Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 41
Reaction dynamics – Part 4

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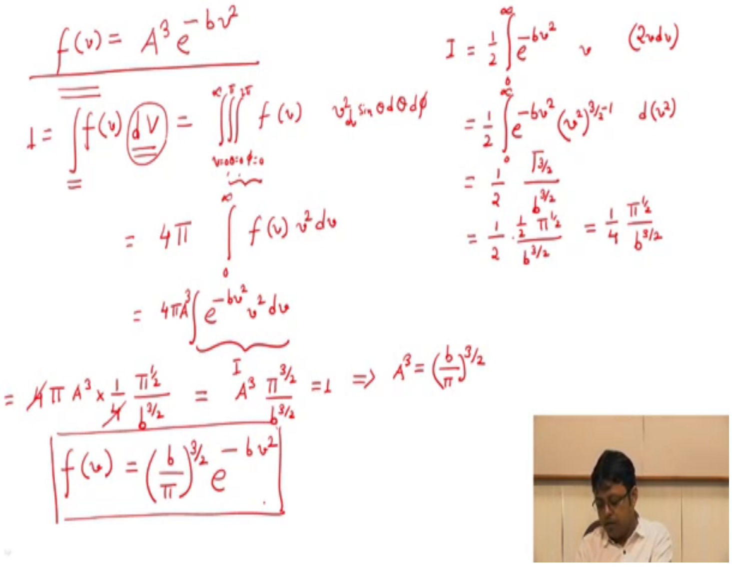

Now, if you remember that the functional form of the distribution function was A cube into e to the power minus b v square and then, we said that we are going to integrate it to get the entire probability because by definition, since it is a probability distribution in the speed, the velocity space ah; so if we integrate it irrespective of any direction. So, that will give me the actual velocity or the total probability and the total probability must be equal to 1. So, if I integrate it over the entire volume, I should get it a the value equal to 1; this volume again it is in the velocity space.

Now, part of the dv that we have already calculated, we have already integrated it over the theta and phi and we know how to integrate it because this volume element was basically v square sin theta d theta d phi and this integration means actually, it is a triple integration between are the this v theta and phi, v going from 0 to infinity; theta going from 0 to pi and phi going from 0 to 2 pi. So, those 3 integrations, I mean out of those 3, these 2 are done already. So, all we have to do is to evaluate this integral, 0 to infinity. So, let me write the other value.

So, the integration of our theta and phi gave 4 pi and then there is a v square and then, we had a dv also and we had basically f of v, v square d v, that we are going to evaluate and that we know should be equal to 1. Now let us write the value of v square. So, that will be sorry f of v that is A cube. A cube also, we can keep out of the integration 4 pi A cube and then we have e to the power minus v b v square into v square into d v. Now for evaluating this integral, we can use a standard integration table but I am not use that ladder actually tell you any general integral, how we can solve this kind of integrals.

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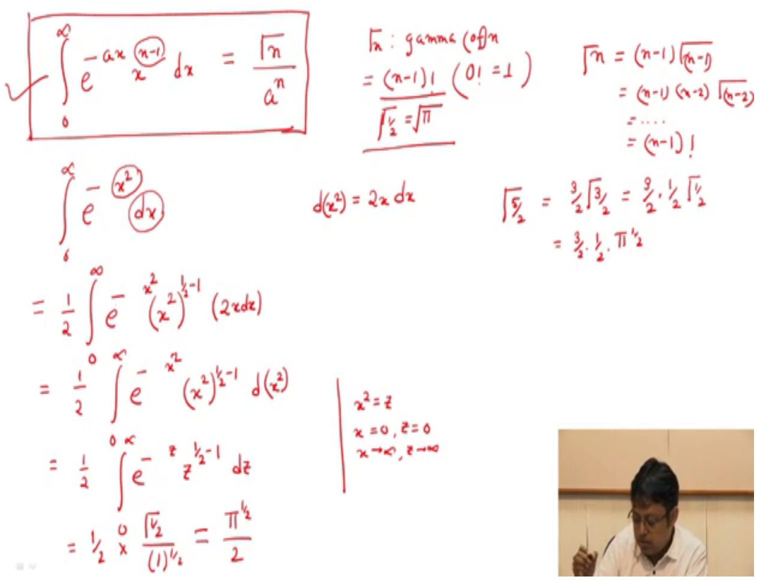

Now, what is this kind of integral? So, suppose I have a very general integral, which is integral 0 to infinity; x to the power n minus 1 e to the power minus x or better write they e to the power minus x first; x to the power n minus 1 dx that is a special function and this special function is known as gamma function. We write it as just like this and the value of the integral v gamma n by e to the power n where this thing is nothing but gamma. It is basically gamma of n.

We call it as gamma n and the value of it is nothing but n minus one factorial and if you by chance get gamma half, that will be nothing but root pi and remember that 0 factorial is 1. I hope you know there were what is factorials. Now let us try to evaluate something. Let us say evaluate here. So, here what we have, it is e to the power minus x square into x square dx some kind of thing.

So, suppose I ask you to evaluate this one, e to the power minus a x square, a for let us first evaluate this one e to the power minus x square d x what is the integral? Now what do we have to do; we have to write it in this form, in this integral from, then only we can directly put the fellow. Now think about it. How to do it first look at the exponent, what is the variable? The variable is x square not x. So, here I have to write it instant of dx, I have to write it as d of x square. So, we know that d of x square is nothing but 2 x dx. So, I have to multiply by 2 x and I have to also divide by 2 x. So, so that is the idea.

So, what I am writing, just follow carefully. I have e to the power minus. Let us let me just write the dx first. So, I am writing that 2 x dx and then, I have to use something like or we can write it 2 x dx later also, that is not a problem. So, I have e to the power minus a x square into I have 2 x dx that will give me the d of x square and then I have to divide it by x that I will write at x to the power minus 1 and I also have a factor of half because to account for this 2 here.

So, x to the power minus one, now I have to write everything in terms of x square because x square is now the variable. So, x to the power minus 1, instead of that I can write it as x square to the power minus half because that is also x to the power minus half minus 1 but instead of writing minus half, I will write it as n minus 1 because in the gamma function formula, it is n minus 1.

So, minus half is nothing but half minus 1. So, this entire thing e to the power minus x square, I can write it like this. So, in the next step what I will do is that and the x is going from 0 to infinity. So, I will write it as half 0 to infinity e to the power minus a x square x square to the power half minus 1 d of x square. You can easily do a change in variable, you can just say that x square is z.

So, when x is 0, z is 0 when x is tends to infinity, z is also tending to infinity ok. So, you can just do a change in variable. So, we can write e to the power minus a z z to the power half minus 1 d z, that is exactly the gamma function formula and that tells you this value will be nothing but gamma n by a to the power n. So, there is a half times gamma half by a to the power half; a is basically here. Let us just evaluate say just e to the power minus x square because this is also will appear somewhere.

So, a is nothing but 1, so 1 to the power half. So, the value of this digression will be gamma half is root pi. So, it will be root pi by 2. Similarly, if you ask what it will be the value of say x to the power e to the power minus x square. So, that also we have to write in terms of gamma function. We can easily write it. So, let us go back now and just try to evaluate this integral; e to the power minus v square b v square v square dv. Now again it is basically v square, so I have to write 2 v dv because in the next step, I will just write it as d of v square. So, that is the trick. Now if I write attached 2 v dv of course, I have to account for a factor half, I am just writing this integrand right now. So, this is a and there are some constants also.

So, the limits are 0 to infinity and then I have e to the power minus b v square. If I have 2 v dv, so there is a v square already there. So, suppose I took, I have stolen one v. So, this v and this v is v square. So, that v, I can write it as v square to the power half right. So, and half, I have to write it as n minus 1. So, that n will be basically half plus 1 or that I have to write it as 3 by 2 minus 1. So, then now we can see how we have written it down, maybe I I should write it in the next line this was basically v and then what I have is e to the power minus v v square, v square to the power 3 by 2 minus 1. So, 3 by 2 minus 1 is half and v square to the power half is v.

So, that is how it we are writing. So, it is nothing but half gamma 3 by 2 divided by b to the power 3 by 2. So, gamma n by a to the power n, so here a is nothing but b the constant. Then you can easily see what is gamma 3 by 2. So, gamma n is n minus 1 factorial that we will do. So, like here n minus 1 means actually. So, let us go once again. So, like you suppose if I have gamma 5 by 2, so that will mean if it is n minus 1, so I can write gamma n is as n minus 1 gamma n minus 1 which is basically n minus 1 into n minus 2 into gamma n minus 2; so, that will that will basically get series which is nothing but n minus 1 factorial.

So, that is the same thing we are doing here. So, if it is gamma 5 by 2 say for example, it will be n minus 1, gamma n minus 1. So, n minus 1 is 3 by 2, gamma 3 by 2. Now, gamma 3 by 2 write it as 3 by 2 into n minus one much. So, 3 by 2 minus 1 is half into gamma half and we already know that gamma half means root pi. So, it will be nothing but 3 by 2 into half into root pi.

So, in a similar token, this one will be nothing but half, gamma half which is we have half in here. We have another half and gamma half is root pi divided by b to the power 3 by 2. So, what we got is this half and this half gets one fourth pi sorry pi to the power half divided by b to the power 3 by 2. So now, you can just put it here. Just for space, I am just writing it here it is basically 4 into pi into A cube into one fourth pi to the power half divided by b to the power 3 by 2 that is equal to 1. Let me first simplify and then we will equate it to 1 and then what we see here this 4 cancels and then what I get is nothing but pi to the power 3 by 2 because pi is nothing but pi to the power 2 by 2.

So, I can write it as A cube into pi to the power 3 by 2 divided by b to the power 3 by 2 that is equal to 1 or we could actually write instead of A cube, we could write actually b by pi to the power 3 by 2. So, the distribution function is now slightly better. I can see that. So, we are writing it as f v, the functional form of f v which was this. So, now, I have written in terms of only one constant. So, I have eliminated A. I am writing A in terms of b, but still I have to evaluate p; b to the power 3 b by pi to the power 3 by 2 e to the power minus b v square. So, that is now the distribution function. Now we have to evaluate b.

Now, to evaluate b, now you can ask the say remember that we said that we will also take help of the fact that the average value of the v square will be nothing but equal to the 3 3 k b T by m; So, which we just started. So, we will just use this fact from the kinetic theory of gases that v square average is 3 k b T by m.

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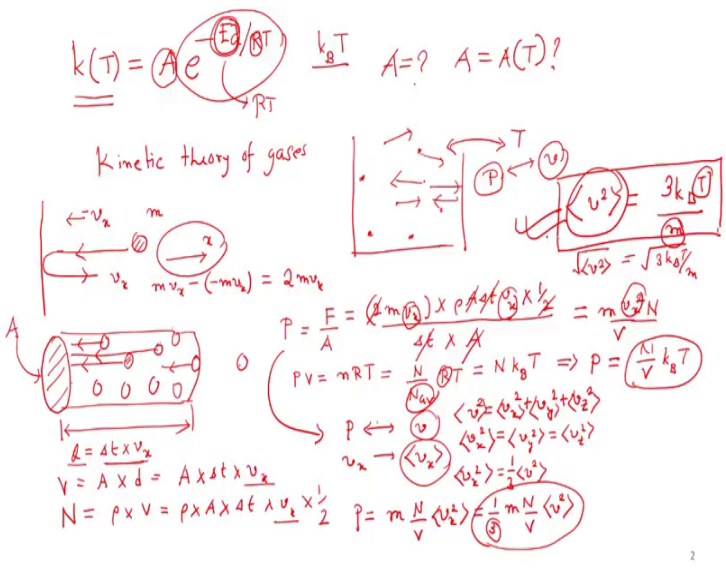

So, now, how will you calculate v square average from this function? It is very easy. So, average value of any quantity.

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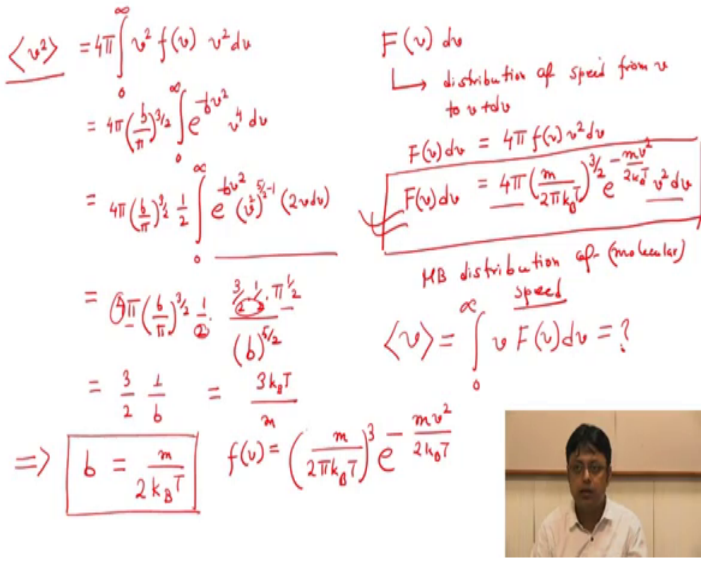

Say in this case, v square average will be nothing but you take the v square, you multiply it by the probability factor and then you integrate over the v and of course you have to integrate over everything, but the 4 pi is already there. So, I am just writing it like this; 4 pi and I am writing it as dv and only integration over v. So, what I get here is that let us just evaluate it. I have 4 pi and then f of v we got already an interesting relation which is basically this one b by pi to the power 3 by 2, e to the power minus b v square.

So, b by pi to the power 3 by 2, e to the power minus v square into v square d v, that integral; now we can easily write this form that it is e to the power minus v square; I have to write 2 v dv from d of v square and then I will have one v here, one half here and instead of v, I can write v square to the power half which is basically. So, this here we had a v squared dv because the volume element was 4 pi v squared dv and together I will have v to the power 4 dv.

So, I will have a v v cube here. So, the v cube thing, I have to write it as v squared to the power n minus 1. So, if I write it as v squared, it is basically v square to the power 3 by 2 and the 3 by 2 I can write it as pi by 2 minus 1. So, that is the entire thing, 0 to infinity and there are some constants which is 4 pi into v by pi to the power 3 by 2.

So, this thing will be nothing but gamma 5 by 2 divided by a to the power 5 by 2. Now also have to write the d here in the distribution function there was a b. So, it will be b to the power gamma n by a to the power n; b to the power 5 by 2. Now you can easily see we are going to get a very interesting relation. So, I have 4 pi here, b by pi to the power 3 by 2 into half. Instead of gamma 5 by 2, you can just slightly directly write down the value. So, gamma 5 by 2 is 3 by 2 times half times root pi and then let us see what we discovered. So, these this half and this half gets cancelled right away sorry, it is not cancelled; it will be the value. So, let us see actually what do you get. So, what we have here, let us just write everything together. I have 3 here and 2 into 2, 4 and 8.

So, that 4 actually gets canceled with this 4. So, ultimately I will have 3 by 2 and it is specific a 2 into 2, 4 into 8 and just write it, 4 into 3 by 8. So, it is 3 by 2 and then just calculate the pi's. So, I have pi divided by pi to the power 3 by 2 and the pi into pi to the power half is pi to the power 3 by 2 and that gets cancelled with pi to the power 3 by 2. So, that is fine. I have b to the power 3 by 2 and b to the power 5 by 2 here. So, that get cancelled I will have only 1 over b and that should be equal to as you know, it will be 3 k b T by m because that is the value of the v square average.

So, we get what is b? b is nothing but, we get 3 and 3 cancels here; basically I will get twice kb or we can just go in the other way. So, this is the value of b. So, the distribution function f of v, now instead of f of v, we are writing every time as what is the exact distribution function, but then when we are integrating it, we are integrating it with v and v plus dv. So, we what we are writing from what will what will write from now or onward, we just introduced a new distribution function.

So, this is nothing but the distribution of velocities, distribution of velocities or distribution of speed from v to v plus dv. So, that we can get; so f of v dv is nothing but, I have to take the original thing f v and integrate it up only over the theta and phi and with the corresponding following element, but that will give me I I without integrating it over v because only the v part and just integrating over the theta and phi. So, theta phi integration gives me 4 pi v square dv.

So, we are just writing it as 4 pi f v dv; there is also v square dv. So, the v square value, now we can write it what was f of v f of v was a cube, but a we wrote in terms of b already. So, we found that it is b by pi to the power 3 by 2. Now b is twice m. So, we can write it as just one minute, it will be 3 by 2 and it will be actually b, b will be m by 2 k b T. So, let us just rewrite it once again f of b is b by pi to the power 3 by 2, b by pi. So, it will be 2 pi k b T to the power 3 by 2 into e to the power minus b v square, b it will be m v square by twice k b T.

So, this distribution function which we are going to use which is already integrated over theta and phi will be nothing but 4 pi into m by 2 pi k b T raised to the power 3 by 2 into e to the power minus m v square by twice k b T into v square d v. So, that is the Maxwell Boltzmann distribution of molecular speed. So, this is the Maxwell Boltzmann distribution of molecular speed. It is not velocity again.

So, what we what we learnt today or what we discussed today so far is that, we started with kinetic theory of gas and then we said that no actually that is not that I mean the gas molecules have a range of velocities. It is not that every molecule is having the same velocity and then we argued that in a I mean statistical ground within a range of velocities, the number of the molecules will be the same and that is what exactly we wanted to calculate.

Now, when we are talking about velocities, actually the thing which we measure is speed and speed is independent of any direction and which means from a velocity distribution, we can construct speed distribution just by integrating over the direction which means actually we are, I mean removing the constraint on the direction.

It is not biased in moving in any particular direction and then we showed how to get the volume element in spherical polar coordinate and we before that prior to that we actually discussed the actual form of the distribution function based on several logical footage where we said that it should be an even function, it should be it should vanish at plus minus infinity and all these things and then we got a distribution function, small f of v. That distribution function is a probability function and then f of v depends also on different but we direction, but we said that it we better actually get distribution function while we are integrating it over all the direction.

And all we are getting is basically the final Maxwell Boltzmann distribution where the directional independence thing is already taken care of. We have already multiplied it by 4 by v square into dv. So, all we have to do is, take this function multiplied with something, say some average quantity that we want to measure and then integrate over only over v because the theta phi integration is already done. So, all we have to do suppose for example which we will see in the next part is that if we integrate, if we want to find the value of average velocity, what we have to do; we have to take this velocity and ask what is the probability just multiplied by the probability distribution and then just integrate over 0 to infinity and you get something.

So, that we will see and we have not plotted the Maxwell Boltzmann distribution yet we will first plot this function. How it looks like and we will also discuss that what are the from how to go from the speed distribution to the energy distribution. So, those things we will discuss in the subsequent parts.

Thank you.