Chemical Kinetics and Transition State Theory
Professor Amber Jain
Department of Chemistry
Indian Institute of Technology, Bombay
Lecture – 12
Problem solving session 2

Hello and welcome to module 12 of Chemical Kinetics and Transition State Theory. In last several modules we have developed a theory for of a collision theory, to be able to calculate a rate constant, a number out for a given reaction. In a last module, we look at a few examples of how to calculate this number. Today we will continue on and solve few more problems so that we become more comfortable. Today not only we will look at numerical problems but a little bit of derivations as well; so let us continue.

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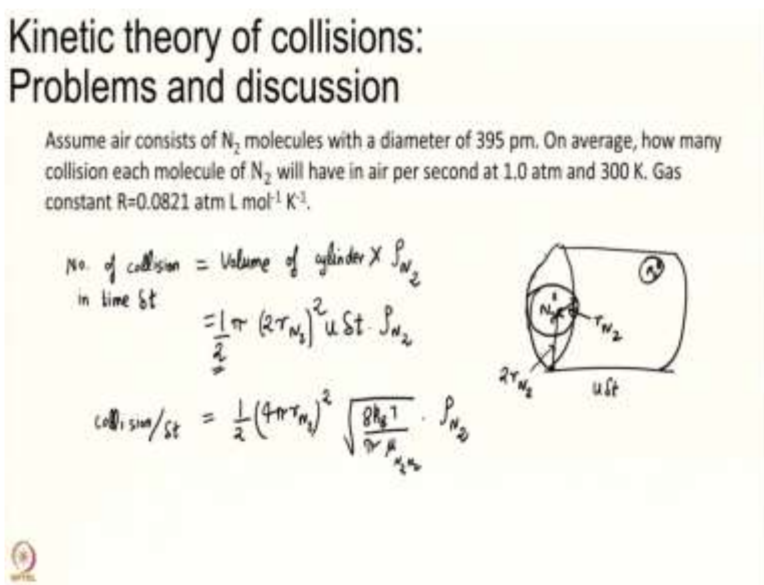

So, our first problem of today is that let us assume our air has only nitrogen gas; a nitrogen can be assume to have some particular radii. I have given you a diameter of 395 pico meter and the question is, how many collisions each molecule of N2 will be having per second; in regular conditions of pressure of one atmosphere and temperature of 300 Kelvin. So, that is our question, so let see how do we solve it; and so the answer is very much related to collision theory.

In collision theory we are finding a rate constant as the rate of collisions, and the rate of collisions is of course directly related to the number of collisions that you are having; so let us start. Let say this is N2 with some radii and essentially we construct the same idea. We construct a cylinder, this is u del t this cylinder's length, you can go back to this proof will be 2r N2; it was rA plus rB, if A and B are different.

A and B are same, so you get 2r N2; and all that we have to do is to find the volume of cylinder. So, number of collisions is equal to; so this is in time delta t will be equal to volume of cylinder, into the density of nitrogen. So, the density of nitrogen will tell me what is the probability that another nitrogen molecule is in here; so that is the idea.

So, this is equal to then pi 2r N2 square, u delta t rho N2. Is this correct or have I missed something? There is a little factor that is missing, a factor of half. So, whenever I have A equal to B, I get a factor of half; why? Because I am double counting the collisions. The N2, this N2 let us me call just A arbitrarily, if it collides with another N2, which is B. N2 B also collided with N2 A, so I have double counted the collision; so that is why the factor of 2.

Again we discussed this is in some detail a few modules back; so please revise that if this is not clear. So, collisions per unit time will simply be half 4 pi r N2 square; and this u in collision theory, we replace by the average speed average thermal speed which is. So, we are going to calculate all of these quantities one by one and multiply them together.

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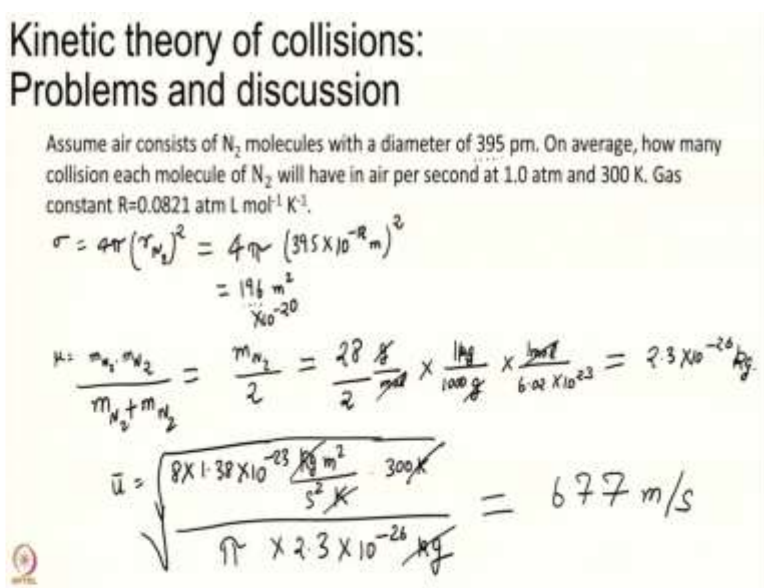

So, first thing was sigma equal to 4 pi r N2 square, we have to be just very very careful of units; never mess on that. 395 pico meter 395 pico meter is 10 to the power of minus 12 meter square; I have calculated this out. This thing is equal to 196 meter square. Just a quick note on how many digits you want to write the answer to? If you will plug it on a calculator; you will of course get many many more decimal places.

But, since my question I was having three significant figures; I have written the answer also in three significant figures. So, that is a general rule of thumb. So, the next quantity I have to calculate is the average speed; but to calculate average speed, first let me get the mass. This is equal to if you can just quickly check this is equal to m of N2 divided by 2, and the mass of nitrogen is what?

A nitrogen is a atomic mass is 14 gram per mole; so, this is 28 grams per mole divided by 2. I want the answer in kilograms in SI units, so I have to convert my unit; if we use grams per mole, you will get completely wrong answer units careful. So, this I convert in 1 kilogram over thousand gram into 1 mole, divided by the Avogadro number; so the gram cancels gram, moles cancels with mole.

And I will get the answer in kilogram and I have done the math; this comes out to be 2.3, into 10 to the power of minus 26 kilogram. So, once you start doing these kinds of calculations, you will actually this thing is wrong; this should be minus 20 here. So, then you keep on doing these calculations. You will also get a sense of what are the numbers you expect together; mass is generally in the order of 10 to the power of minus 26 or 10 to the power of minus 27.

This reaction cross section is generally in this order of 196 like 100 Armstrong square; so get sense of these numbers. So, even if you make a mistake, you will be able to quickly see; you will be able to sense, your sixth sense will tell you that something is not right. Finally, I have to not finally. But, I have to calculate that thermal speed as 8 kB 1.38 into 10 to the power of minus 23, what is the unit of kg?

Kilogram meter square second square Kelvin; 300 Kelvin divided by 8 k T divided by into the mass. And the mass I have found is 2.3 into 10 to the power of minus 26 kilogram; also Kelvin cancels with Kelvin, kilogram cancels with kilogram. And I will get square root of meter square per second square, which is same as meters per second. So, this I can again plug it on a calculator and I get it as 677 meter per second.

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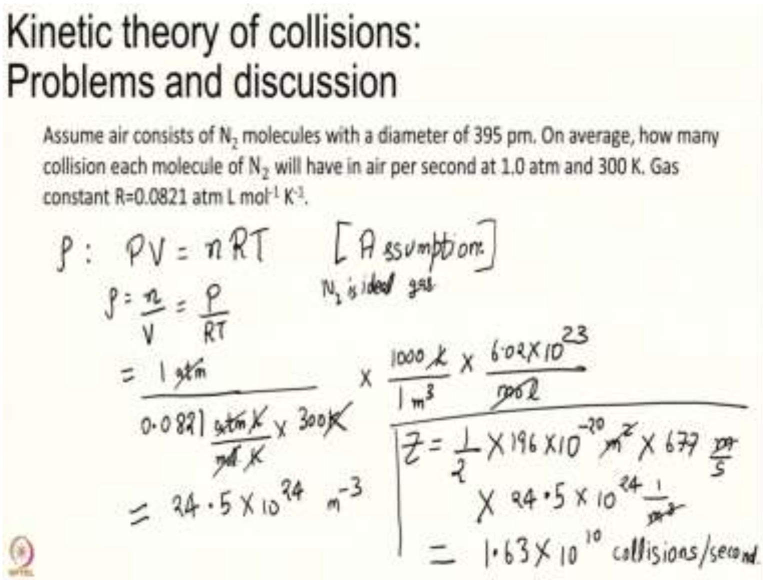

Finally, I have to calculate the rho, I have to first to get the pen; rho, so to calculate rho I am going to use ideal gas flow. Anytime in the question to calculate something you are making an assumption that is fine to do so, if it is a reasonable assumption; but if a mentioned what assumption you are making, N2 is ideal gas.

So, my answer will be valid under this assumption, so rho is nothing but n over v; which is nothing but P over RT, which is nothing but 1 atmosphere. R I have given already in appropriate unit's mole Kelvin, into temperature is 300 Kelvin. So, what is the unit of rho I am looking at? Rho is a density and density should be it is a number density. So, I want to cancel liters with meter cube, so I will have thousand liters in 1 meter cube; and I will have 6.02 into 10 to the power of 23 per mole units.

Pay attention, if you do not practice you will not get this right; liter cancels with liter, mole cancels with mole, Kelvin cancels with Kelvin. And everything else is just plugging it on a calculator, which gives me 24.5 into 10 to the power of 24; something atmosphere also cancels correct meter minus 3. So, make sure that my numbers are right; I am functioning them myself on a calculator, and there is certainly a chance that I have made a mistake.

So, it is upon you to make sure that these numbers are correct; sorry I still have to find the final answer, which is now easy again my bad. So, finally the collision was half into sigma, which we found to be 196 into 10 to the power of minus 20 meter square, into thermal speed. Which we found to be equal to 677 meter per second, into rho which we have found equal to 24.5 into 10 to the power of 24; 1 over meter cube. So, if you do all these, first thing is that units will cancel, meters square meter square with meter cube; and I will get 1.63 into 10 to the power of 10 collisions per second per molecule of N2. That was already built into my equation.

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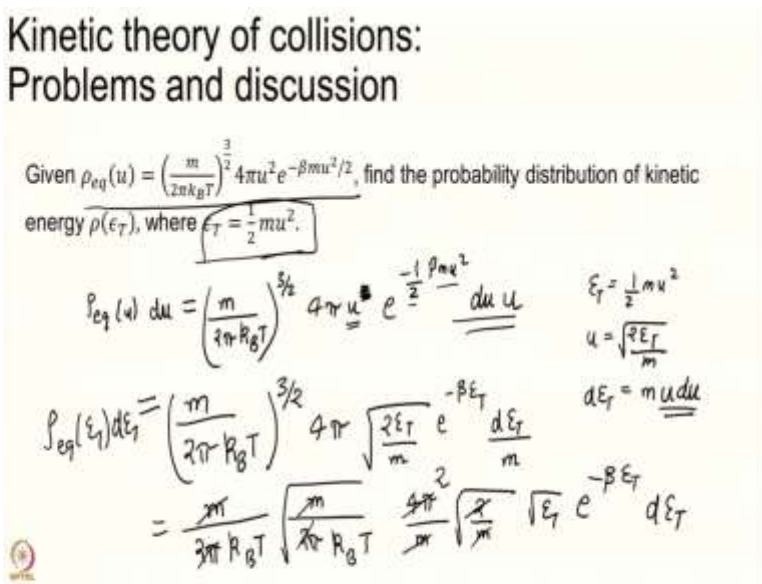

So, let us look at the next question, this is about transforming between different variables. It is extremely important and collision theory is really built upon it. You should be comfortable in converting between different variables; so this is something we have done in one of in while deriving. But, let us do explicitly once more; I am doing this again because it is very important, you should practice this a lot.

So, I have given the rho equilibrium in speed, and the question asked to find the distribution in energy in kinetic energy this one. So, how do we do it? Remember the volume element. Again I can promise you if you do not practice, you are going to forget volume elements in your exam; so we are going to do it carefully. First thing is we write this rho with a volume element du, and this is given to me; so what do I do? E is half mu square.

First notice u equal to 2, this is simple manipulation, this is not hard; and d epsilon is mu du. And I will just play around with it, you can do it in any fashion that you like. I have u square here, I will take this, I will write as u here; one u I will take and write here. So, I get u into du which I will use here; so this I will write as m over 2 pi kB T to the power of three half, 4 pi you, u is root 2 epsilon T over m, e to the power of minus beta.

A half mu square is epsilon T, u into du is dE over m; so, I can simplify this a little bit. Again more you practice, more you will become comfortable on how to do these kinds of tricks; these comes only and only with practice no alternate. You cannot just watch these lecture series and become comfortable with this.

4 pi over m root 2 over m root epsilon T, e to the power of minus beta epsilon T d epsilon T. So, let me just write this seems to be correct; this has converted now. So, I will see several factors are going to cancel; m cancels with m, 2 pi cancels here with to give me 2, anything cancels, yes; m cancels with m, this two cancels with this two.

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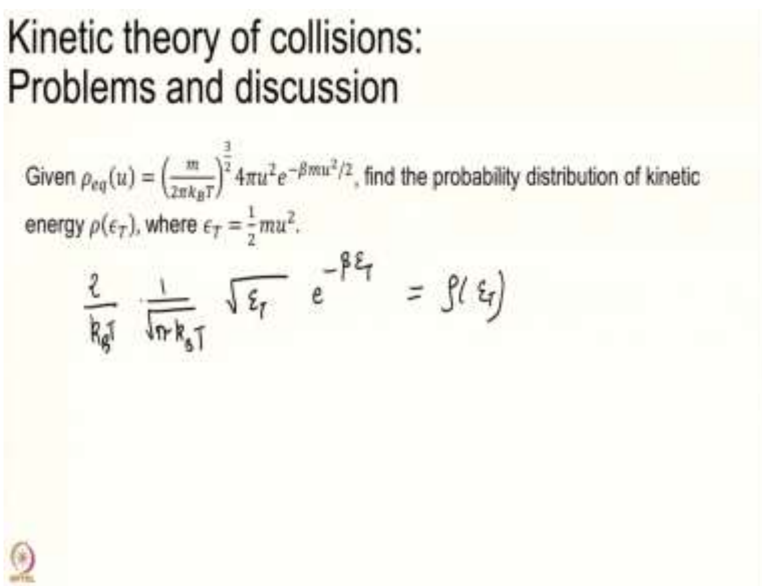

So, the net result I get is I have written it here, you can simplify this. 2 over k T into 1 over root pi kB T root epsilon T, e to the power of minus beta epsilon T; this is equal to rho of epsilon T. So, you can go back to one slide, make sure that this equation is correct; I have cancelled all the factors correctly. So, this is about transformation of variables very important concept.

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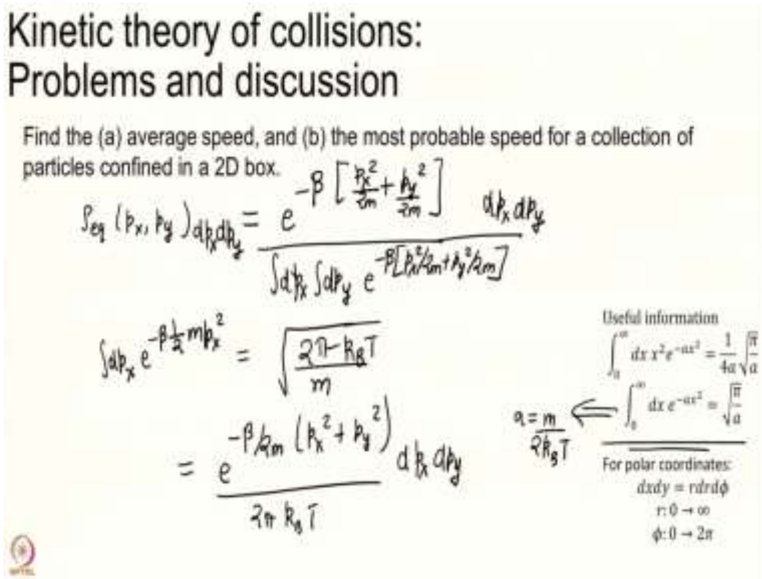

So, our second problem is to calculate average speed and most probable speed in 2D; so we have actually solved more complex problem which is of freely. Here we will solve problem now in 2D; so we will have to go back towards basics. How we derived and written in 3D and follow that proof in 2D; we have to be just very very careful. So, what is our basics? Well are basics says the Boltzmann's distribution; that will always be true.

I have only 2D so I am writing only px and py, minus beta H; and the H here is only Px square over 2m plus py square over 2m, and never forget your partition function. So, earlier we have done the same thing but with Pz as well; so it was more complex. So, I had p plus Pz square as well as integral over Pz in the denominator. Why I have to be converting units between different variables? And when I do that what do I do? I always keep track of volume element. First let us find out the denominator.

So, let us calculate d Px e to the power of minus beta half m px square; this integral you can find here. And in this if I have to convert a will be equal to m over 2 kB T; so this is equal to m pi divided by a, which is m divided by 2 kB T. So, this thing then becomes equal to e to the power of minus beta over 2m Px square plus Py square, divided by 2 pi kT, d Px d Py.

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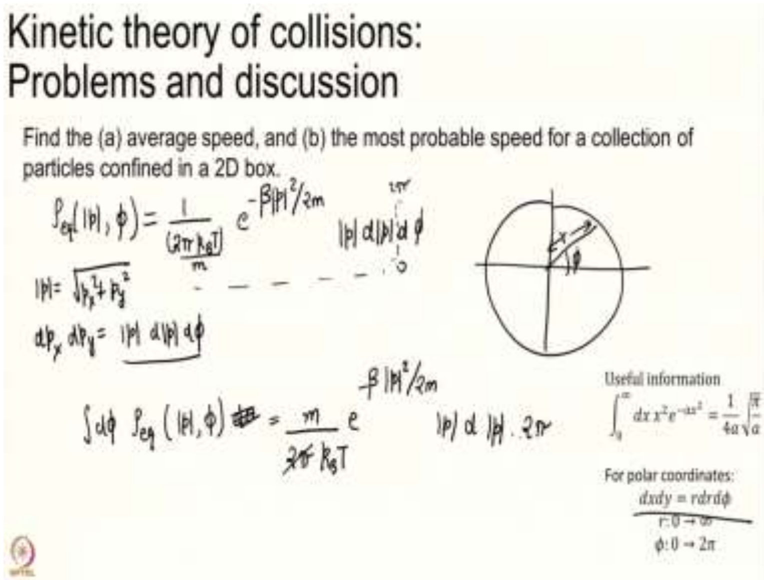

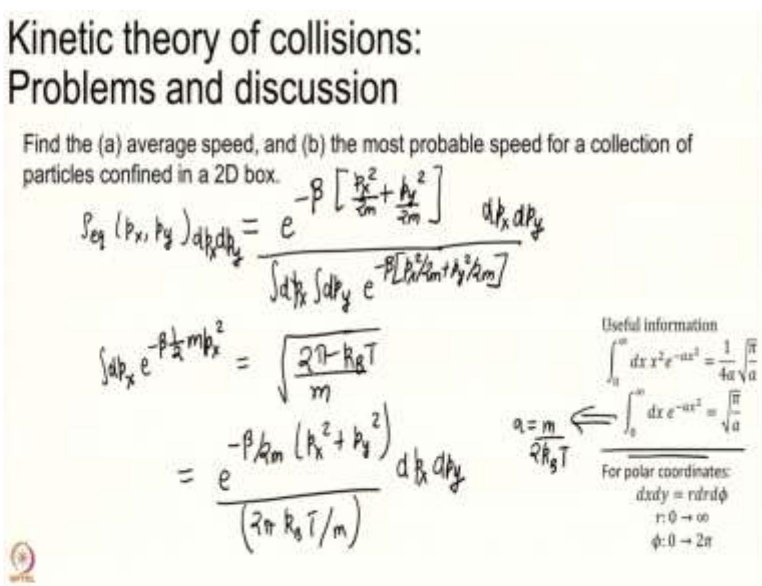

So, the next thing is we have to move to polar coordinates; in 3d we went to spherical polar coordinates of r, theta and phi. Here we will have only 2D, so we are going to move to polar. So, we will take the rho that we had in the last slide, and we want to move to P comma phi. So, this will be equal to now we will convert, so what is our basis? P is root of Px square plus Py square; and importantly we will see this thing here d Px d Py is mod P d P d phi.

So, this will be equal to 1 over 2 pi kT over m; so that is simply this factor. I think I have forgotten the divided by m here. So, this thing keep on going back to pen. E to the power of minus beta I had Px square plus Py square, which becomes mod P square over 2m into the volume element, so this thing. Now, the point is I do not care about phi, I only care about the overall speed overall momentum. So, what do we do?

We integrate over phi, just like we integrated over theta and phi in 3D. So, this thing I want is integral over d phi over d sorry d phi; so this is easy. We note that most of the terms here are independent of phi, as everything is independent of phi; and I simply multiply this by 2 pi if I get an integral here, from 0 to 2 pi. Everything here is independent of phi, so it is an easy integral; so I will just cancel 2 pi.

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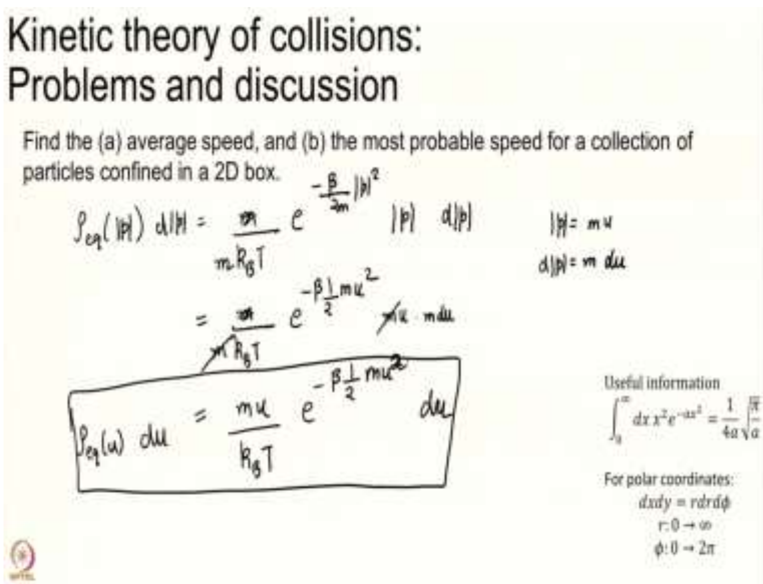

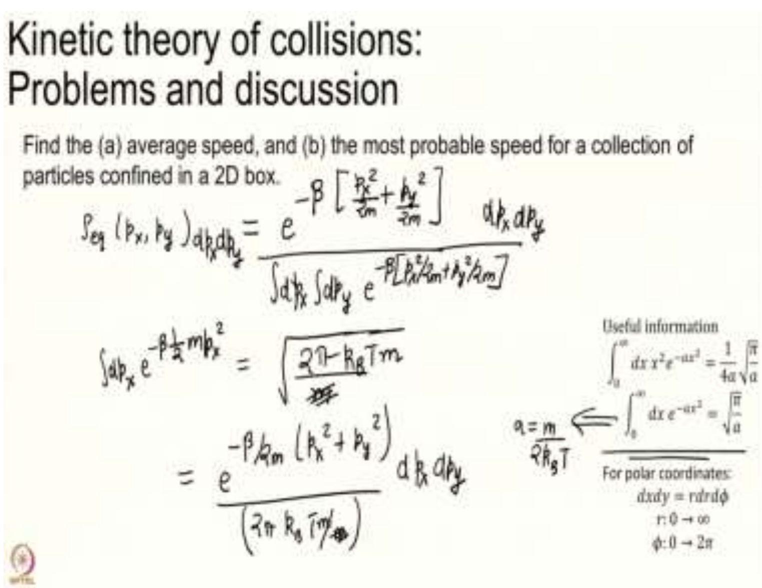

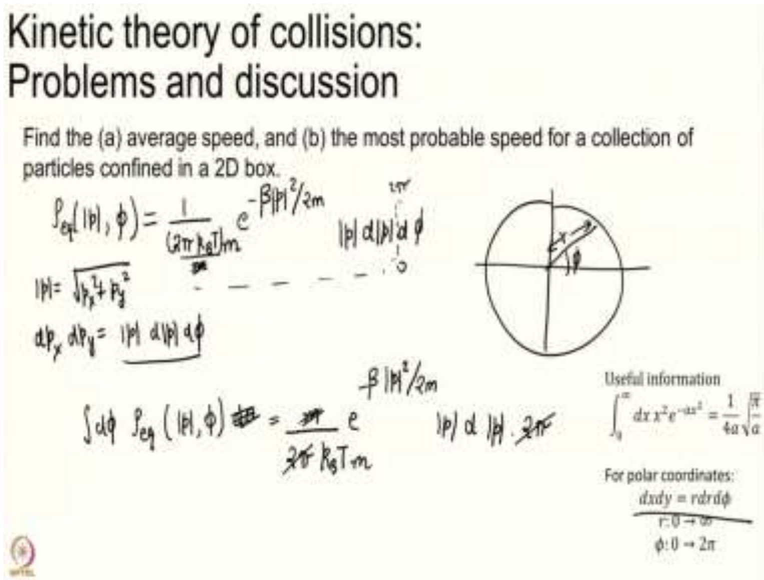

And I get let me go back m over kB T, e to the power of minus beta over 2m mod P square mod P. now, we are going to convert to speed which is momentum; so P is equal to m u dP equal to m du. So, we will just replace these things carefully; so if do these things here, you can quickly verify. This is mu square mod P becomes mu, and dP becomes m du; I have made a mistake here.

This is m in that in numerator, this m is in the numerator, this thing will carry on. M in the numerator here, so this m is here, my apologies. So, one m is supposed to cancel and I get mu over kB T, e to the power of minus beta half mu square du. So, once we have found the equilibrium density, we will then find the average speed at most probable speed.

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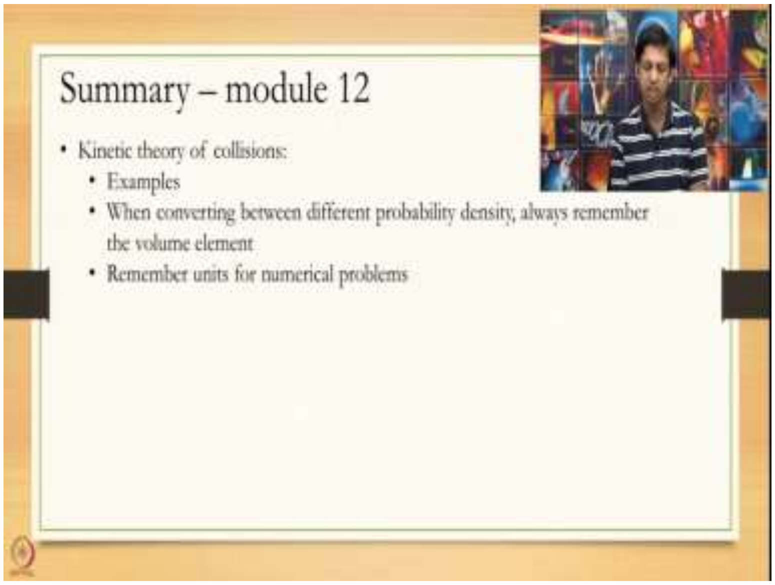

In summary, today we have solved many few more examples; two important points to note. When you are transforming in between units, remember your volume element; when you are doing a numerical calculation, remember your units. Thank you.