Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 33
Chemical Kinetics: Mechanisms – Part 2

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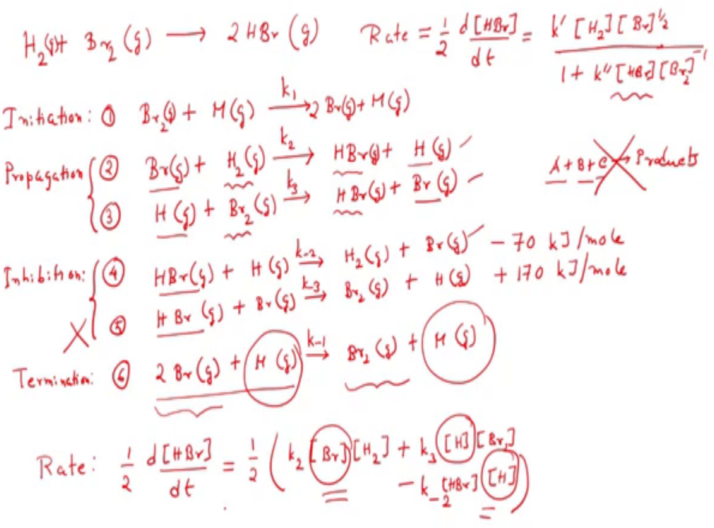

$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$ Rate $= \frac{1}{2}\frac{d[HBr]}{dt} = \frac{k'[H_2][Br]^{1/2}}{1 + k''[HBr][Br_2]^{-1}}$

Initiation: ① $Br_2(g) + M(g) \xrightarrow{k_1} 2Br(g) + M(g)$

Propagation ② $Br(g) + H_2(g) \xrightarrow{k_2} HBr(g) + H(g)$

③ $H(g) + Br_2(g) \xrightarrow{k_3} HBr(g) + Br(g)$

$\cancel{A + B + C \rightarrow \text{Products}}$

Inhibition: ④ $HBr(g) + H(g) \xrightarrow{k_{-2}} H_2(g) + Br(g)$ -70 kJ/mole

⑤ $HBr(g) + Br(g) \xrightarrow{k_{-3}} Br_2(g) + H(g)$ $+170$ kJ/mole

Termination: ⑥ $2Br(g) + H(g) \xrightarrow{k_{-1}} Br_2(g) + H(g)$

Rate: $\frac{1}{2}\frac{d[HBr]}{dt} = \frac{1}{2}\left(k_2[Br][H_2] + k_3[H][Br_2] - k_{-2}[HBr][H]\right)$

If you remember we also discussed a particular reaction which looks very simple H 2 plus B r 2 both in gas phase producing hydrogen bromide in gas phase. But the rate law observed rate law was fairly complicated and the rate that was observed which is half d H B r we can write the rate in terms of the products like this.

Here there is only one product H B r which was k 2 sorry k prime; k prime is one of the rate constants. And if you remember that it was something like 1 plus k double prime H B r into B r 2 minus 1.

So, this is fairly complicated rate law; the absorbed rate law which does not follow which does not it suggests immediately that it is the reaction did not happen like 1 H 2 molecule and 1 B r 2 molecule just came and collided together to form H B r. Then the rate will be very simple then the elementary step is just by molecular collision and the rate will be just some observed rate law, times H 2 concentration, times B R 2 concentration, it will be as simple as that.

But since the observed rate law is very complicated ah; so, people studied this reaction and devised the mechanism. Now what happens? This reaction actually proceeds to something known as radical pathways. So, here radicals are generated and these radicals are free radicals are extremely reactive. Radicals means there is no lone or bond pair of electrons there are bond pair and lone pair of electrons, but in addition you have an unpaired electron that is why it is called a radical.

Now, these are by the way neutral radical; it is not cationic or anionic radical. So, what do you have? You have to have some step which actually initiate the reaction; initiate the radical reaction. We call that first step as initiation where these bromine, bromine molecule actually collide with something; that something we are writing as M. We will come to that; what do you mean by M? And then this is step number 1, then it is it forms actually 2 bromine radical plus M and these bromine radicals are also in gas phase plus M which is test phase.

Now, that M can be any spaces; so, basically it is a collision only activated dissociation of bromine 2 into 2 bromine radical; it can be a bromine molecule itself. So, it can be the hydrogen molecule itself; so, sometimes it can be also the wall of the container. So, it says that somehow some of the bromine in the reactive mixture. So, in the reactive mixture initially had bromine and hydrogen and then initiate it is initiated by actually the a free radical which is the bromine radical.

Now, you could think also that the H 2 also breaks and forms H radical, but the bond energy of H 2 is much higher; it is much much more difficult to break an H H bond than to break and B r B r bond. So, the first step is basically initiated by the bromine radical; then once this bromine radical is initiated, it can react with hydrogen gas and it can abstract a proton from it. And then it can form H B r which is the product plus it forms the hydrogen radical.

Now, any radical species is very reactive as I said; now this hydrogen radical can also in the very same way, these are all gas phase species react with the bromine molecule and abstract 1 bromine atom from H B r and give bromine radical that. So, you can see that one radical B r is generating the other radical and here also the H radical is generating the other radical. So, these will this process will continue because you are regenerating some other radical which actually regional back the old radical and this continues. So, this is something like a chain reaction and it just amplifies itself and in the in the process you form H B r and you just consume H 2 and B r 2.

So, this step is known as the propagation and then you could also have inhibition. In the sense you could think that sometimes these radicals are actually trapped and one of the trapping will be; if the product H B r actually traps say hydrogen radical in the system to form H 2 and bromine radical. Or this product H B r can also trap a bromine radical and then giving rise to bromine molecule plus hydrogen radical.

Now, as I said this is known as inhibition and you can easily see inhibition means these 2 steps; propagation was these two steps together. And you can easily see that this H B r now actually is basically a forming or entry at the product which is H B r is actually inhibiting the process, it is actually scavenging the radicals H and B r. And that is why you see in the rate equation H B r comes in the denominator; so, too much higher concentration of the product H B r can also cause the inhibition.

So, that is a hint that H B r is causing inhibition for this reaction to propose this mechanism. Because in the observed rate law, we see that it H B r comes in the denominator. So, then also you have a termination reaction which will be just opposite of the first reaction who are basically 2 bromine atoms in presence of a third body actually gives you B r 2 plus M. Now you can argue that this is the probability it will be very less of course, it will be very less because it is a 3 body collision. But the point here is that when the 2 bromine atoms collide; they can form a bond then some energy is released and there should be a third body to take up that energy.

So, that is why you considered a 3 body collision here exactly it is not like a 3 body collision like we said that it is not possible to have a 3 body collision and form something like A plus B plus C going to product and we said that we would not consider this kind of elementary reaction because they are not possible. However, here we are saying a slightly different it is a by molecular reaction; it is 2 bromine atoms forming bromine molecule, but it released energy has to be taken up by a third body which is not a reactive species here; it is just there which is absorbing energy it may be the wall of the container also.

So, it is not like that there are 3 reactants forming product; it is just there are 2 reactants there forming product, but the third part is just absorbing the excess energy. Now also we can simplify further in the sense that this particular reaction; this equation number 5; it is actually endothermic in the sense that it needs heat to be supplied to for this reaction to happen. And this heat is pretty substantial for endothermic reactions remember that we always use a positive sign because heat is required for this reaction.

So, it is energy supplied from the environment the surrounding that is why it is a positive thing versus these other inhibition reaction is exothermic which means heat is released by 70 kilo joule per mole. And the first one the fifth one is basically the other inhibition reaction which was endothermic by 170 kilo joule per mole. Now endothermic attractions under normal condition is very very unlikely to happen because you need much more heat to be supplied.

So, we can also right away from the beginning ignore this step. So, you basically have in average we have total 5 steps; now you can also put some red constant for each of these steps I write k 1 here and k 2 for this step k 3 for this step. And this reaction is nothing, but the inverse of the reaction 2. So, we can write the rate constant as k minus 2 for this reaction k minus 3, but we will we are anyway not going to consider this one. And for this reaction you mean eventually you can write as k minus 1 because it is just the opposite of the first reaction.

So, now let us the device I make a rate law based on this mechanism using the steady state approximation of the intermediate radicals. And the radicals are hydrogen radical and bromine radical and you see that what is the rate of the reaction by the way? So, the rate of the reaction is expressed as half d H B r d t and that is wherever you have the H B r d t; so, H B r is formed in this reaction.

So, step number 2; so, it will be k 2 times B r into H 2 and it is also formed in step number 3; which is k 3 that is why I am writing a plus sign into H into B r 2. And plus we see that it is consumed in step number 4; we have ignored step number 5. So, we will use a minus sign it is k minus 2 H B r into H. So, we can write it here ; it is minus k minus to the minus 2 into H 2; sorry it will be H B r into H H B r into H. So, we see that in order to get the rate law we have to know what is the concentration of B r? And what is the concentration, what is the concentration of H radical?

Now, we will use the steady state approximation for these 2 intermediates and see what happens.

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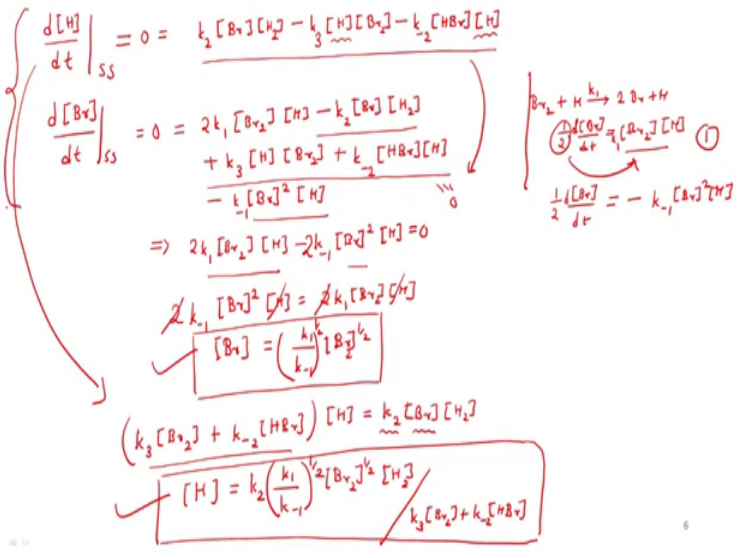

$$\left.\frac{d[H]}{dt}\right|_{ss} = 0 = k_2[Br][H_2] - k_3[H][Br_2] - k_{-2}[HBr][H]$$

$$\left.\frac{d[Br]}{dt}\right|_{ss} = 0 = 2k_1[Br_2][M] - k_2[Br][H_2] + k_3[H][Br_2] + k_{-2}[HBr][H] - k_{-1}[Br]^2[M]$$

$$\Rightarrow 2k_1[Br_2][M] - 2k_{-1}[Br]^2[M] = 0$$

$$\cancel{2}k_{-1}[Br]^2\cancel{[M]} = \cancel{2}k_1[Br_2]\cancel{[M]}$$

$$\boxed{[Br] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[Br_2]^{1/2}}$$

$$\left(k_3[Br_2] + k_{-2}[HBr]\right)[H] = k_2[Br][H_2]$$

$$\boxed{[H] = \frac{k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_{-2}[HBr]}}$$

$$Br_2 + M \xrightarrow{k_1} 2Br + M$$

$$\frac{1}{2}\frac{d[Br]}{dt} = k_1[Br_2][M] \quad ①$$

$$\frac{1}{2}\frac{d[Br]}{dt} = -k_{-1}[Br]^2[M]$$

Now, first let us consider the H radical; so, we will say that these d H d t under steady state is 0 which is d H d t you can easily figure out where it appears; it appears in the second equation, it is consumed in the third equation. So, the second equation was bromine reacting with H 2; so, it is k 2 bromine into sorry; it will be bromine radical into H 2 minus we have k minus 2. Or we can first write the k 3; you see the third step it is consumed H into B r 2 H into B r 2. And then see where it appears again; so, it appears again in reaction number 4 where it is again consumed by action of H B r.

So, reaction number 4; a direct constant k minus 2 H B r into plus H alright; similarly we can write d B r d t under steady state is 0; now bromine appears in many classes. So, the first step which is bromine 2 plus M it is formed, but then see the first reaction; it is bromine 2 plus M forming the 2 B r into M. Now let us just right it here it is 2 B r plus M; if I write the rate of this law rate of this step with respect to bromine I have to write half d B r d t is bromine 2 into M.

So, which means d B r d t will be 2 times bromine 2 into M; now we are only writing the d B r d t terms we are collecting the d B r d t terms; so, you have to multiply it by 2. So, just keep that in mind; so, this half actually we are taking on the other side. So, which means it is 2 times k 1 you should be k 1 sorry k 1 into B r 2 into M. And then we have let us see the reaction number 2; reaction number 2 will be it is consumed.

So, it is k 2 into B r into H 2, reaction number 3; it is again regenerated which is k 3 into H into B r 2. I am just following the hydrogen formation reaction wherever actually a hydrogen radical is generated the bromine is radical is consumed and vice versa. And then you will have a fourth step which is basically hydrogen and hydrogen bromide reacts.

So, then bromine must be formed there; so, it will be plus k 2 k minus 2 into H B r into H. And the fifth step we ignored and the sixth step will be just nothing, but the reverse of the first step and you can see here the sixth step. So, it is basically bromine is consumed, but; so, or long will be B r square into M. So, it is consumed; so, it will be k minus 1 into your squared into M. Now you cannot first see what is the solution for H radical from this equation? So, that will be easier.

So, see here where H appears. So, H appears here, H appears here and before that you can you can first solve it as H radical or B r radical whichever way. So, let us first simplify this now look at this part minus k 2 plus k 3 plus k minus 2. So, this is just negative of this part and this is already 0. So, the negative of this part will also be 0. So, what we can write using the first basically this is from the H equation or hydrogen radical equation; we can just remove this entire part. And then we can write 2 k 1 into B r 2 into M minus k 2 minus k minus 1 B r square into M that is equal to 0 because this part which I have underscore here is also 0 because of this.

Now, you can simplify it and get the expression for bromine. So, you can just put this term or this term on the other side and then you can easily see that the bromine square will be nothing, but equal to or we can just write it like this for the typing; k minus 1 into bromine square into M that is nothing, but 2 k 1 bromine into M and this M now cancels. So, that is why you wrote it as M because it will not appear in a rate equation, it can be H 2, it can be B r 2, it can be one of the container, it can be one of the radicals. So, it is just a coalition (Refer Time: 18:49) activated process and this is just a third body.

And then we can actually see that the bromine steady state concentration is nothing, but twice k 1 divided by k minus 1 into bromine. The square root of everything, but I am just writing the rate constant separately and the concentration of bromine separately. Now you can use this; so, this is basically the expression for bromine that we need to solve the rate of the reaction. Because in the rate of the reaction remember the both the concentration of bromine as well as H appears.

Now, we also need to solve the H equation; so, we can right away write it from here. So, we see that the steady state concentration of H; if we just take that thing common you can write it like this. So, we see that k 3 into B r 2 plus k minus 2 into H B r times H is nothing, but k 2 into B r into H 2; now B r already we know we will just replace the value B r here.

So, hydrogen atom radical concentration will be nothing, but k 2 into B r. And that instead of B r we are writing it as twice k 1 divided by k minus 1 to the power half. So, it is k 2 and this is basically we are writing right now B r expression is this times B r 2 to the power half; times there is a H 2 concentration here divided by this entire thing which is k 3 B r 2 plus k minus 2 H B r.

So, we see that this is the expression for steady state concentration for hydrogen radical. So, this is for bromine radical, this is for the hydrogen radical; so, we got these 2 terms which is fairly it looks really complicated. And then we have to now solve the d H B r d t which is the rate of the reaction. So, let us now solve it what is the d H B r d t. So, for that you just see this reaction what is the expression for d H B r d t. So, that will be our half d H B r dt let us write it.

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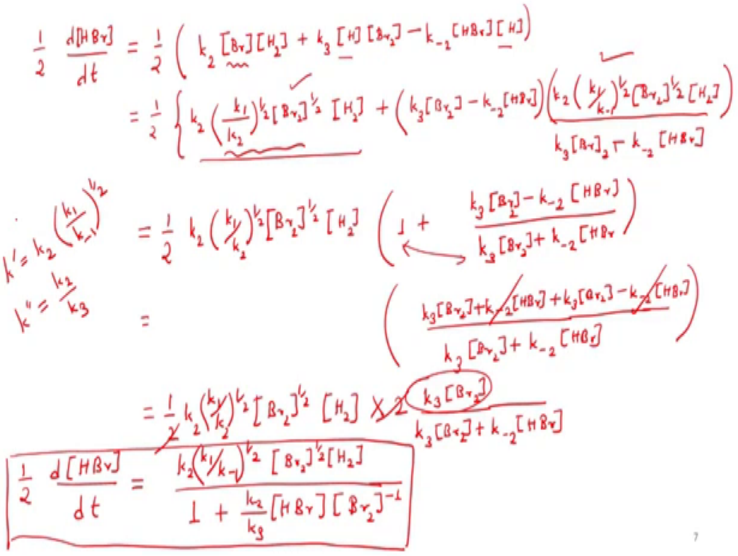

$$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{1}{2}\left(k_2\underset{\sim}{[Br]}[H_2] + k_3\underline{[H]}[Br_2] - k_{-2}[HBr]\underline{[H]}\right)$$

$$= \frac{1}{2}\left\{\underline{k_2\left(\frac{k_1}{k_2}\right)^{1/2}[Br_2]^{1/2}[H_2]} + \left(k_3[Br_2] - k_{-2}[HBr]\right)\left(\frac{k_2\left(k_1/k_{-1}\right)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br]_2 + k_{-2}[HBr]}\right)\right.$$

$k' = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}$

$k'' = \frac{k_2}{k_3}$

$$= \frac{1}{2}k_2\left(k_1/k_1\right)^{1/2}[Br_2]^{1/2}[H_2]\left(1 + \frac{k_3[Br_2] - k_{-2}[HBr]}{k_3[Br_2] + k_{-2}[HBr]}\right)$$

$$= \left(\frac{k_3[Br_2] + \cancel{k_{-2}[HBr]} + k_3[Br_2] - \cancel{k_{-2}[HBr]}}{k_3[Br_2] + k_{-2}[HBr]}\right)$$

$$= \frac{1}{\cancel{2}}k_2\left(k_1/k_2\right)^{1/2}[Br_2]^{1/2}[H_2] \times \cancel{2}\frac{k_3[Br_2]}{k_3[Br_2] + k_{-2}[HBr]}$$

$$\boxed{\frac{1}{2}\frac{d[HBr]}{dt} = \frac{k_2\left(k_1/k_{-1}\right)^{1/2}[Br_2]^{1/2}[H_2]}{1 + \frac{k_2}{k_3}[HBr][Br_2]^{-1}}}$$

So, half the H B r d t is nothing, but half times; let us see what we wrote here; it is k 2 B r into H 2 it is basically that step 2 it is forming, step 3 it is forming and then it is consumed only in one particular step which is reverse of step 2.

So, let us write k 2 B r H 2 and k 3 H B r 2 k 2 and we have B r into H 2 that is the basically reaction of bromine radical which is generated in step 1 with H 2. And then the third step which is basically the generated H radical from reaction 2 is reacting with bromine and then it is decomposing in step 4; if you remember this one. So, H B r in H step 5 we ignored; so, it will be k minus 2 into H B r into H; so that is the overall thing. So, we have to write or insert the expression for the bromine; so, it is half times.

Now, bromine let us see what is the expression for bromine it is 2 k 1 to the power half divided by k minus 1 and bromine it will be B r 2 sorry if the 2 is should be inside B r 2 to the power half. So, let us write it k 2 times 2 k 1 divided by k 2 to the power half B r 2 to the power half into H 2. So, that is basically the expression for bromine and then we have H we have to write for H we can actually take it common. So, you have k 3 into B r 2 minus k minus 2 into H B r that entire thing multiplied by the concentration of H.

Now, the concentration of H is this let us write it k 2 to k 1 divided by k 1 k minus 1 to the power half. It was k 2 and just k 1 and did you see it once again it is k 2; 2 k 1 divided by k minus 1 to the power half. And then you had B r 2 to the power half divided by 8 into H 2 into H 2 half and then you had a division by k 3 B r 2 plus k minus 2 H B r alright.

Let us go back and just check the equations; so, here for the bromine steady state equation, if you remember the last step which is here the step number 6; there actually 2 bromine atoms are generated. So, again from the same logic like it is basically half d B r d t for the step number 6; just like step number 1 had this half factor is minus k minus 1 into bromine square into M.

So, there will be a 2 factor; so there will be a 2 here. So, which means it will be 2 into this; so, these 2 will cancel. So, there will be now 2 here and for that similar expression for hydrogen there will be now 2 here, so it will be just k 1 by k minus 1. So, here there will be any 2 here there will be any 2; now how to solve this thing? So, you can see that this entire expression k 2 into we can actually just take common for this part. So, this half times k 2 into k 1 by k 2 to the power half into bromine to the power half into H 2 and inside parenthesis you have 1 plus.

So, you have you have taken this part common this entire part common which I am writing in the first bracket. So, this and this taken common; so, this I have 1 plus and half k 3 B r 2 minus k minus 2 H B r divided by k 3 B r 2 plus k minus 2 H B r. So, then I can just proceed with this; so, this will be nothing, but if I just act these 2 k 3 B r 2 plus k minus 2 H B r. And so, it will be k 3 B r 2 minus sorry plus because I am just multiplying by 1; k minus 2 H B r. So, that term will cancel you can see it plus k 3 B r 2 minus k minus 2 H B r.

So, this term cancels with this term; so, we will be left to it twice k 3 into B r 2. So, that 2 let us write it, so this will be nothing, but times twice k 3 into B r 2 divided by k 3 B r 2 times plus k minus 2 into H B r. And it is multiplied by this entire thing half k 2; k 1 by k 2 to the power half, bromine to the power half and H 2 you can see that we are almost closed here.

So, the rate of the reaction; so, this half and half will cancel and what we see here we can actually divide the numerator and the denominator by B r 2. So, we can just rewrite it; so, what we got? Half d H B r d t is let us just arrange the constants which is k 2, k 1 by k minus 1 to the power half. Then we have B r 2 to the power half H 2 divided by ; we are dividing both side and there is also in k 3 remember there is a k 3. So, we can write it as k 3 into k 2 and then we have or we could actually divide it by not only B r 2, but we could divide the numerator and denominator by k 3 B r 2.

So, then this factor becomes 1 plus will have k minus 2 divided by k 3 times H B r and there is also B r 2. So, that will be B r 2 to the power minus 1 ; yes I think we are correct yeah. So, this is the rate expression that we saw that we observed experimentally; as we see that if it is even if it is a fairly complicated rate expression we can actually express the entire thing.

This will be actually B r 2 to the power half because now B r should come in the rate expression. And you can see that this observed rate which we had started with we could recover and here. So, that k prime is nothing, but a combination of constant which is k 2 into k 1 by k minus 1 to the power half. And the other constant k double prime the way we have written it at the very beginning, it will be k 2 divided by k 3.

So, as we see that we can actually get the mechanism of this reaction very very correctly by assuming that the reaction happens through the radical pathways. And there are some hints from the observed rate law that the H B r is coming in the denominator which means actually H B r reacts as an inhibitor. And also you see that these nice arrangement here of this or the nice analogy that we had developed throughout using also a fact that this is an endothermic reaction.

So, this elementary step we discarded and finally, by using all this thing and going through all this exercise; we discovered that yes actually the reaction follows the observed rate law. And not only that the rate constants also can be recovered the observed rate constant; there are two rate constant k which you wrote as k prime and k double prime.

They are also described as something like combination of the rate constants of the elementary steps which is k 1, k minus 1, k 2 k minus 2 and k 3. So, we will one more thing we can see here. So, we can see that all the rate constant k 2 k minus 2, k 1 k minus 1 and k 3 they appear in the rate equation; only thing is that k minus 3 which is the reverse of this which is the endothermic reaction that does not happen; it is obvious because we are ignoring.

So, to summarize we saw that how a very I mean simple looking reaction H 2 plus B r 2 is giving you 2 H B r can have a very very complicated read law. But we can actually devise a mechanism which satisfactorily explains the observed rate log; under steady state approximation of the intermediates which are very much reactive intermediates, which are hydrogen radical and bromine radical.

So, now we are all set to discuss the catalysis part, but before that we will first consider or we will first discuss the unimolecular reaction. And then we will discuss little bit about the Arrhenius equation and then we will follow the enzyme then we will have a discussion on the enzyme catalysis.