Introduction to Chemical Thermodynamics and Kinetics
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Lecture - 37
Chemical Kinetics: Mechanisms - Part 6

Now, we will continue on the mechanism of our reaction, and we will discuss slightly different topic right now which is processes on solid surface, what happens when you use a catalyst which is in solid phase.

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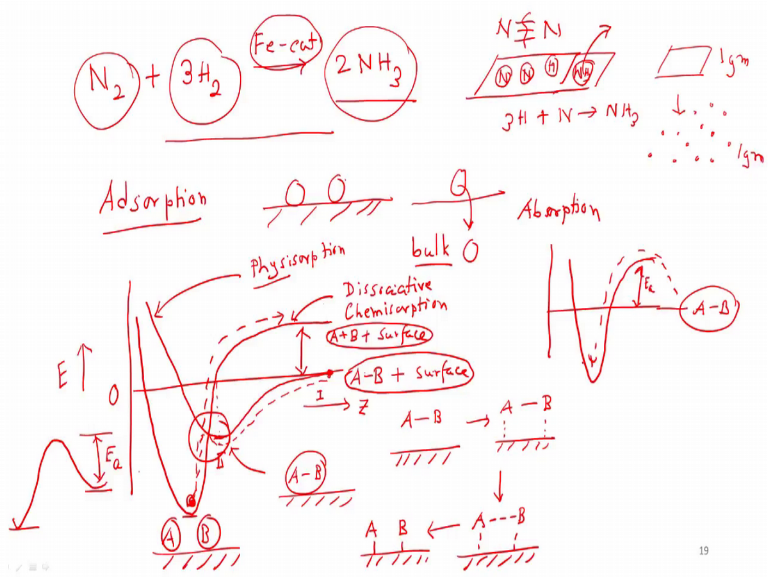

Now in many cases you know that this is a very important process the for example, when you have a read about this reaction that ammonia production from nitrogen and hydrogen. So, that is energetically less favorable, but if you use platinum I mean iron catalyst on platinum asbestos.

So, then the activation energy of this reaction is pretty much down and, then you see the reaction proceeding at some ambient temperature. Now for this I mean this was a revolutionary discovery because, if you remember ammonia is used in fertilizers and nitrogen and hydrogen are just you can actually get it in abundance particularly nitrogen and, then in nature plants or the bacteria residing in the roots of plants, they do this process of nitrogen fixation and, that is how they the plants get nutrient, but if you want to produce ammonia not only for fertilizers, but also in many industrial processes, the ever found that just using this catalyst, the rate of the reaction increases by whole a lot, and then the question is how basically the iron works here.

So, so that process will we are going to discuss today. So, going to basically develop a model that will describe the mechanism of this not only this reaction any surface reaction and, particularly will give you an example of surface catalysis, this is an example of surface catalysis by the way. So, they are actually use iron particles and once you suppose you can actually do it on an iron surface where so, this reaction is slow the reason is this nitrogen bond, it is very difficult to break.

And what happens on iron surface these bonds can be easily broken and, you get free nitrogen atom adsorbed on the surface and, also you have free hydrogen atoms absorb or this surface and, then these hydrogen atoms and these nitrogen atoms react together to give you ammonia. And the process happens on the surface iron surface itself and once the ammonia forms on the surface, it comes out of the surface and that is how the reaction happens.

So, iron actually acts as a catalyst and one more point I want to emphasize here. So, usually you do not use a plate of metal or piece of metal, the reason is if you use you can ask this person that if you take a piece of metal and, then break it into many small pieces in the size of say some few tens to a few hundreds of nanometers, or slightly more, then you can easily show that the volume is fixed, but the surface will actually the total surface area will increase, or you can say the surface to volume ratio will also increase.

Since these are all surface processes, if you can actually you say 1 gram metal in this form versus 1 gram metal in this nanoparticle form, you will see that there is a huge enhancement in surface moment you break the piece of metal into small small particles, that is why people use small they use actually a metallic powder, or something like that. So, that the surface area is increased, now the process of a gas which is attached which attaches on the surface this process is known as adsorption.

Now, it has a meaning why we are calling is at adsorption because, you have a surface and the molecules are sitting on the surface that is it they are not penetrating the surface, if it penetrates our surface and goes inside means it goes into the bulk medium, then this process is known as absorption and you already know that, we are talking about adsorption.

Now, the question is why adsorption is will occur. So, it must be energetically favorable. So, then you can ask this question fine can we have energy diagram in this case it is a potential energy diagram are describing this process of adsorption. So, what I am plotting here is basically energy or the potential energy and suppose this is the 0 of energy. Now 0 of energy is arbitrary by 0 of energy I am saying that this X axis is the distance from the surface for example, and when I am saying that it is the molecule, which you get adsorbed is far away from the surface. So, it has no interaction with the surface. So, that point I am talking at to be 0 of potential.

Now, suppose we are bringing the molecule towards the surface meaning, we are just moving in this direction and, then what will happen is that as it is brought closer, then the molecule the there will be an attractive interaction and that is why the molecule will get attached to the surface. And this will be the nature of the potential. So, you see that at some point at some specific distance from the surface, the potential energy is minimum and, then what happens that again if you want to bring the molecule suppose this is the molecule and, this is the surface and if you want to bring it more closer together, then the electrons on the molecules and the surface electrons on the surface they start repelling each other. And then actually you will have a repulsive force.

So, there will be a best position or best equilibrium position what the energy will be minimized. Now this process where just suppose I am starting with a molecule, which I am calling as say A B molecule. So, there is a bond between A and B, suppose a and b are atoms or it they may be a fragment of a molecule and, this state is A B plus surface it is basically A B and surfaces are far apart.

Now, when I reach here so, here A B is basically stuck on the surface. So, this A B is stuck on the surface. So, that is basically known as it is physically stuck there is no chemical change in this process. So, that is why we call this as physisorption it is a adsorption, but it is a physical adsorption. Now you can think of a process just like I told that when nitrogen get adsorbed on iron surface, the N triple bond N breaks so, then you get down nitrogen atoms. So, that is actually causing a dissociation. So, that is a chemical process.

Now, you can think that I can also have a chemical process, where the molecules get dissociated. So, we will have a similar curve. Now that curve will look like something like this, I will just discuss in a minute why I am drawing this curve like this, let me just remove this, now you see here I am calling this curve as chemis option as opposed to physisorption had just it was physically observed.

Now, what happens here if the molecules get dissociated, then I am calling this curve as chemists absorption. So, far apart these molecules will be A plus B plus surface. So, look at the very intricate difference between the fizzes option thing, when the molecule is far apart it is a molecule A B, but the A B bond has not been broken and there is no interaction between the surface and, what I am showing here the chemisorption instead, it is basically the molecules is dissociate at the E bond has broken and there is a surface, but there is no interaction between the atoms and the surface.

So, when that process happens that interaction should be much stronger than this interaction. So, this potential energy will be much much deeper, than the chemisorption state also you see that this curve the chemisorption curve in the asymptotic regime asymptotic regime in the sense that it has basically, it has I mean much larger distance from the surface, in that regime if I think that so, that energy difference will be nothing but the A B molecule and the A plus B atoms, or it may be the fragments.

So, a bond has been broken which means this will be there will be some energy difference between the A B and A B, A plus B and of course, the A plus B will be of higher energy because, you have supplied energy to the system and that is why the bond has broken, or in the other way other sense if the bond is formed from A plus B to A B, then you will release some energy. So, A B is always stable as that is why this curve lies at the bottom. Now what happens when nitrogen atom molecule approaches the surface, initially we have here we basically start from here, and then so, initial step is a physisorption, always actually there is a physisorption that actually precedes, or that happens before chemisorption and, then what happens you cross this little barrier that is shown here and you come to the chemisorp state.

So, this chemisorp state is nothing but A and B stuck on a surface. So, as soon as it is chemisorbed it is dissociated. So, this so, this is why sometimes we call it as dissociative chemisorptions. So, it is physisorption does not dissociative it is just a physical attachment it is a weak attachment, but chemisorption is a strong attachment where basically the metal is now forming a bond with the so, what is happening here. So, I had an A B bond and, then you can you can draw it like this. So, this is basically the state here state one say and, then at state 2 where I am at physisorp state. So, you can argue that it basically it is looks like this.

So, I have a b, but I have a very weak interaction with the surface and, then what happens it crosses a barrier and when the it crosses the barrier near the barrier the situation is like this. The A B bond is being broken and the A 2 surface and B 2 surface bond is being formed and finally, you will have the A B bond completely broken and a new bond has been formed between the A and surface and B and the surface. And that is how the N triple bond N also breaks, but it involves multiple steps because, you have to first make the triple bond to double bond, then double bond to single bond and, then the single bond to no bond something like that.

So, all these things are happening. So, now suppose the A B molecule is chemisorp or actually it is dissociated. Now when it goes back; so it now goes back following this curve meaning when it goes back it actually goes back as a dissociated atom. So, that can happen that may not happen, if the interactions of these atoms if the surface is strong it may not happen, but the point here is that you can actually cleverly use a surface which in many cases is a metal surface and, bring a molecule and then dissociate it and then if you heat it up maybe you can actually weaken that metal to atomic bonds and, then you can actually dissociate it into atoms.

However, you may not be able to do it in the gas phase because, you have to supply a lot of energy to break the bonds in the gas phase, but what happens is that there is a physisorption state. So, it is weakly attached and then there is a barrier, but this barrier now you can see this barrier here, if I just magnified it is something like this physisorp state is going into the chemisorp state.

So, this is the minimum physisorp state and, there will be a minima of the chemisorp state. So, this barrier which we will discuss detail in later is called an activation barrier and, that activation barrier is very small and that is why the surface catalysis works. So, there is a physisoption and there is a chemisorption and, prior to chemisorption there is a physisoption and that is why it is already energy is lower and, then you have a chemisorp state.

If you ask this question that if the physisorption did not happen, what will be the case. So, the chemisorp state is something like this and, then there is the suppose know physisorption which means actually now the molecule starts from here, in the asymptotic limit. Now it has to somehow come and cross this barrier which is this. So, it has to proceed through a path, which is something like this and, then only it can do the kbs or then it can only dissociate.

So, now you see that there is a huge difference between a physisorption followed by chemisorption and on the dissociation by chemisorptions. So, that is why surface catalysis that is the inherent way of thinking intuitive way of thinking, why surface catalysis works, it is it only works lowering the height of the barrier and, that is connected to the rate constant through arrhenius equation that we will be studying later.

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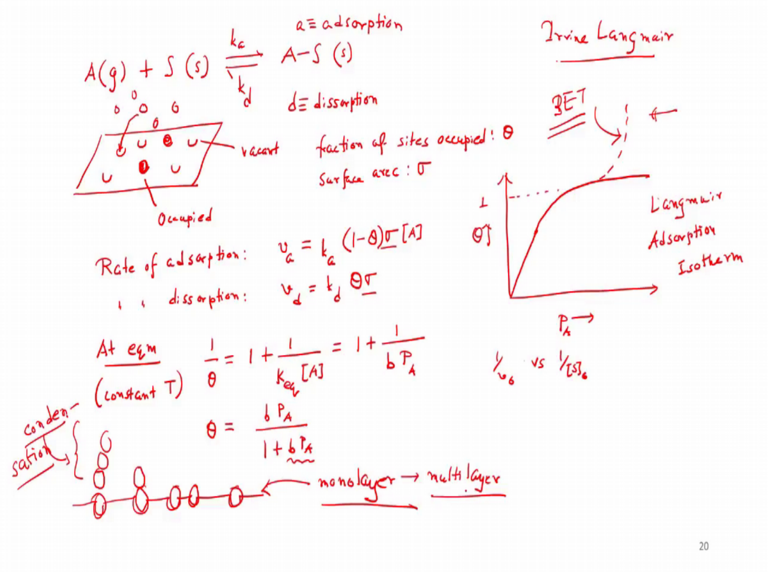

$$A(g) + S(s) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} A\text{-}S(s)$$

a ≡ adsorption

d ≡ dissorption

fraction of sites occupied : θ

Surface area : σ

Rate of adsorption : $v_a = k_a (1-\theta)\underline{\sigma}[A]$

" " dissorption : $v_d = k_d \theta \underline{\sigma}$

At eqm (constant T)

$$\frac{1}{\theta} = 1 + \frac{1}{K_{eq}[A]} = 1 + \frac{1}{bP_A}$$

$$\theta = \frac{bP_A}{1+bP_A}$$

$1/v_0$ vs $1/[S]_0$

Now, the question is how we model develop a kinetic model to describe the mechanism of such process and, the mechanism is very simple and this mechanism was put forward by Irrine Langmuir an American physical chemist who did a lot of work on surface science. So, what Langmuir said is that suppose you have an gas which is A and, then you have a surface which is solid. And then there is a fast equilibrium between the gas adsorbed on the solid. So, this is now as if it is a solid state. So, the gas is attached to the solid and, then the forward rate we call it as a rate of absorption and the reverse rate we call it as a rate of desorption.

So, d stands for desorption, it is opposite to adsorption a is adsorption. Now there is a fast equilibrium between them and the question is how do you quantify this equilibrium. Now you cannot actually calculate what language suggested is that suppose, we have some available sites where the molecule can come and sit. So, suppose these are molecules these are floating in gas. And, then the molecule will come and sit on the surface. So, then you will have a molecule stopped on the surface. So, at any point of time you can think, there are always some sites which your vacant site and some sites which are occupied. So, like these are this is occupied because no other molecule can sit on that and here it is basically a vacant site.

So, let us consider the fraction of this vacant site fraction of free site, or vacant site they say I am calling as theta and, then also consider that the surface area a is just take a number say little notation let us call it as a sigma, usually we call use the sigma for surfaces. Now what language said the rate of adsorption, rate of adsorption which is the forward process will be nothing but if I just call it as a v a, that will be nothing but proportional to how many sites are vacant. So, instead of writing the theta as of happened, I can write it as a fraction of sites occupied as theta, I mean this is just a notation.

So, then the adsorption will be dependent on how many what fraction is available. So, that fraction this since this is a fraction it will be 1 minus theta. So, that fraction is basically available, it will also that fraction times the area will be the number of available sites because, we are using a fractional notation. And times it will also depend on the concentration of A because, you have more number of gas molecules here of course, the rate of adsorption will be more it is as simple as that and, you have a rate constant associated with it is the forward rate constant.

Similarly, the rate of desorption will also be equal to something like it will be now dependent on theta, because theta is the rate of occupied size how many sites are occupied into sigma, but it would not depend on the pressure of the or concentration of the gas because, it does not matter, because it is just absorbed on the surface and it is just going into the gas phase. However, if we have more number of molecules in the gas, then there is a chance to go on sit on the surface, but if it is only already on the surface. So, then it is a spontaneous process which is basically going into the bulk phase or the gas phase. So, and then associated here we also have a desorption rate and at equilibrium at a fixed temperature.

So, the rate of adsorption and desorption will be same and, we can just equate these two equations and you can see that the sigma thing gets cancelled. So, you can readily solve it and you can show it, that I will get 1 by theta is 1 plus I am just skipping this for the time being some equilibrium constant which I am calling it as K equilibrium. So, you get a ratio of K desorption K adsorption by K desorption that you can write it as the ratio as a equilibrium constant times the concentration of A, but usually do not use concentration because, it is a gas to solid surface adsorption. So, instead of concentration you write it in terms of the partial pressure or pressure.

So, if there are multiple species then there will be partial pressure, otherwise it will be just pressure. So, you just write it as a same equilibrium constant it would not be the same equilibrium constant because, moment I write it in terms of pressure, then there will be other factors like I have to divide by P 0 the standard pressure and convert the concentration into pressure. So, then there will be some factor multiplied by the equilibrium constant, but that will also be another equilibrium constant that, I am writing it as b and then pressure of A. Now we can also write what is the value of theta.

Now, theta you can just rearrange, it you will see that it will be b into P A divided by 1 plus b into P A. If you want to plot it the adsorption this is known as adsorption isotherm because, we said that we are doing this experiment at constant temperature. So, if we plot this thing theta the rate of the fraction of sites occupied versus the pressure of the gas, you will see that at no pressure, I can actually ignore this term b into P A compared to 1. So, it is linearly proportional to P A. So, it will have something like this and at a very high pressure, then this term will be a very high compared to 1.

So, it will be b P A by b P A so, then actually fractional saturate. So, it will go like this where basically this is a saturation point theta is a fraction so, it can maximum of theta can be 1. So, we see a car which is very interesting because, we saw this curve in Michaelis Menten equation. If you remember that when, we were plotting the initial rate v 0 versus initial substrate concentration that also looked a similar way. Now the in the physics is very similar because, if you think that in the Michaelis Menten situation what we had is that we had enzymes and each enzyme had a particular site for substrate binding.

So, you can think that there will be some free enzyme and, there will be some engines which are already occupied and in the in the language, language and it is the same here also, there are sites the sites are site each site you can think of an 1 enzyme and 1 molecule binds to 1 site only binds to 1 molecule not to multiple molecules that also, we I mean kind of are good or in a model we basically that we put that constraint. And if you think in that way, then there is a not much difference between the enzyme catalysis and these surface catalysis, although enzyme catalysis is in homogeneous catalysis in the sense enzyme substrate and everything the product is in the surface here, there on in different phase.

So, that is why we call it as a heterogeneous catalysis, this ammonia production from nitrogen and hydrogen because, there is a gas phase and there is a solid phase which is the metal surface. So, it is a 2 phase system and that is what it call it is as a heterogeneous catalysis. Now the concept is very similar that is why you are getting similar nature of the curve. Now one more thing so, this is known as a language option isotherm, but in real life what you what you see here that once I have this these were the surface sites I can just draw it like this, suppose these are the surface sites and when you have enough pressure, then the molecules are coming and sitting on that and all sites are occupied then you cannot have further molecule.

So, here actually what land more absorption isotherm says is that you stop at the mono layer formation, mono layer in the sense that only 1 molecule layer 1 molecule thick layer is there not multiple molecules, but in reality what happens is that, when you have a particularly low temperature, when you have this situation then that other molecule can sit on this molecule and, other molecule can sit on this molecule. And then you can actually go from mono layer to what is known as multi layer and, after certain point actually you cannot control this moment to increase the pressure, you will see all the molecules are sitting on the surface because, that is what is known as condensation.

So, you have seen that if you take a metal surface at cold temperature and put it in a say or any surface in a say cloudy day or when we have enough humidity in here. So, you see will see that water vapour actually condenses on the surface. So, condensation means actually you have multiple layer because, you can see the layer. So, which means actually there are several atomic several molecule are sitting vertically and, that is basically shows the condensation.

So, attaching of one molecule is facilitating, the attaching of multiple molecules and, then the curve will not look like this after certain pressure, you will see that this curve will just blow up and for that actually we cannot explain from Langmuir absorption isotherm. So, this is known as Langmuir maybe you can draw it as a dotted line like this, adsorption isotherm and then this scarf there is a model for that it is known as BET model, but will not discuss it here which actually discusses this multilayer adsorption case.

So, Langmuir absorption is limited to only those situation where it forms only mono layer and, it just stops at the mono layer formation and no multi layer formation is I mean no multi layer formation occurs further.

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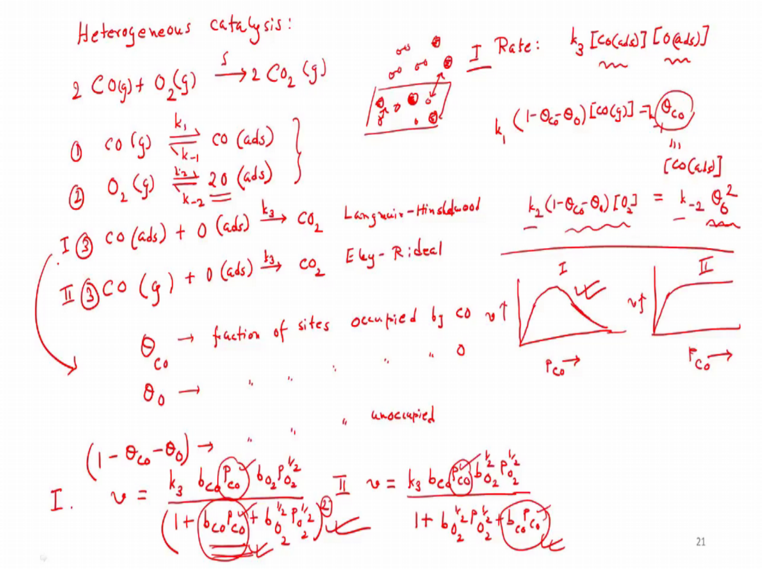

Heterogeneous catalysis:

$2CO(g) + O_2(g) \xrightarrow{S} 2CO_2(g)$

① $CO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO(ads)$

② $O_2(g) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2O(ads)$

I ③ $CO(ads) + O(ads) \xrightarrow{k_3} CO_2$ Langmuir-Hinshelwood

II ③ $CO(g) + O(ads) \xrightarrow{k_3} CO_2$ Ely-Rideal

θ_{CO} → fraction of sites occupied by CO

θ_O → " " " " O

$(1-\theta_{CO}-\theta_O)$ → " " " " unoccupied

I Rate: $k_3[CO(ads)][O(ads)]$

$k_1(1-\theta_{CO}-\theta_O)[CO(g)] = k_{-1}\theta_{CO}$

$\theta_{CO} \equiv [CO(ads)]$

$k_2(1-\theta_{CO}-\theta_O)[O_2] = k_{-2}\theta_O^2$

I. $v = \frac{k_3 b_{CO}P_{CO} b_{O_2}P_{O_2}^{1/2}}{(1+b_{CO}P_{CO}+b_{O_2}^{1/2}P_{O_2}^{1/2})^2}$

II $v = \frac{k_3 b_{CO}P_{CO} b_{O_2}^{1/2}P_{O_2}^{1/2}}{1+b_{O_2}^{1/2}P_{O_2}^{1/2}+b_{CO}P_{CO}}$

Now as I said that this model I can use for catalysis and by catalysis again I talked about heterogeneous catalysis. Now instead of the nitrogen higher and hydrogen reaction producing ammonia, we will talk about some interesting reaction where carbon dioxide carbon monoxide and oxygen both are gas and, in presence of a surface they form carbon dioxide.

Now, the question is what is the mechanism of this reaction. Now 2 mechanisms were proposed and so, the first mechanism says at the first part of these 2 mechanisms is same. So, you have carbon monoxide gas which actually in presence of the surface is going to the carbon monoxide in the adsorb state, this will be just like what we just developed through Langmuir mechanism. And then you have oxygen gas which is also getting adsorbed, but this case it is a dissociative chemisorptions. And then the first model which is known as the Langmuir or (Refer Time: 27:33) model it says, the reaction happens between the adsorbed carbon monoxide and the adsorbed oxygen atom and then you will have CO 2.

So, this is basically the final step at the rate determining step and the other model says no actually there are carbon monoxide adsorbed, but these oxygen atom sorry, there are carbon monoxide as the, but they do not react with with the adsorbed oxygen species. The carbon monoxide in the gas phase actually reacts with the adsorbed oxygen species to give you CO 2.

So, one mechanism so, this is mechanism 1 and this is mechanism 2 and, this 1 is known as one more or Langmuir Hinslawood mechanism and, this is known as Eley Rideel mechanism. So, the both mechanism said there is a initial step see oxygen has to be adsorbed on the surface. And the O double bond O has to be broken otherwise this reaction on proceed and the question is I have on the surface, I have oxygen attached, I also have carbon monoxide, I am just drawing it like this.

Now, the question is there are also oxygen molecules here and, there are also carbon monoxide molecules here and, these are oxygen atoms by the way. So, I should draw it like this. So, this is O 2, this is carbon monoxide. Now the question is the reaction between this carbon monoxide and that attached already absorbed oxygen atom, or it is between 2 surface faces. So, it can happen that the molecules get absorbed and get dissociated. So, there are oxygen atoms and there are carbon monoxide atoms and on the surface they are now working they are now reacting. So, it is not it is a collision on a surface which means it is a two dimensional collision.

So, you can actually model it by in a very interesting way by using two dimensional distribution of Maxwell Boltzmann distribution, but we will not discuss it right now, because we will discuss it at the very end how to use Maxwell Boltzmann distribution to discuss the reaction rates, or get an expression for the rate of the reaction. Now the first model we will try to solve and, you see that it is very easy to solve because I will give you a hint how to solve it.

So, you have to have basically the two sides here. So, you can say that they are one type of site where carbon monoxide is attaching, or suppose that there are these sites are same, but you say that this is basically the fraction of sites fractional surface sites basically, which are occupied by carbon monoxide and, then you can also say that there are also fraction of oxygen which are op sites occupied by O atoms and so, the fractions which are fractions of sites unoccupied will be nothing but 1 minus theta CO minus theta O.

So, that is very important here. So, you have some type of site and that both model when you develop it you have to consider this, now it is very easy so, you just calculate what at the so, or your rate of the reaction here will be nothing but for the first mechanism for mechanism 1. The rate of the reaction will be nothing but k 3 into CO absorbed. Let me write it like this CO ads times, you have oxygen atom absorbed. Now you have to find these two numbers from the reaction from the first two equilibrium and, this is as simple as that and we have already described it how to do it. So, we can quickly do it. So, it is basically k 3. Now if you go back you will see that here, what do you what you are seeing here is that theta is basically we need the pressure actually.

So, so again the rate of forward reaction and rate of reverse reaction will be same and, for the first equilibrium you can write it that the rate of adsorption, which is 1 minus theta 0 C O minus theta O times carbon monoxide in gas that is concentration will be equal to the rate of desorption, now desorption means actually it is only theta 0 and, then there will be some rate constants. So, it is k 1 I am calling this as step 1 say this is step 2, this is step 3, this is also step 3. So, step 3 differs for these 2 mechanism, I am calling this as k 1, this is k minus 1, this is k 2, this is k minus 2.

So, this will be k minus 1, then and then we will just take the ratio all we need is basically the ad sub species concentration, or the here actually you cannot write the concentration you have to write in terms of the fraction, just remember that because it is the co adsorbed will be nothing but proportional to theta 0. So, that is equivalent to saying the CO absorbed.

And similarly for oxygen also you can write it is a dissociative oxygen. So, remember that that forward rate will be nothing but k 2 into 1 minus theta 0 minus theta O into O 2 and, the reverse rate now you have in the stoichiometry is 2 O. So, it will be if you if you ask this question just from your kinetics knowledge. So, it will be just oxygen whatever is their oxygen theta for oxygen that will be squared because, it is a 2 factor is there. So, will have basically k minus 2 into theta O and that will be basically squared and, then you can actually solve it for this thing and this thing.

So, all you can actually easily see it. So, if I just bring it here and call it as equilibrium constant that t just C theta oxygen that part will involve actually a square root So, ultimately if you solve it. So, you will get very interesting equations, I am just writing the final solution for the mechanism 1, you will get the rate of the reaction which is k 3 into CO absorbed into that O absorbed that will be nothing but if I write it in terms of partial pressure, I could have written it in terms of b and P also.

So, it will be nothing but k 3 k 3 will always be there and, I will have b CO and pressure of carbon monoxide multiplied by b O 2 and pressure of O 2 to the power half because, you can see that when I solve for theta O on the left hand side all these things had to be so, I have to take the square root that is right the square root is coming and, divided by I will have basically 1 plus b CO b CO and that plus b O 2 to the power half and b sorry P O 2 to the power half.

And for the second mechanism you will have v is equal to k 3 times for the other mechanism sorry for this first mechanism there will be a square, you can actually work it out and it will be k 3 into b CO and b O 2, or maybe you can write the pressure term together b CO and b O 2 P O 2 this will be always half divided by I will have one plus b O 2 to the power half P O 2 to the power half and plus b CO and P CO.

So, we will see that we saw that there is a square term in the denominator. So, if we plot it now that how the theta versus P follows, if it follows the mechanism 1, then you just think about it at the low pressure say I am plotting it as a partial pressure of carbon monoxide because, if you change the partial pressure of oxygen that do not matter because, the oxygen part is the same in both cases and because, it is oxygen adsorbed species that actually reacts, but for carbon monoxide perspective it is very different whether, it is carbon monoxide adsorbed or whether it is the carbon monoxide which is in the gas phase.

Now, the question is if I do that then I will see P CO and then if you ask this question what is the rate of the reaction of the fraction or we can actually plot the rate of the reaction here. So, at a very low pressure of P CO think about it what will happen, then I can ignore this part P CO and, if we ignore it then I will have 1 plus b O 2 and P O 2 and in the numerator, you can see that it will be linearly proportional to P CO. So, it will be something like that.

In both cases it will be true, but in the very high pressure limit what will happen is that now you can actually ignore this part I mean this will be nothing but only this part. So, you can think that this part will be so, high. So, mechanism 2 I am also plotting together. So, for low pressure regime it will be similar it is just linearly proportional and very low pressure and, then because this term is very small and you can neglect it compared to other terms. So, then with respect to P CO it will be linear, but in the very high pressure limit when I have this term dominating P CO over the other 2 terms, then in the Langmuir remember there is a square. So, it will go inversely at as P CO because, there is a P CO here, there is a P CO square here. So, it will be 1 over P CO and in this case it will just perfectly cancel. So, it will be just saturated.

So, this will show up here where like this Eley Rideal, but Langmuir in the high very high pressure limit it will be 1 over P CO. So, the overall curve will look like something like this. So, you will see that these 2 mechanisms actually predict very two different behavior of the reaction rate, versus the partial pressure of one component which is the carbon monoxide and, then experimentally it was found that it actually follows this curve which means this mechanism, which Langmuir and himself proposed is the current mechanism and not the other mechanism which Eley and Rideal proposed, but Eley and Rideal mechanism holds for other reactions, not for this particular reaction carbon monoxide and oxygen.

So, the reaction proceeds had between in the rate determining step, it actually the step actually involves collisions or reactions between 2 adsorbed spaces, it is adsorbed oxygen with absorbed carbon monoxide whereas, the Eley and Rideal said that it happens between 1 absorbed species which is carbon oxygen atom and, the other species is in the gas phase you can have at carbon monoxide absorbed, but that does not react with oxygen according to Eley Rideal mechanism.

The carbon monoxide in the gas actually comes and hits the oxygen atom adsorbed and then it forms carbon dioxide. So, in this particular example it follows the Langmuir Hinshelwood mechanism. So, we will stop our discussion on the mechanism of reaction here. So, this part is slightly different than the earlier parts in the sense that it is a heterogeneous thing that we are discussed and, it involves a surface just like we had a small discussion on surface chemistry after chapter at the end of as a part of the lecture or module 9, where we discussed first the application of thermodynamics.

So, one was equilibrium electrochemistry. And the part 2 was basically the surface chemistry. So, in that same way we just kept the surface chemistry towards end. So, that it is a slightly different from the others because, usually you talk about everything as a bulk phase and all the reaction kinetics or the thermodynamics.

So, you mostly have discussed for the bulk phase and, this is 1 unique example how surface catalysis helps and surface catalysis works and, nevertheless surface catalysis is very very important particularly these heterogeneous catalysis. And for heterogeneous catalysis we all survive because, if the ammonia production was not demonstrated by (Refer Time: 42:17) we would have diet and by now, because of crisis of food because it ammonia as a very very important constituent for fertilizers all right.

So, just conclude our discussion on the mechanism here. And, next we will start the reaction dynamics.

Thank you.