Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 42
Reaction dynamics - Part 5

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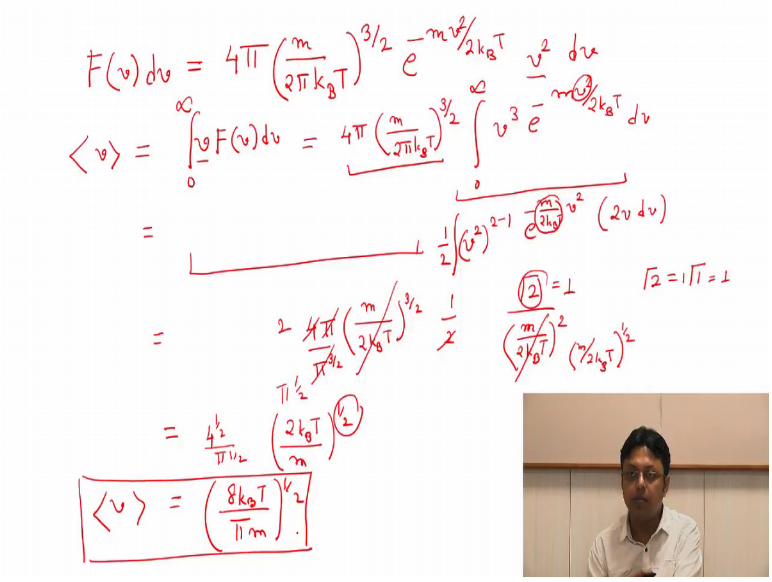

So, we discussed about Maxwell Boltzmann distribution and we got a distribution function F of v d v, we are writing it as F of v d v and that is 4 pi into m by 2 pi K B T raised to 3 by 2 into e to the power minus m v square by twice K B T into v square d v. So, that was the distribution function or it is known as the speed distribution function.

Now, suppose we want to calculate the average value of speed. So, we want to calculate this average value. So, this average value will be given by. So, any average quantity which is a function of velocity, you have to multiply with the probability distribution and integrate over all possible velocities or speed. So, that will be equal to. So, we take it out 4 pi into m by 2 pi K B T raised to the power 3 by 2 and then you write. So, it will be it is a v here and there is a v square here.

So, together it will be v cube e to the power minus m v square by twice K B T and d v. So, I am keeping all the constants outside. Now, this integrant we just solve. So, again this is we will just write it in terms of the gamma function and the way we can write it is that.

So, the term here is v square. So, write it as 2 v d v and then it will be e to the power minus m by twice K B T that is a into v square and then we will have only v squared left here because I have already taken out v squared here and then there will be half multiplied by all the constants which you have written here sorry not here this constitute. Now, this v square now, we can write we have to write it as n minus 1 remember that. So, it is basically v squared to the power 1.

So, what we can write it as it is v squared to the power 2 minus one. So, it will be gamma 2, this integrant value; it will be gamma 2 divided by a to the power 2 and what is a is this constant m by 2 pi K B T to K B T 2 K B T, sorry, m by 2 K B T and square of that. So, what we what do you see here gamma 2 is nothing, but n minus 1 gamma n.

So, it will be 1 into gamma 1 and gamma 1 is n minus 1 factorial which is 0 factorial which is nothing, but 1. So, we will have only m by 2 K B T whole square and inverse of that that is the value of the gamma function and we also have half here, let me write the constant now. So, the constant was 4 pi into m by 2 pi K B T, I am just writing it in a slightly different way m by twice K B T to the power 3 by 2 and then there was a pi that I am taking out pi to the power 3 by 2.

So, what we get is this is equal to 1. So, as you can see m by 2 K B T this is 3 by 2 and this is 2 means it is you can just write it as 4 by 2. So, I will be left with 1 m by twice K B T in the denominator and so, it is 4 by 2 and this is 2 by 2. So, I will be left with square root of that and then these 2 cancels with this I will have 2 here and what I have is let us see here and have one pi to the power 3 by 2 here and this is pi. So, this will cancel giving rise to 1 pi to the power half.

So, at the end of the day what we are getting is I will have 2 times pi to the power of half and divided by m by 2 pi K B T that 2 K B T that we can write it as twice K B T by m raised to half, then we can actually put everything inside the parentheses and keeping in mind that to another power half. So, if I put 2 inside that will be 2 I can write it as 4 square root of 4. So, this 4 and ah; so, instead of 2, I can write it as 4 to the power half and then put everything inside. So, it will be 8 pi K B T by m I think the pi is in the denominator not in the numerator so, which is divided by pi to the power half.

So, it will be nothing, but 8 K B T by pi m to the power half. So, this is the value of the average velocity now you can also ask you can now plot it the Maxwell Boltzmann distribution and now just ask this question where basically what is the value of this of these all these parameters that we got.

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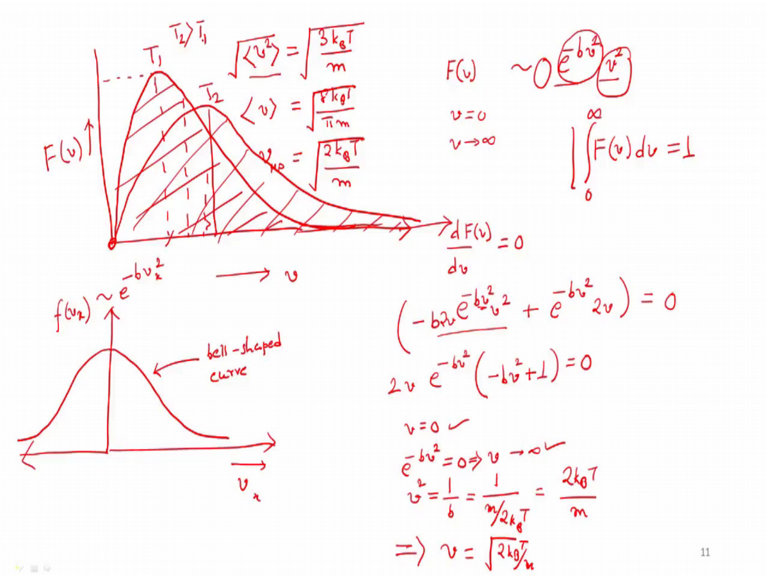

So, if you plot the Maxwell Boltzmann distribution again remember that it has basically 2 terms F of p d v that actually goes as e to the power minus some constant into v square into v square d v.

So, if I just plot it off v versus v that is how it will look like and then what we will have is that think about it at v equal to 0 the function will be 0 because this term is 0 and when v tends to infinity the function actually goes to 0 because of this term. So, very high and very low velocities are actually the probability of that is actually 0.

So, this function will look like something like this and then what you get here is that you have something with some where the function actually picks up now remember that this is a well speed distribution if I had plotted the velocity distribution which is F of x that we discussed at very early. So, that is that has a form of e to the power minus b v x square. So, if I plot v x along this axis remember that velocity can take both positive and negative values.

So, that function is known as Gaussian function or this is sometimes known as it is a bell shaped curve and this is called a bell shaped curve and here note the striking difference that I am getting this term v square term when I actually considered that this is a speed distribution which does not have any preferential direction. So, that is actually changing the entire thing. Now, we can actually proceed along the same direction and try to find out what is this maximum probability or what is this maximum distribution maximum the distribution. So, that maxima to get it you have to just take the derivative of that function with respect to velocity and then to find the maxima you have to just take it to be 0.

So, you can easily get it. So, there is some constant here, but we do not care because the constant will be anyway 0 because we are just equating it to be 0. So, if I take the derivative. So, follow it carefully. So, it is a chain rule in differentiation first take the derivative of e to the power of minus d v square.

So, it will be just e to the power minus d v square and it will be minus b and times you have e to the power minus d v square into derivative of v square with respect to v. So, that will be 2 v. So, that enter term should be equal to 0. Now, what you see here is very interesting thing that we have if you look at it here that if I take e to the power minus v square v into e to the power minus b square common, then we will have minus b into v plus 2 that is equal to 0.

Now, we have 3 possibilities one is v equal to 0 that is just one of the minimum and the second possibility is e to the power minus b v square that is 0 that happens when v tends to infinity and the third thing. So, e to power minus v squared equal to 0 means v tends to infinity. So, these are 2 location of the minimum. So, this is the first minima here and the second minima at basically at infinity you can actually draw it more nicely ok; so, at very high value.

So, this is also the second minima it goes to its not actually the minima should not be here actually it is just exponential square take. So, tends to infinity the very high value and also the third condition where is giving me that v is 2 by b and remember what does b was m by 2 pi K B T. So, 2 K B T; so, it is basically m by twice K B T if I just put it a on top that will be it should be one let me just check quickly it is 2 v and when I take the derivative it is basically yeah. So, e to the power v square when I take the derivative or to take also the derivative for v v square that will give me 2 v.

So, what I can take as common is v and this will be then you check once again this will be then v square yes it has to v square and this 2 will cancel this will be just one and then

I will have v square is equal to one by b. So, twice K B T by m or we can say that when just write it here that v is nothing, but twice K B T by m square root now this v is we write it as v most probable meaning what is the most probable velocity and we see that you have 3 different kinds of velocities. So, one is the v squared average which we already got from kinetic theory of gases and that we know that will be 3 K B T by m.

But usually we take the square root of that because it is a it has a dimension of velocity that is known as this is basically mean square velocity. So, taking the square root we call it as a root mean square velocity that is square root of 3 K B T by m and we just showed that the average velocity is nothing, but 8 K B T by pi m square root and then right now we showed there is a v and I am writing it as mp; mp in the sense is the most probable velocity or the it basically is the where the curve actually maximizes and that is nothing, but twice K B T by m square root of that. So, what we see here.

So, this is twice K B T by m and then the 3 K B T by m and 8 K B T by m you just have a look at it. So, 8 by pi pi is 3.14. So, it will be always greater than 8 by 3.14 will be greater than 2, but of course, it is less than 3. So, the average velocity will be somewhere here; so, to the higher than this value. So, this will be the v average position of that it is it is highly quality the way I am writing it right now and the r m s velocity will be somewhere here which is the highest value.

So, you see that average velocity means actually what is the average number of molecules or the what is the mean of this distribution is like now you can see that that actually depends on the area under the curve also now this is a probability distribution remember that and if I take the area under the curve that should be always equal to 1 because we know that F of v d v, it is a probability distribution integrated from 0 to infinity should be equal to 1.

Now, we can ask a question that suppose, we go to a high temperature. So, what will happen or lower temperature if we increase the temperature you can see that the function goes as with respect to temperature; there is a functional dependence inside b and there is also v squared both of them actually are dependent on temperature. Now, if you plot it then you can easily figure out this curve will actually get more and more flattened and this value of this most probable distribution will actually shift towards right and all the velocities actually shift towards, right and the curve will get more and more flattened in the sense that.

But area under the curve will still be the same it will be still in if we integrate it should be equal to one always. So, this is drawn at two different temperatures say t 1 and t 2 where t 2 is greater than t 1. Now, one more interesting thing to look at is this kind of curve.

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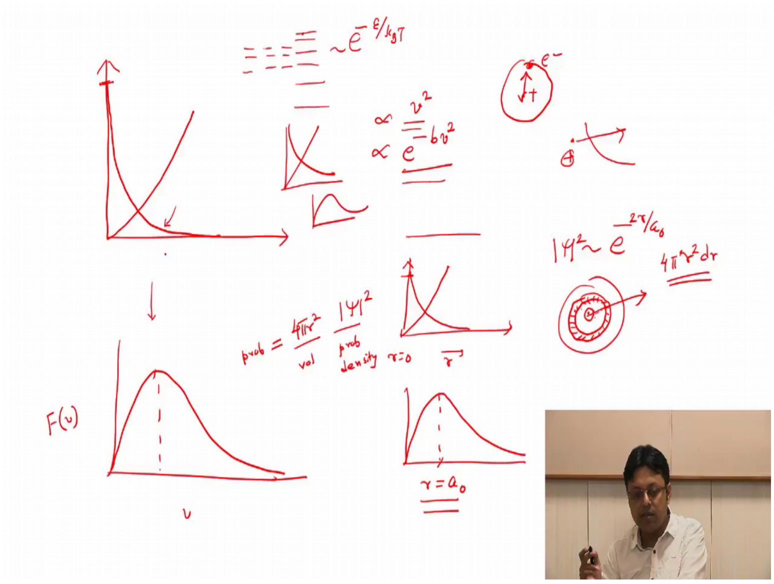

Where actually I have two different functional variation one is v squared and one is e to the power minus some constant into a v squared.

So, think about it if I plot it very separately e to the power minus b square will be very sharply decaying function of v and v square actually goes as this it is a quadratic function. So, the product of them actually something like this. So, as you can see that e to the power minus v square picks up at v equal to 0; however, that v equal to 0 the function is not maximum because of this term is also there.

So, that is making the function at 0. Similarly, at a very high value, e to the power minus v squared is 0, but v squared is a very high value, but you do not get a very high value there because now this is basically bringing it down. So, at somewhere here where both the functions have some values they are actually get the maximum similar type of behavior you will also see in many other situation for example, when you discuss the in quantum mechanics.

So, when you study these hydrogen probability density or probability distribution along the radial coordinate for say a ones orbital and the functional form for ones orbital is the wave function actually it goes as e to the power minus r by a 0. So, if you go from go away from the nuclei the electron this is the basically probability amplitude decreasing.

So, square of the probability amplitude decreases as e to the power minus 2 r by a 0 that is a decaying function of r that psi square mod psi square which actually is directly related to the other probability density; however, you never get the maxima at r equal to 0 which is at the nucleus the reason is you actually measured the probability density, but not the probability.

So, which means so, if this is the atom or you are talking about probability density as you go away from the nuclei. So, you see that probability density drops, but when you measure the probability you have to multiply it by a volume and that volume means actually you have to consider a small sphere around it and that volume of the sphere or if you just go somewhere here.

You have to consider again volume of a spherical shell that we kind of calculated and when you multiply the volume of the spherical shell you remember that that will come as 4 pi r square d r, we already calculated it in terms of v that that was 4 pi v squared d v it is the same thing. So, that actually is a quadratic function and that goes as like this. So, when you plot the actual probability which is multiplied by 4 pi r squared.

So, it is the volume and this is the probability density. So, density times volume is the probability. So, you have two functions which are actually maximizing or minimizing at two different extremes.

So, what do you see actually this function will go also as a with from an with a maxima somewhere else neither at r equal to 0 or equal to infinity and that for the one is atomic orbital, you can easily show that this maxima will come at r equal to s 0 over s 0 is above radius which actually both found to be the radius of the electron or of the if you think that ok. So, the electron is classically or writing as a particle around the nucleus. So, that distance is basically a 0 known as both radius.

So, that you can easily figure out from in quantum mechanics also; So, this kind of curve come and many different places also in degeneracy or in the in the Boltzmann distribution where you talk about rotational levels there also you will see that fine if I go to very very high additional levels that your Boltzmann distribution goes as e to the power minus e by K B T that we will discuss a little bit.

So, chances of getting a particle at a very higher level is much less. So, it actually drops down, but the number of steps are also increasing in a number of steps for a particular energy which is known as degeneracy factor that also goes as it is it goes as some factor to 2 j plus 1 we are not let us not go into the details, but the point here is that since that is also going high you get a increasing value of that and together you will see that these two functions actually goes through a maximum.

So, the point here the this kind of nature of the curve you will encounter at many places not only in maxima Boltzmann distribution, but also in some other systems like rotational levels when you are talking about probability distribution in the rotational levels or even in particle in a box also 3 D box and the degeneracy factor is increasing, but then.

So, basically the long story short there are two always mathematical forms of the inside the function one is trying to basically maximizing the function at 0 and minimizing the function at infinitely the other one is has just the opposite effect that the actual function is a product of these two parts and which goes through a maximum and now you can ask this question.

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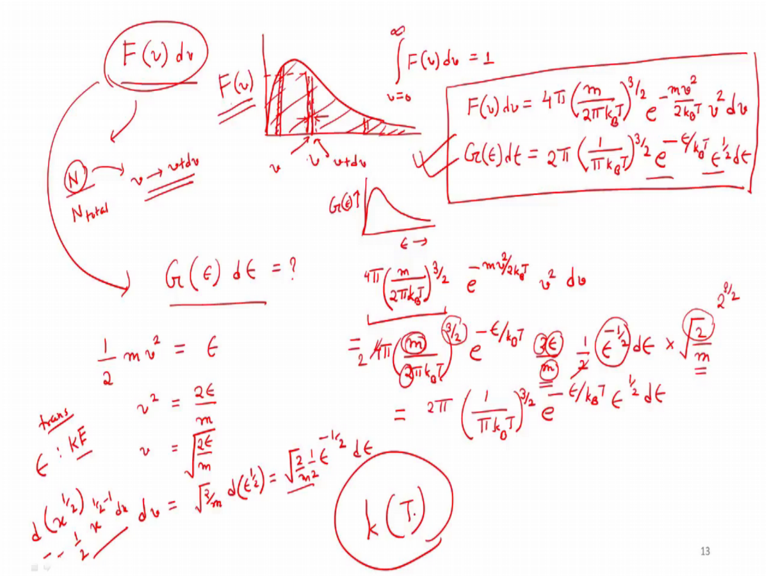

So, we got a function which is a maximum and distribution function are the velocity speed distribution function now what is the meaning of this d v. So, if I plot F of v versus v.

So, if I ask you; what is what is the what is the probability at finding the molecule and v that is not a very good question to ask the reason is as I said that the exact number of molecules those are actually fixed for a narrow range, you have always is whenever you are talking about probability and you are not talking about this in the same sense like hydrogen atom.

We are not talking about probability density we are talking about probability which is basically probability density times the volume in this case it is F of v is nothing, but probability per unit velocity range. So, what we talk about is actually to get the actual probability you have to talk about probability in a narrow range which is a p 2 p plus d v and that is this function.

So, this function will tell me the fraction of molecules because this is still a probability. So, some number of molecules divided by the total number of molecules this number of molecules is nothing, but they are those number of molecules which lie whose speed lie in the range v 2 v plus d v at any time and again on a statistical ground. We said that this number for a very large system will always be fixed because some molecules are entering in this region and others are living.

So, you always talk about particular width in the distribution and then once you integrate this curve it is nothing, but you take at various position of the v and for every v, you just calculate, what will happen? What is the area element if I go from v to v plus d v and in that way you basically build up the area under the entire curve and that is the meaning of integration and then you realize that F of v d v.

So, that is basically the area under this curve and if I integrate over all the area which means I am varying now v from 0 to infinity that should be equal to one. So, this curve is known as actual area normalized curve now the question is from this distribution, can I actually get a distribution which actually say is in terms of the energy something like this can I.

So, because that will be very useful to understand reaction kinetics or reaction dynamics that when a reaction is feasible or not now to get that we need to just use a very simple relation we know that half m v square is the kinetic energy and here energy means the kinetic energy itself. So, whatever I have the v squared term I can easily replace it by this and then you can easily say that. So, v square will be twice epsilon by m or we can write it as v is nothing, but square root of twice epsilon by m.

So, the speed distribution we wrote it as if you remember that it was 4 pi into m by 2 pi K B T raised to 3 by 2 e to the power minus m v square by twice K B T v square d v. Now we have to replace these terms. So, that we can write it as am not; right now writing this one e to the power minus m v square. So, you know that half m v square that will be the kinetic energy. So, this is nothing, but e to the power minus epsilon by K B T by the way when I write epsilon and call it as a energy it means that it is actually translational kinetic energy always.

So, because it is a maximum Boltzmann distribution of molecular speed; So, it is a translational motion that we are talking about and then instead of v square we can directly write twice epsilon by m and now for d v you can write it when just taking the differential on both side.

So, it is square root 2 by m into d of epsilon to the power half. So, d of epsilon to the power half if I take the differential it will be F epsilon to the power half will be square root of 2 n. So, it is nothing, but derivative of this or differential of this.

So, that is nothing, but half x to the power half minus 1 into d x something like that. So, you get epsilon to the power minus half and there is a half factor here and d epsilon. So, let us just put it here. So, it will be half epsilon to the power of minus half d epsilon and in the front you have 4 pi into m by 2 pi K B T. Now, if you just rearrange the terms. So, that will be.

So, look at it here carefully. So, I have an this is raised to 3 by 2. Now this 4 pi and there is a 2 here. So, I can write it as 2 pi yeah we follow to right to this factor here square root of 2 by m. So, it will be also my multiplied by square root of 2 by m and then you can see here this m and m to the power half by 2 is m to the power 3 by 2 and that will cancel with this m to the power 3 by 2.

So, what will be left to it and there is a square root of 2 here and there is a 2 here. So, I can write these together as 2 to the power 3 by 2 because these 2 I can write it as 2 to the power 2 by 2 and this square root of 2 is 2 to the power half. So, I will have 2 pi and that 2 to the power 3 by 2 will also cancel with this 2 to the power 3 by 2.

So, in essence; I will have one over pi K B T raised to 3 by 2 e to the power minus epsilon by K B T epsilon to the power minus half and this epsilon will give me epsilon to the power half d epsilon. So, that is basically the Maxwell Boltzmann distribution of molecular energies.

So, let us write it clearly. So, what we just got that we got basically to the distribution function in terms of molecular speed that we write it as F of v d v and that is 4 pi m by 2 pi K B T raised to the power 3 by 2 e to the power of minus m v square by twice K B T into v square d v and if I just convert it into the energy distribution I am writing as g of d epsilon d epsilon.

So, that is 2 pi into one by pi K B T raise to 3 by 2 e to the power minus epsilon by K B T epsilon to the power half d epsilon and see that this energy distribution is also will have a shape something like these it has a exponentially decaying function, but it if I just plot it epsilon g epsilon versus epsilon.

So, there will be a decaying function, but that that decay is not too fast decay like the Maxwell Boltzmann distribution and the rise is also not too fast there are actually it was v square squared of velocity here actually it is epsilon to the power half.

But the overall nature will be I mean over a qualitative thing will be same it is one function that is raising with respect to epsilon and the one function that is decaying. So, it will have slightly different curve which is something like that, but yeah then the quality of nature will be same now.

So, to summarize; so, we have got basically two distribution functions one is Maxwell Boltzmann distribution function in of speed and other one is the energy and we will see how this energy distribution function will be useful in calculating or estimating the rate constant and remember that is our goal, we have to calculate these k of t or this rate constant at as a function of temperature and see what is happening.