Introduction to Chemical Thermodynamics and Kinetics

Dr. Arijit Kumar De
Department of Chemistry
Indian Institutes of Science Education and Research, Mohali

Lecture – 40
Reaction dynamics – Part 3

Now, let us extend the same kind of treatment to 3 dimension because actually the molecules are moving in a 3 dimensional space. So, their velocities are also having components in all 3 directions, we experience and visit and now let us ask this question how, what is this differential volume element and for having the speed in the range v to v plus dv, dv x and or, simultaneously speak v x to v x plus dv x v y plus v y plus d d v y and v z to v z plus dv x. What is that following element and how we can actually integrate it over, we can get an element which is independent of the direction.

So, which means actually, instead of a circle, it will be a sphere in the velocity space. It is not a coordinate space; it is a velocity space.

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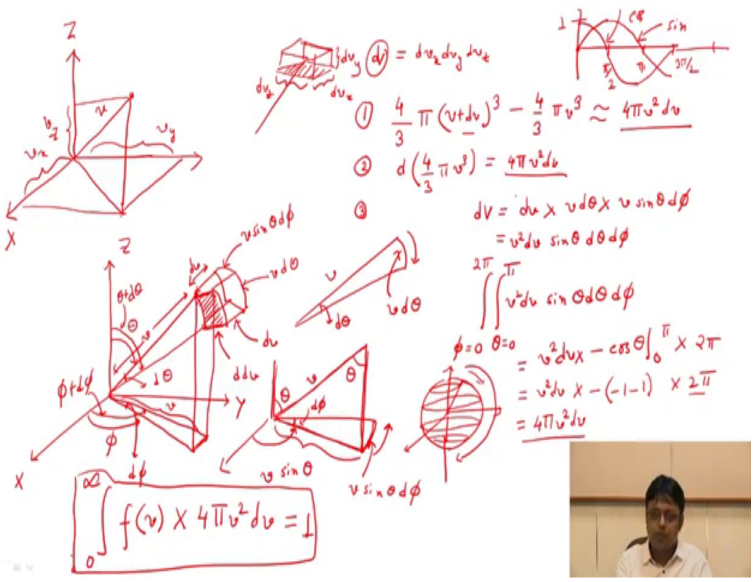

So, as before you can argue that, let us first draw the 3 dimensional space. So, I usually prefer to draw the xyz axis like this. The reason is when you make this correction, you just choose the x axis and then rotate it along y axis, a towards the y axis. So, if we just take this axis and rotate it towards y axis, then your z should point out. So, this is known as just like my right hand.

So, this will be, you can you can just say. So, from x to y if I rotate; so, z should point out. So, that is known as a right handed rule. If I had chosen it the other way, if I switch any 2 of them like, if I write x for this and y for this then it will be a left handed system. You can easily show it, you can easily realize it.

Now, suppose, this is an arbitrarily oriented velocity vector which has velocities along x, y and z; So, the x component of the velocity is if I just draw, if I just draw a projection on the x y plane. So, and then just draw a line here. So, this is the x component velocity and similarly, we will just write it like this and similarly, this will be the y component of the velocity.

So, this is v y, this is v x and this is the v z. So, this is the x, y, z components of it and then we are also saying that we went from v x to d v x, sorry it is basically from here, we want to want in this direction. So, we can actually draw it slightly separately. So, this is the vector and we want to say, suppose this is the velocity vector and then what we are doing we are moving v x to v x plus d v x which means actually in this direction and then we are also going to v y to v y plus dv y in this direction and simultaneously.

So, if I just move it that way, I will get an area element and then I will also go in the upper direction to say to z to z plus d z and then I will get volume elements. So, that is 3 dimensional volume where basically this side is d z, this side is d x and this side is d y.

So, that is that the volume or if you just write it as d v is d v x times, this is not d z actually this will be d v x because this is a velocity space d v y and d v z. So, that is basically d v, it is a small v, dv x, d v y, d v z and then we are asking this question fine that d v we do not want because we want a d v independent of the direction.

So, then we can do it in many different ways; it is it is basically a velocity vector and then you are sweeping the angle and then if you sweep it all possible direction, you will get a spear. In the 2 dimensional, you are getting a circle. In this case, you get a sphere because you are going in all possible direction and then you can ask this question fine, I got a sphere independent of the directions and then I am just only changing the length of the basically the radius of the sphere from v to v plus dv.

And then you can just easily calculate what is the volume content within these, this would not be actually the annular shell thing. Now this will be actually a shell which is known as a shell. Shell is something like you have a big sphere and you have an inner sphere which is a small sphere inside the big sphere and this small radian which is just lying between this outer sphere and the inner sphere is called the shell. Now what is the volume of the shell? So, that you can easily calculate by all these 3 methods, that I said in the earlier part. So, the volume of a sphere is 4 third pi r cube. So, here it will be 4 third pi v plus dv cube which is basically the outer sphere minus 4 third pi, the inner sphere is just only v v cube.

And again, you can approximate that d v square term and d v cube term, I will ignore. So, you can easily figure out that will be 4 pi v square dv and you could directly asked this thing that fine, it is a differential volume of this sphere 4 third pi v cube that will directly give you 4 pi v square d v because you see the integration of v cube is 3 v square that 3 will cancel and the third thing which will just show you now, is fine.

So, I will go instead of writing it in the Cartesian, rectangular Cartesian coordinate, I will go to the spherical coordinate, coordinate and then in the spherical Cartesian coordinate, I have basically 3 parameters ; one is the length which is the v which is just like this and then I have this angle which I called as phi, which it max with a Paul x axis to the y axis, that was the sense of rotation of positive phi this is y and this is z but then I also have another angle, which is basically this inclination angle, which I call as theta.

So, this theta is called as I think azimuth angle. Now, the question is what will be the ranges of phi and v and theta. We can go from 0 to infinity but here actually we are keeping v fixed and going from v to v plus dv. So, change it from v to v plus d v. So, this is nothing but d v and then simultaneously we will change the phi to phi plus d phi. So basically, if I just draw it like this. So, this is phi plus d phi.

So, that this small angle is nothing but d phi and simultaneously we have to go to theta to theta plus d theta, that also you remember; d v change I am doing a slightly later. So, basically I got some sweep in the phi and then I am also sweeping down meaning, I am going from theta to theta plus d theta. This is nothing but theta plus d theta and then this small angle will be nothing but d theta and then if I do that, then I generate this surface and then simultaneously, I will also increase it in the d v direction.

So, then I will get a volume. So, this volume I am asking the question, what is the volume element? So, or the d v for this, so instead of going from d v x, d v y v x to v x plus v d x in the rectangular Cartesian coordinate sense, I could have also got a differential element by going from v to v plus d v by changing the length of the vector a little bit by differential amount, sweeping the vector long phi which is basically this is a vector and if if you consider this is the plane and then we are basically sweeping it like this. So, this is the phi angle and then we are also saying that let us also sweep it down little bit. So, that is the theta angle and if you sweep that way, you can actually generate a differential volume element. Now, the what is the volume of this?

So, this is we can actually approximate to be a rectangular parallelepiped where actually the volume will be nothing but multiplication of the length of the sides. So, one side is straightforward, this is basically d v because you remember this was d v. Now, what about these other two sides? Now think about it this side, which is here or here is nothing but here. So, this side is nothing but what is this by the way.

So, this is nothing but again the v itself and if this angle is small, so we can write it is nothing but v d phi. So, this side is v into d phi. Now what about this site which we got by sweeping the azimuthal angle, so that you can again see that this is also sorry, this should not be d phi v into d phi, I am coming back to it.

So, this length is v. So, I am let me just write it once again. This is v and that I am sweeping this theta, I am sweeping by d theta. So, if this is v and this is d theta, so then this will be v times d theta. Now, let us calculate what is this? What is the change due to the change in phi from phi to d phi? So, that we took a projection on this plant which we are generating once again. Now, look at it carefully now what is this angle? This angle is theta. So, this angle also should be theta because this is the z axis and this is the perpendicular to the x y plane. So, these two lines are parallel.

So, if this is theta, this angle also should be theta. So, if this is theta, I know that this is v. This is the length of the vector velocity vector which is just the speed the magnitude of the velocity vector and then if this is theta, this is nothing but v times sine theta and then, what we did is that this v sin tan theta now we swiped and got something swiped along this axis and this sweeping is. So, if you remember this was my x axis, this was my phi and this was my d phi, this is the small d phi thing.

So, what will be this arc length then? This arc length will be nothing but the length which is v sin theta into d phi. So, this is, this already we showed it is v d theta and the other side which is this side is v sin theta d phi. So, if I just multiply all these thing, one axis was. So, this differential volume element is should not write it as d V. I can, I can just write it as d capital V something like that. So, that is here also I should write it as d capital V, the volume element it is v to v plus d v. So, that is giving me one side as d v, theta to theta plus d theta that is giving me one side as v into d theta and phi 2 phi plus d phi is giving me, v sin theta d phi.

So, what I am getting is v square sin theta d theta, sorry d phi and there is also and d v yeah. So, I am just collecting the terms. So, now I have to integrate over theta and phi because I am just keeping the length same. I have done an incremental change and I am doing a sweeping along this any direction and that will give me the volume of these spherical shell ; shell means it is just the, just that structure that lies between two concentric spheres. Now what it means is that the that volume will be nothing but integration of our this thing over changing the theta from 0 to something, the phi 0 to something.

A phi integration is always 0 to 2 pi as you have seen like. So, we just saw in the 2 dimensional case that the phi is basically all this angle. Now theta how much you have to change; that is the question. What are you doing think about it? It is basically a sphere and at the center, I have x, I have y and this is z. Now, I had a vector like this and if I sweep the angle phi, I will generate this thing and then I will sweep the theta also in this direction.

So, if I sweep the theta, I will get another circle. I am sweeping theta and phi together. So that way, I can actually generate the entire surface if I sweep the theta all the way from here to here which means, the theta variation is nothing but from 0 degree when it is aligned along the z axis to all the way to minus z axis which is basically 180 degree or pi.

Now, this picture you have seen in geography just like a these are my latitudes and longitudes. So, latitudes as basically have 0 to 360 degree or 2 pi and longitudes are 0 to 180 degree or phi. So, that way you can actually construct the surface of a sphere; exactly the same concept we are using here. So, now, if you integrate it, this v comes out of the integration it is v squared d v. So, this now v integration and then integration over sin theta d theta is a basically minus cos theta evaluated between the limits 0 and 2 pi.

So, you can easily ask this minus cos theta evaluated between 0 and 2 2 pi sorry, 0 and pi not 2 pi and integration of d phi is just phi and the limits are 0 to 2 pi. So, that is giving me 2 pi as before the circle 2 dimensional case.

So, cos theta cos 0 is 1 and cos pi is 0; So, it will be basically minus of 0 minus 1. So, it is 1 away. So, what we will have is nothing but, sorry cos pi is actually 1 minus 1, we I was if the it is always better to remember it in this way. So, you have pi by 4, pi by 2, 3 pi by 4 and pi. So, cost actually is plus 1, when it is pi by 4, when it is 0. So, then actually let us just draw pi by 2 and pi by pi that way yeah. So, it is 0 at 90 degree and then it is minus 1 at pi and sin will be basically 0 at 0 degree. It is plus 1 at pi by 2, it is 0 at pi and it is minus 1 at basically another pi by 2 radial which will be pi plus pi by 2.

So, 3 pi by 2, something like that and at that point cost will again come to 0. So, this is the cost curve, this is the sin curve. Anyways, so cos pi is nothing but 1, sorry minus 1; so, this integration will be times it is minus sign is there minus 1 minus 1, this cos 0 is plus 1, but it is the lower limit of the integral. So, that will give me actually 2 factor. So, this will be nothing but that 2 and that 2 pi I am writing as 4 pi v square d v which is exactly the same value we are getting whichever way you do it. So, I showed you three different methods for calculating the differential volume element in in basically in 2 dimension first.

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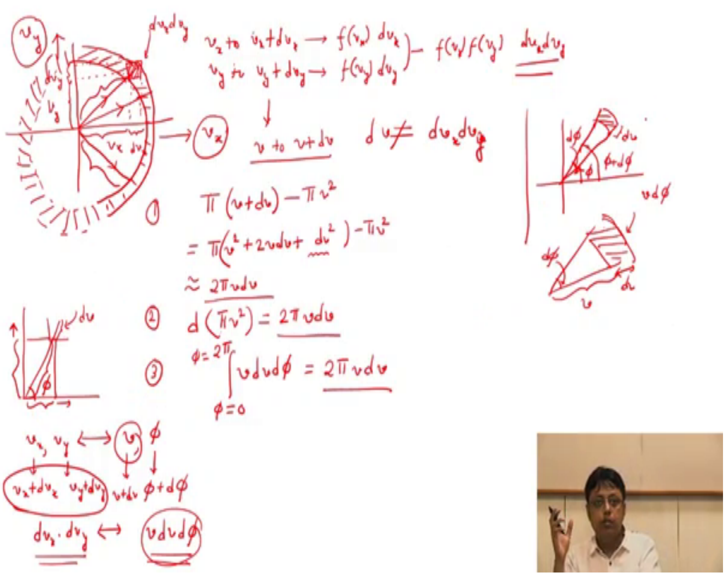

And then in 3 dimension and we showed that that 3 dimension one is the one which we need.

So, then the question is, we know that there is a f v or which we already calculated.

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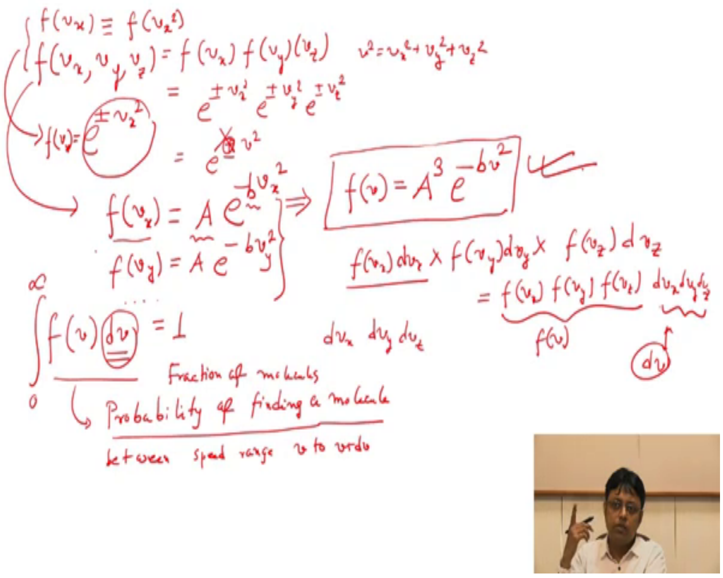

So, f v is nothing but this function which is this, f is A cube into e to the power minus b v square and then we are multiplying by a volume which is basically independent of the direction. So, that differential volume where add a multiplying because then we will get a probability and then if we integrate also over all the velocities, then we will get actually it is a probability distribution which is that should give rise to 1, which means if I take now f v and multiply by the volume element 4 pi v square d v and integrate it over all the d v range; d v range should be 0 to infinity. It is not minus infinity to plus infinity because v x can or v y or v z can go from minus infinity to plus infinity because it is a velocity.

So, it has a direction. So, plus minus directions are there, but v is now a magnitude of the velocity, independent of the direction and that is why you did all this calculation to make it that independent of direction what is the value because all we are interested in the speed distribution, not the velocity distribution. So now, if I integrate the speed, speed is just a magnitude of velocity which cannot be negative. So, it goes from 0 to infinity and that integration should give me 1. So, that integration will first evaluate in the next section and then you will see, how we can write I can will see basically how we can get the parameters and how we can get to the Maxwell Boltzmann distribution.

Thank you.