene does not adsorb. Because rate is proportional to the propylene partial pressures. So, propylene does not chemisorb on the surface; that is one thing. So, there are certain postulations which have been observed during the experiment. And, now the mechanism is revised right.

So, the mechanism which is something like here first cumene adsorbs on the surface of a catalyst. And, gives some adsorbed cumene right adsorption of cumene this is the first step. Then, this adsorbed cumene transform into some adsorbed benzene and the propylene which is not adsorbed directly the cumene. And, the on the surface of the catalyst which is adsorbed transform into a benzene propylene which will go into the gas phase. And, benzene which is some adsorbed benzene on the surface. And, finally this benzene disrobes and gives you the product benzene and the site is vacant right. So, propylene does not adsorb.

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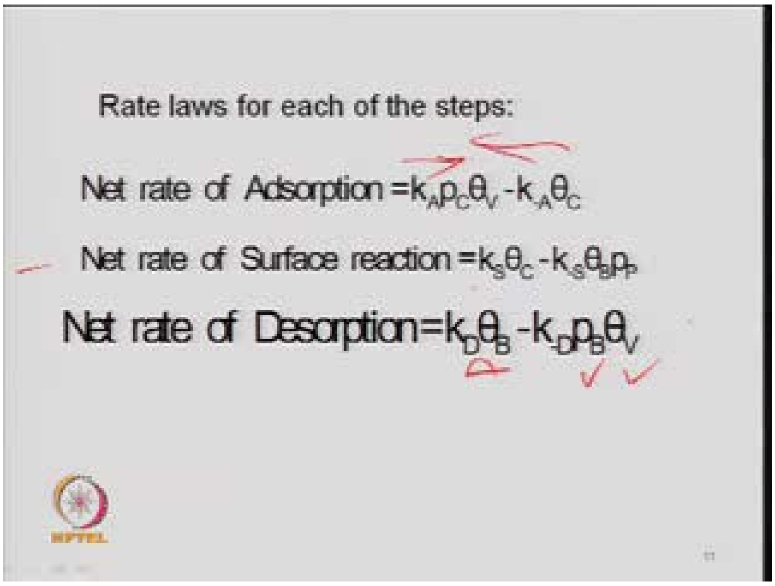

Rate laws for each of the steps:

Net rate of Adsorption $=k_A p_C \theta_V - k_{-A} \theta_C$

Net rate of Surface reaction $=k_S \theta_C - k_{-S} \theta_B p_P$

Net rate of Desorption$=k_D \theta_B - k_{-D} p_B \theta_V$

So, these is just an example problem where to clarify or how to get the expression or finally get the model discrimination or identify the parameters of the model. So, rate laws can be defined for each step. So, general rate law that net rate of adsorption of A I am not saying that they are faster at equilibrium. So, net rate of das of A right. So, for this is first reaction adsorption of A. So, rate of formation of this adsorb cumene which is nothing but rate catalyst for the forward site multiplied by the partial pressure of cumene times the concentration of the vacant site right; that is the forward site reverse is C sigma transform into this. So, rate is proportional to the concentration of the adsorbed cumene site. So, this rate constant times the partial pressure of cumene times the concentration of vacant site minus the desorption rate constant times the concentration of adsorbed cumene right; that is net rate of adsorption of cumene which has been shown here right.

So, K A times the partial pressure of cumene times the concentration of vacant site right forward reaction rate. So, this is reaction in the forward direction and this K minus A which is desorption rate constant times the concentration of the sites which are already adsorbed by cumene. So, by cumene is being this job; so that is the reverse reaction rate. So, net rate is the just like in reversible reaction for the homogenous system you write. So, rate of forward reaction minus rate of the backward reaction these are net number of molecules of cumene adsorbed. And, when you say that this is very fast and at equilibrium; then this should be 0; net rate of adsorption is 0 at equilibrium right.

If none of this step is rate controlling as I said before also then you have to make the overall that is at steady state net rate of formation of intermediate will be 0. So, here the reaction is very fast and at equilibrium one can write the rate of forward reaction is equal to rate of backward reaction. Similarly, for surface reaction so second one is your surface reaction here. So, concentration in this is your forward site of the reaction will be proportional to the concentration of C sigma which is your adsorbed species. And, reverse site this is depending on the concentration of adsorbed B like theta B and the P is in gas phase. So, partial pressure of P right.

So, here it will become K S times theta C the concentration of cumene which is adsorbed minus reverse reaction which is K minus S times the concentration of adsorbed benzene times the partial pressure of propylene. So, this is net rate of surface reaction. And, if I say surface reaction is rate controlling this step will be written as the rate controlling and other two will be written very fast. And, these two will be at equilibrium and then you can find out theta B theta C using these two right. And, net arte of desorption for the third one desorption step here B sigma benzene which is adsorbed now will disrobe.

So, rate of benzene desorption is nothing but the rate constant in the forward direction times the concentration of the benzene which is adsorbed theta B right minus the desorption step that is the site. So, that will depend on the partial pressure of the benzene and times the concentration of the vacant site. So, this is written here. So, K D rate constant for desorption of benzene times the concentration of the benzene which is already adsorbed. Because desorption will depend on those concentration and minus K minus D which is the reverse reaction rate constant times partial pressure of benzene times the vacant site. So, any step can be rate controlling right and other rest can be assumed as a they are at equilibrium right. So, one can postulate the overall rate. So, here we are just shown the different step case by case.

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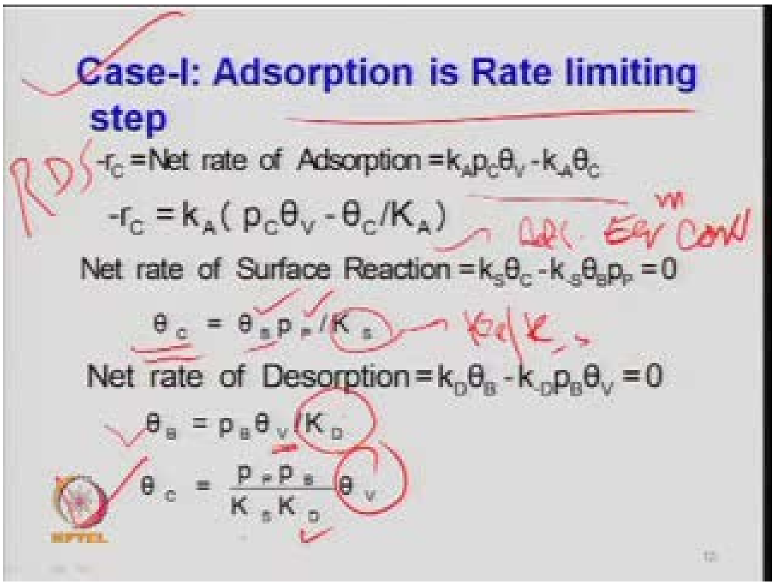

Case-I: Adsorption is Rate limiting step

$-r_C$ = Net rate of Adsorption $= k_A p_C \theta_V - k_{-A} \theta_C$

$$-r_C = k_A (p_C \theta_V - \theta_C / K_A)$$

Net rate of Surface Reaction $= k_S \theta_C - k_{-S} \theta_B p_P = 0$

$$\theta_C = \theta_B p_P / K_S$$

Net rate of Desorption $= k_D \theta_B - k_{-D} p_B \theta_V = 0$

$$\theta_B = p_B \theta_V / K_D$$

$$\theta_C = \frac{p_P p_B}{K_S K_D} \theta_V$$

So, first may be that it adsorption is rate controlling as I said that model discrimination right and parameter estimation. So, you have suggested a mechanism. So, mechanism suggested is like this the first step hypotheses a mechanism based on some experimental clue. And, then you had just written the rate expression because assuming that each step is at elementary step. These steps are assumed elementary step of the reaction right. So, and then now we are postulating that there may be 3 post possibility; the system may be rate controlling or this system may be rate controlling or this step may be rate controlling right 3. So, either one is rate controlling or second or the third right. So, is you have to take 3 different cases; if 1 is controlling then these 2 will be very fast and at equilibrium right and so on so on.

So, you can develop the model and then finally evaluate the parameter. So, this is what I am doing here. So, the first one is the adsorption as the rate controlling step. So, if your adsorption is rate controlling then your net rate of disappearance of cumene; that is the adsorption is given in the first step here because this is the rate controlling now. So, by overall rate of reaction will be given by this expression right in the first case. So, here partial pressure of cumene is known parameter. But theta v is concentration of the vacant sites which is not known. You have to find out in some of known parameter same thing for theta C is not known. So, that can be determine by using this 2 right. So, because they are fast and at equilibrium. So, this has been done here so rate of adsorption which is written here.

Now, you can take K A out; so this is becomes P c times theta v minus theta c times K A divide by K minus A right. So, this is basically 1 upon K adsorption equilibrium constant. So, this is the equilibrium constant now right rate of forward reaction divide by rate constant for the forward reaction divide by rate constant for the backward reaction. And, that is the definition of adsorption at equilibrium constant. So, basically this K A k a upon K minus A this is your K A right.

So, surface reaction as I said because this is rate determining rate controlling RDS. So, the for RDS is this the other 2 step s are at equilibrium. So, rate of forward reaction is equal top rate of backward reaction or net rate of formation of that species is 0 net rate of reaction is 0. So, K S times theta C minus K minus S times theta B times P is equal to 0. So, from this one can find out the concentration of adsorbed cumene right.

The surface sites which are covered by the cumene is theta C; so that can be find out. So, this is you write theta C so theta C is represented as fraction of the sites covered by the cumene right; one can write C C also concentration of the sites covered by cumene. So, any definition can be used. So, theta B times partial pressure of this because theta B times p t divide by this is again here K S; here this expression which is written equilibrium constant and K s divide by K minus s right.

So, that is adsorption equilibrium constant for surface reaction right; rate of forward reaction divide rate constant for the forward reaction divide by rate constant for the backward reaction. So, that is the equilibrium constant for this reaction right; same thing for the third reaction which is desorption. So, K D times theta B minus K minus B D times P B times theta B is equal to 0. Because this reaction is again very fast and at equilibrium or net rate of formation is 0.

So, in that case again one can find out theta B. So, theta B it will be simply P B times theta v divide by K D divide by K minus D. So, rate constant for desorption divide by forward rate constant divide by the reverse rate constant. So, that is your adsorption equilibrium constant or desorption equilibrium constant. So, equilibrium constant for desorption of benzene right. So, one can write K D subscripted again B right for the benzene. So, theta B is known theta C which is written in terms of theta B. So, theta C can be calculated because theta B is unknown here. So, theta and this is now theta B which is again here theta B is unknown right but you can write it in terms of total site balance. So, theta C is equal to pressure times theta B. So, theta B is substituted like this P B times theta B. And, the other two equilibrium constant K S and K D are in the denominator. So, the still you need to find out is this theta B.

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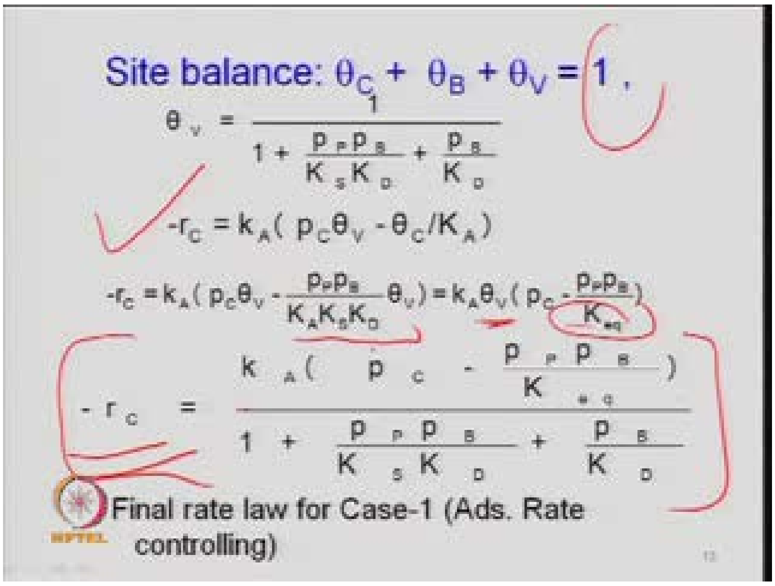

Site balance: $\theta_C + \theta_B + \theta_V = 1$,

$$\theta_V = \frac{1}{1 + \frac{p_P p_B}{K_S K_D} + \frac{p_B}{K_D}}$$

$$-r_C = k_A(p_C\theta_V - \theta_C/K_A)$$

$$-r_C = k_A\left(p_C\theta_V - \frac{p_P p_B}{K_A K_S K_D}\theta_V\right) = k_A\theta_V\left(p_C - \frac{p_P p_B}{K_{eq}}\right)$$

$$-r_C = \frac{k_A\left(p_C - \frac{p_P p_B}{K_{eq}}\right)}{1 + \frac{p_P p_B}{K_S K_D} + \frac{p_B}{K_D}}$$

Final rate law for Case-1 (Ads. Rate controlling)

So, let us look at the site balance right. So, site balance you know that the cumene is being adsorbed on the surface, benzene is being adsorbed but propylene is not adsorbed. So, the sites total number of sites if you say right, fraction of the site if I talk one right sigma of all theta I. So, that is 1 right. So, fraction of the sites these are theta C covered by c fraction of the sites covered by D and the fraction of the sites which are vacant right. So, summation of all these will be 1 or in other words you can say the concentration of sites adsorbed by cumene plus concentration of sites adsorbed by benzene plus concentration of vacant site is equal to total concentration of the site c t right.

So, this is basically c c over c t this is c b over c t and this is c v over c t what I have already discussed. So, one can very easily find out from this because theta v is known now; so minus r c which is net rate of disappearance of cumene right. So, rate of disappearance of cumene which was defined here like this right. So, you have defined in this form now so substitute the value of theta v and theta c; and you get the expression here. So, K A times P C times theta v minus theta C and all these terms are now known right. So, substitute it here in this. So, this is k A times P C times theta v and theta C substituted already calculated.

So, P p P B divide by K A. Now, this equilibrium constant for the adsorption reaction, surface reaction and this is the desorption of benzene right times theta v. So, you can further simplify this. So, theta B can be taken out. So, K A times theta v and in bracket you have now P C minus P p P B divide by this other rest of the term right; K equilibrium constant for the overall reaction. Because what is your overall reaction this. This is your overall reaction right C gives you P plus B.

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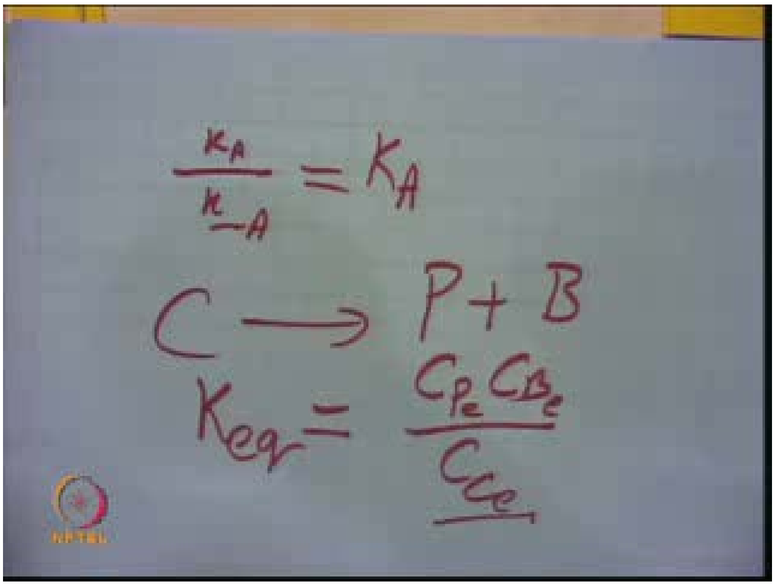

$$\frac{k_A}{k_{-A}} = K_A$$

$$C \longrightarrow P + B$$

$$K_{eq} = \frac{C_{P_e} C_{B_e}}{C_{C_e}}$$

So, what will be K equilibrium constant at this overall equilibrium constant which you get from thermodynamics will be simply the concentration of P times, concentration of B divide by the concentration of C right. And, that is written there in terms of either write partial pressure. So, this is at equilibrium right equilibrium composition; so which is written here K equilibrium. So, this term which is if you see there that is nothing but the combination of all these rate constants here. So, P p P B which has come from theta C if you substitute that which you have already done. And, K A times theta v times P C is here P p P B right which is written here P c c B divide by your third term c c right in the denominator which is your concentration of c. And, that has been just written in terms of combination of all these which is K A K S K D. And, the whatever in terms of the total or overall equilibrium constant for the reaction.

So, the basic meaning of this is that the overall equilibrium constant of the reaction is known to you from thermodynamics. So, and the term which is reported here and this in the form of because these are beyond equilibrium. So, when the equilibrium arise for this reaction this suppose if I say 80 percent conversion. So, after eighty percent the rate of for forward reaction is equal to rate of backward reaction for overall reaction. You cannot achieve more than that conversion is that is the meaning right. And, for a given condition of temperature and pressure if you disturb your equilibrium you can get more.

So, these kind of membering type of reactors can be used or some the molecular distillation type of react reactive distillation; what you call now a days. So, these type of reactors can be used. But when you have the for a given reaction at given condition of temperature and pressure the equilibrium conversion can be that is what written in terms of C P here right the concentration of e at equilibrium. So, that is so when there is equilibrium these all are the concentration at equilibrium. So, which it means one can define the concentration at equilibrium or the conversion either way. So, these term are just defining that the driving force a kind of driving force which is required for a reaction to happen.

So, if this driving force is not there or the rate difference is not there will not be any chemical reaction. So, this gives you the idea that how far you are deviating from equilibrium. So, which is P C minus P B P P P B upon k equilibrium and that is just talking one can look at in terms of the P C; that is the concentration of C minus that at equilibrium what when you define the rate. So, that can be just to check whether your when the concentration of cumene reach to the equilibrium composition their will not be any further conversion.

So, that is what from thermodynamics one can find out that what is the equilibrium conversion; and accordingly the conditions can be decided. So, your rate of net rate of disappearance of cumene is simply now written K A times P C minus P p P B upon K equilibrium. And, divide by 1 plus which is the term here written in the form of Langmuir Hinshelwood because theta v is known now.

So, from this theta v is equal to 1 minus theta C minus theta B substitute the value of theta C and theta B. And, then you have the expression something like this which is here in the denominator. So, 1 plus P p P B divide by K S times K D for equilibrium constant and plus P B upon K B. So, this the final rate expression for the disappearance of the cumene when adsorption of cumene is rate controlling remember. This is a one specific case or the rate expression which will say that the if adsorption is rate controlling. Then, it should depend on the partial pressure of C that is cumene; it should depend partial pressure of B, it will be depending on the thermodynamic equilibrium constant right. And, what are the terms defined in the denominator of the equation right.

So, this will give you a kind of guideline that whether the reaction is rate controlling or right for a given conditions. So, if adsorption is rate controlling our rate should be match to this kind parameter. So, there can be other case second case which is the surface reaction is rate limiting. And, similarly so for surface reaction again you have to proceed all these steps during the reaction. So, I will continue it next time. So.

Thank you.