Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 39
Reaction dynamics – Part 2

So, let us first discuss the reasoning that will have this situation or.

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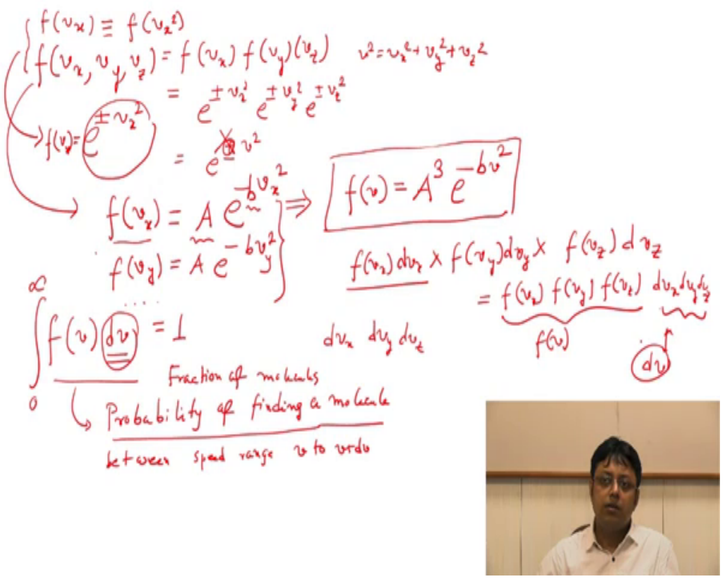

This condition that the joint probability will be product of individual probabilities and also the first condition that f of v x is an even function of v x and we asserted that it will be something like v x square. So, if we write it together, so the probability distribution will be something like e to the power minus plus or minus v x square 1 or v square, why, the reason is goes as like this.

So, we know that v square is v x square plus v y square plus v v z square. So, you can say that f of this quantity, f of v x into f of v y into f of v z, it will be nothing but e to the power plus or minus v x square into e to the power plus or minus v y square into e to the power plus or minus v z square, because if you add all of them either plus or minus which you do not know yet.

So, then I will get I, if I take the plus sign, it will be v s square plus v y square plus v z square which will be nothing but v square and that make sense because this probability f of v x in v y, v z has to be the probability of having this velocity component along x is v x and simultaneously along y is v y, along z is v z which means we are calculating some v where v square is equal to v square x square plus v y square plus v z square and that we directly get from this argument. Now whether the plus sign will be correct at the minus sign ; now if you can think that if I take the plus sign, so it very large velocities. So, this will, this distribution will blow up. So, when v goes to infinity it will be very high. So, that is very very highly unlikely.

So, this plus sign cannot be possible; however, if v or say any of this velocity say all right now, let us talk about only the velocities if the v x can go to plus minus infinity, but if I retain the minus sign, then either it goes to minus infinity or plus infinity that will basically if I take the minus sign then e to the power plus or minus infinity squared will be 0. So, it will probability of having the molecule at a extremely high or extremely high speed in either direction will be very very low.

So, just by logic, will say that f of v x will have a form of e to the power minus v x square, but of course, there will be some constant we are just writing this arbitrary constant as b v x square and also there will be some other constant because we are just keeping this as an arbitrary constant which you can evaluate later.

So, the functional form of f of v x will be nothing but A into e to the power minus b v x square and so, similarly f of v y will be a into e to the power minus b v y square because this A and b are just arbitrary constant and which are independent of the direction. It is just the functional form. It does not matter whether it is x, y or z. So, if it is f x the corresponding term will be x if it is f y, it will be v y if it is z it will be v z. So, we can now say; so, what will be the f of v f of e will be nothing but the product of f of v x into f of v y into f of v z.

So, I will have something like A cube into e to the power minus b and then all these v x square v y square and v z square add up. So, that will give me e to the power minus b v square. So, that is the functional form that we are getting for the velocity distribution. So, for the speed distribution and it just we just got it from the velocity distribution and also are going that f of v y will also be e to the power minus b v x square, sorry it will be v v y and similarly for f of v z and all these three, is giving me this speed distribution.

Now the question is what is this, this is the distribution function of course. And we are going to evaluate it what is the what is that evaluation, but before that, let us consider that usually when you evaluate it, you have to integrate the f of v d v that should be equal to 1 because this is a probability distribution and since this is the speed, speed cannot be positive or negative. It will be from 0 to infinity.

However we have to now calculate d v in terms of d v x, d v y, dv z which means, what is d v or f of v d v f of v d v means, it is basically the probability of finding a molecule which is basically the number of molecules divided by the total number which you can also say the fraction ; fraction of molecules instead of probability of finding a molecule between speed range v 2, v plus dv, but what the functional form we got from f of v x if we just ask this a similar question what is f of v x, dv x that basically tells you, it is the probability of finding a molecule with a x component speed v x to d to v x plus d v x.

So, all we have to do right now is to ask this question, how we can get from a the d v x. So, so joint probability will be nothing but if you if you ask this question that the what is the joint probability? Joint probability will be of having a molecule from speed velocity v x to v x plus d v x in x direction simultaneously, the y component velocity from v y to v y plus dv y and simultaneously, the z component velocity as from v z to v z plus d v z that will be nothing but f of v x into f of v y into f of v z into d v x, d v y, d v z.

Now, the first part we already calculated it will be nothing, but f of v, but this is not how to calculate basically this to and connect it to the d v because d v is independent of direction whereas, d v x, d v y, d v z have some direction. Now to give you a better feeling of what I am saying is that, let us consider just a 2 dimensional distribution. Suppose the molecules are moving on a plane and so we can actually draw it in a Cartesian coordinate and suppose this axis tells me the v x and this axis is for v y.

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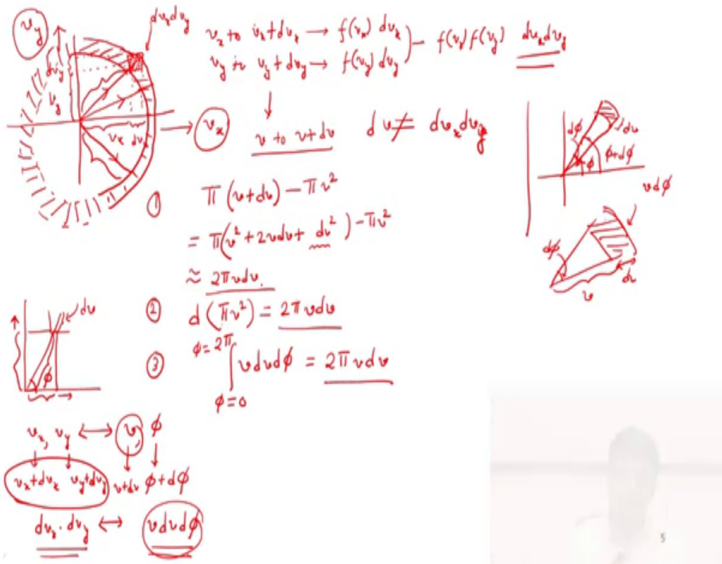

So, I only have two components of velocities. And suppose at any point, the velocity is along this direction. So, I can always say that fine, I can this will be my basically x component projection will be v x and then I have a range always. So, the range is v x to sorry v x plus d v x.

So, suppose this is d v x and this is v y plus v y plus d v y. So, now, the question is, if I had taken the number of molecules with this kind of distribution where the velocity is v x to v x plus d v d v x minus v x plus d v x and simultaneously, v y to v y plus d v y and then we ask this question from this information that what is the number of molecules are the probability of the molecules of having the molecule having the speed in the range v to v plus dv, then that is independent of direction meaning if I had chosen the velocity along this direction.

This number will be the same; whichever direction you choose the speed it does not matter because speed is independent of direction. So, this quantity, since it is independent of direction which it means is that, what I have to do is that instead of calculating this d v x d v y, what is d v x, d v y? d v x, d v y is nothing but the volume element of the in this case actually it is the area element because it is a 2 dimensional thing. Now remember that function was f of v x into d v x and that function was f of v y into d v y. So, their joint probability was f of v x into f of v y into d v x d v y. So, that is I have shown here what it is it is dv x, dv y.

So, that is a small infinitesimal area element in the velocity space always remember that this is not a position space, this is a velocity space now ah; however, when I calculate the speed I only calculate the length of the vector which is equivalent to v. Now the length of the vector is v here, length of the vector is also v here. Now, v 2 v plus dv means actually, this now dv will be independent of any direction; which means, we have to calculate this dv as this particular area, this entire area basically because that area will now correspond to the d v times v.

So, what I am trying to say here is that. So, in the velocity space, if you look at a particular direction, then you can always say that find this vector actually represents the value which is simultaneously having the speed in the x the velocity in the x direction as v x minus v x plus d v x and the y direction will be v y plus v y plus d v y, but I am not interested in calculating that. I am interested in calculating the speed independent of the direction.

So, and then I say that the speed will be just v into some d v. Now the question is what is this dv? Now, dv means, now it is basically if I wrote at this velocity vector along any direction keeping the lengths m it is the same v f v y and since it is a 2 dimensional plane, I will get a basically circle and around the circle, I will get an annular region which is now my d v.

So, d v is not actually d v x, d v y; d v is actually d v x, d v y and then you have to integrate this d v x, d v y over the entire range independent of the direction. So, that is very important d v is not d v x d v y. You can get d v from d v x, d v y in a very clever way, but we are just, we will just show you in a minute, but if there is an alternative way to calculate, how you calculate d v. Now, it is very easy now what you are asking is that all you are asking is that you have an circle which has a diameter basically v plus d v. So, the area of the circle is nothing but pi r square. So, in this case it will be pi v plus d v and then what I am asking is that what is the area of the inner cycle circle.

So, then actually I will get all these annular circle at the area of the annulus circle. So, that area will be nothing but you can easily do it pi v square. So, it is v square plus 2 v d v plus d v square minus pi v square. So, you can see that this pi v square will cancel. Now this d v square a d v is already a small number. So, dv square we can ignore. So, the ultimately it will be 2 pi v d v. Now you could easily get it in another way.

So, the what I am saying is that the, if I have a speed which is equivalent to v and then if I just calculate what is the probability of having the speed in the range v 2 v plus d v, then this volume element will not be just equivalent to d v x into d v y because it is now independent of the direction. So, this volume element will be nothing but some factor into some factor we have to consider and that factor will be just we can get it by integrating over this area, fractional area independent of any direction.

So, that we showed it to in one way because this is just 2 dimensional things. So, it is a annular area means actually there will be 2 circles and if you just take the difference between the area of this 2 circle, outer minus inner approximating the making one approximation the d v square is almost 0, then you can easily get it.

You could also you know get it just directly. So, what we are saying is the differential element of an circle. So, it could directly write. So, it is it will be nothing but a differential area element around the circle. So, area is pi v square. So, it will be nothing but 2 pi v d v ok. This is the same logic actually which you just said earlier or you could do it in a very different way and this different way is that fine, what we are doing is that fine we are varying, this is basically v x.

We are varying v x to v x plus d v x and we are varying v y to v y plus d v y. Now instead of that what we are saying right. Now it will be independent of the direction which means natural choice could be to use the spherical polar coordinate. Now what is the spherical polar coordinate; instead of say v x v y, will write it as the length of the vector which is v and then this angle which we call as say phi and phi can take value from 0 to 2 phi if we just complete a circle right.

So, all we need to know is what is the relation between them, but how we can write v x, v y in terms of v and phi and then all we are going to do is to integrate it over the entire interval and entire area. We will just vary phi because this v is not changing v where taken fixed the length of the vector because it is a velocity, it is a speed and which can be resolved into v x and v y, but v x and v y has a particular direction.

So, if you choose some other direction that will be different v x by v y, but the speed is the same. So, that is what we are interested to calculate a speed independent of the direction. So, we have to rotate this vector and find what are the what is the area. That is exactly what we are going to do. So, now, you can ask this question fine think about it;

what is this thing, what is this d v thing. So, this is basically you can think of a d v ; the small d v. And then you can always say that if. So, what we are going to do is that, we are changing in v x to basically v x plus d v x and v y to v y plus d v y in the spherical polar sense, you are keeping remember this v fixed. What you are doing is that, you are keeping fix v fixed you are basically sweeping phi to phi plus d phi.

So, the how the now the question is, how this d small volume element you are generating in the spherical polar sense. So, we will just draw it again. So, let us draw it somewhere maybe here. So, what I am trying to say here is that you had a velocity vector. So, you did not change the direction. So, it was fine here and now you have rotated it to phi 2 phi plus d phi. And you have moved also ah; v to v plus d v we are keeping of course, you have also changed it to d v and then you are rotating it by d phi. So, you have generated this area. Now the question is; what is this area? You can easily figure it out. So, if this angle is now d phi.

Now, if d phi is small, then we can write this entire area as, look at it here. So, what is this length, this length is so, basically we are calculating this infinitely small area and this length is nothing but v. So, if this is v and this angle is d phi and if d phi is small then you can approximate that this arc length will be nothing but p into d phi. So, that is just following the trigonometry.

So, what we are getting is nothing but this area which is in the rectangular Cartesian coordinate, I got it by this and the area was just d v x times d v y and that area, we can also get by changing v to v plus d v and doing an increment in the phi from phi to phi plus d phi and that area is nothing but. Now this length is d v and this length is v into d phi.

So, what I will I will get is v d v into d phi. So, it is basically d v times v into d phi. So, that I am writing as v into d v into d phi. Now that is basically the infinitesimal area which we get, but then to make it independent of the direction, what we have to do; we have to take this infinitely small area and integrate over all the phi’s because we are not changing the v here. We already we said that we little bit increment in v, v to v plus d v, but now we ask this question what is the distribution independent of the direction because any direction I take the speed distribution, it should be equal.

So, that annular area, I can get it by integrating this infinitesimal area over the angle for phi going to 0 to phi going to 2 pi and that will be very straightforward in integration of d phi is on the phi. So, you will get 2 pi v d v. So, whichever way you do it or whichever we want to visualize it, I am getting this annular area as 2 pi v d v. Now we can extend it the same thing to 3 dimension because it is not only v x to v x plus d v x or v y 2 v y plus d v y it is also v z to v z plus d v z.

So, which means actually, now I will have 3 variables. So, we will see that, it this 3 variables are actually I mean there will there will actually, want to solve it you know you know rectangular in all this why is which we have developed for the 2 minus dimensional case. So, in the 3 dimensional case also, we will see that there exist a very interesting situation, which we are going to discuss in the next section.