Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 38
Reaction dynamics – Part 1

Hello everyone, today we will start the final part of our course which is reaction dynamics. Now, we will discuss first how one can actually model the reactions and get an expression for the rate constant. So, that it resembles the Arrhenius rate equation because if you remember that Arrhenius found an exponential dependence on temperature one over temperature.

And then he found that it can be connected to some energy which is some kind of barrier a reaction of the reactants phase in order to form a product, it is an energy barrier. And we discussed it in the last lecture and we will we will see today how one can formulate and or get an expression for the rate constant and to begin with we will we will just discuss their reaction dynamics in the gas phase only.

Commencements reaction dynamics we would not discuss here because that is a beyond the scope of our that I mean of our of this course. And also we will first discuss just to you might have studied kinetic theory of gases little bit in your high school, but we will again do a quick review so, that everyone is on the same page. And then we will start what is known as a Maxwell Boltzmann distribution of molecular velocities and then we will use that to calculate the reactive cross section and from that we will calculate the rate constant.

Now, this after this lecture you can actually go back and read or have a look at the lecture number 9 part 2. So, 9 part 1 we discussed about electrochemistry or equilibrium electrochemistry where we just discussed the electro motive force and writing it in terms of connecting it in term in with the reaction free energy. And then the in the part 2 of lecture 9 or module 9 was actually discussing the that transport phenomena.

So, that is a kinetic phenomena in some sense so, you can the also you could have also had listened to this do that video after the kinetics part. because, that has that is the only time dependent part which we discussed under thermodynamics and that part we called as this dynamic electro chemistry not the equilibrium electro chemistry.

So, you can go back and again have a look at that particular part. So, then it will be very clear we plumbed it together that time the reason is it is under both the lectures where or both the topics are under the electro chemistry. Although the first part was under equilibrium relations that is connected to more thermodynamics and the second part is connected more to kinetics. Now to begin with our 2 reaction dynamics so, we will be talking about gas phase reaction dynamics and again just to.

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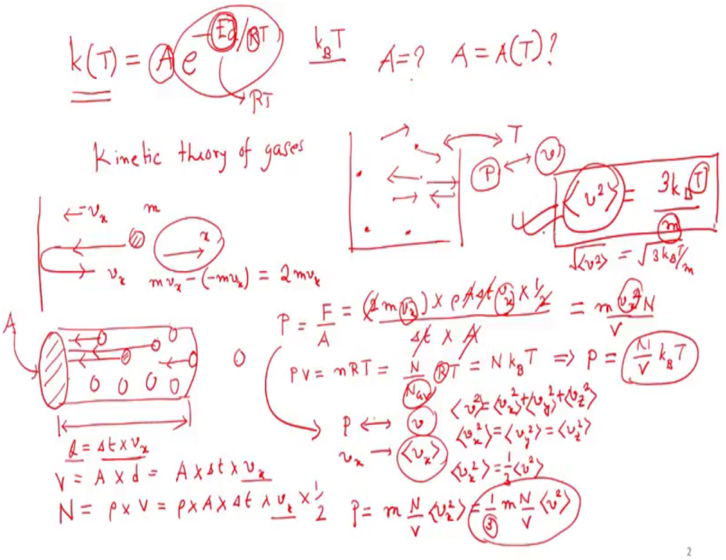

Remember, we want to find an expression for the rate constant that looks like the experimentally determined value which Arrhenius block and particularly we want a physical explanation for this activation energy. And sometimes you can see that I probably wrote k B T in the other day instead of RT, but that just means that you were talking about only 1 molecule or 1 mole.

If it is one mole then you write this n if the same activation energy is part 1 molecule then you write k B T if it is 1 mole than you write RT. So, that is obvious second thing is that this pre exponential factor which Arrhenius got.

So, second thing is that this pre exponential factor which are Arrhenius observed experimentally. The question is what is it? I mean can you get an expression for this?

does the rate constant depends only temperature like only through this term? Or also this pre exponential factor is has some time dependence? Those questions we will answer today and in this lecture.

Now, to begin with let us first discuss the kinetic theory of gases and all of you know what is the kinetic theory. The kinetic theory of gases was developed by many many people and most significantly by Clausius and also by largely by Maxwell and also by Boltzmann.

So, what we are right now discussing is the pre Maxwell Boltzmann development where the physicist were thinking about gas molecules to be composed of all these gas molecules are basically move in a random erratic motion and that is known as the kinetic theory. And this motion is connected to the absolute temperature of the gas.

Now, the first thing first what you can calculate is since molecules are moving. So, if you push them in a container this molecules will strike the wall and bounce back do something like that and this bouncing back or this collision will insert a pressure on the wall.

Now, if kinetic theory is correct then you can calculate this pressure and then which you can measure because pressure is an macroscopic quantity. And then you can actually get an expression of the pressure in terms of say molecular velocity something like that. So, that we are going to first derive.

Now, suppose we have an wall and a molecule is coming in this direction. Now, although I am writing the molecule like this strictly speaking in kinetic theory of gas the molecules were or the particularly for the ideal gases the molecules are considered at this point mass. So, they do not have any dimension, but they have some mass say that mass is m and suppose this is the x axis and the velocity component along the x this is v x. Now, suppose the molecule does a collision and there is no energy exchange between the molecule and the wall and so, it is a kind of elastic collision. But, the momentum change if we take this as our positive x direction.

So, the change in momentum is the final momentum which is m v x. So, the initial momentum according to this will be minus v x, minus the initial momentum which was minus m v x. So, which is nothing, but twice m v x. And all we are going to do is that this to calculate the pressure is pressure is nothing, but force per unit area and force is connected to this rate of change of momentum. So, that we are going to use I mean just from Newton’s law.

Now the question is if you were discussing this choice of this x axis which is in the positive in this case, I could have chosen in the other way. So, what we are saying is that it is the overall magnitude change here so, of the momentum so,. So, if we had chosen the other way it will be just minus twice m v x, but it does not matter we had only concerned with how much magnitude it is changing? What is the total change in momentum? Now, consider that this is for only 1 molecule and to calculate the pressure we have to calculate out the force.

So, we have to calculate some cross sectional area on the wall. So, suppose this area is A it is an arbitrary area and we have to ask this question fine how many molecules are basically striking this wall? And what is the total change in momentum? Now, to calculate how many molecules you need to calculate you need to know the volume ok. So, what volume will choose? So, suppose we are asking this question at some time delta t how many molecules actually are within this zone? So, that will be fixed by if the if the time is delta t if I multiply by the velocity of the molecule which is v x.

So, that distance will be covered by any molecule which is lying within this linear distance because any molecule lying outside here. So, that will take a longer time to cover this to come and hit this wall. So, within this distance we mean that or within this distance is given by this whatever molecules are there they will strike and.

So, the volume is given by nothing about this area times this distance which is a times delta t into v x. And then what we have to calculate the number of molecules which is striking that number of molecules is given by nothing, but the density of the molecules times the volume. because, density is the number of molecules per unit volume and multiplied by following it is nothing, but the numb there and num nothing, but this number of molecules.

Which are within this cylindrical volume within the cylinder who will actually which will strike the wall within this time delta t so, this is the number and then into delta t A into delta t into v x. So, the total change in momentum which is basically force that will be equal to each molecules change in momentum is twice m v x and it will be multiplied by rho A delta t into v x. Now, we are not interested in the that will be not the force, force is basically rate of change of momentum remember.

So, to calculate the rate we have to divide by delta t of course, because it is within the delta t interval how many how much momentum was changed. And then if I divide it by the area I will get the force per unit area which is nothing but the pressure.

Now, in this calculation we actually assume that all the molecules which are within this cylindrical container or cylindrical volume are actually moving towards left, but molecules have equal probability of moving towards left or right. So, we have over counted the number of molecules. So, we should actually calculate when you calculate it. So, we have to calculate it by multiplying another half here.

So, let us just write the half here v x into half and now you can see these 2 and this half cancels and also I am dividing by area to get fresher, this arbitrary area cancels and this delta t cancels. So, these are just arbitrary parameters.

So, what I am left with is nothing but m into v x we have and then rho and rho actually instead of rho we could write it as v n by v. It will be clear why I am writing the rho again as n by v. Now, this pressure if the gas obeys the ideal gas equation then we know that PV equal to n RT. Now this n is the number of moles so, better actually we denote our old n as capital N, which is the total number of molecules

So, we are just multiplying it just a minute it will be m rho was density and we had m and let us write is v x v x square. And then if we had a rho and the wrote we are writing as N by V.

Now, we know that PV is equal to nRT and what is n? n is just number of moles. So, which means actually it is definitely N divided by N Avogadro number. So, total number of molecules divided by Avogadro number times R times T. Now, you can see that this R by a navigator is nothing but the Boltzmann constant. So, we can also write that it is N into k B into T.

Now, you can easily now calculate what is P from ideal gas equation, P is nothing, but N by V into k B into T. we could have written it as rho and just kept the rho in the above equation, it is just obvious that this N by V terms will cancel.

So, what we get ultimately is an interesting situation that mv x square is nothing but k B T. Now, you see this pressure will be what the way we have written it is this pressure is getting contributed by only x component of the velocity, which is not very correct because the molecules are moving in all possible directions.

So, what do we have what are you could try it actually at this point is that how this pressure is connected to the velocity? Which velocity? That velocity which is basically the independent of the direction; And also think about it this the way we have written the velocity it we are written on particular velocity every molecule has, but that is also not true on average the molecule will have say average of the velocity, which you can write it as v x average.

Now, the question is how you will connect this average velocity with the just the magnitude of the velocity which is nothing, but the speed so, which is independent of any direction. Now, we know that this v squared which is just the length of the or the modulus length of the a velocity vector is nothing but v x square plus v y square plus v z square.

And we also know that v x square should be identical to what the average value of the v x square should be identical to average value of v y square or should be identical to average value of v z square. Because, the gas usually is isotropic in nature and the top equation also you can average out.

So, these two conditions give that vx square is nothing but one third v square average. So, you could directly write it here instead of this v square, where now using that we have to use the average velocity. And so, the expression for the pressure will be mass times N by V times v x square average, which is nothing but one third of v square average. I am writing the one third at the beginning n by v into v square average.

Now this expression you compare with this expression because those are 2 expression for the pressure and you can easily get the value of v square average.

So, you get that v square average so, we get that v square average is nothing but you can see this N by V will cancel. So, we will have this k B T we will have these 3 k B T because these 3 will be multiplied with the k B T by mass or sometimes we also are interested in calculating the root mean square average. So, which is nothing but you take the v square average and then square root it and that will be square root of 3 k B T by m.

So, this is an expression of the velocity on the average not velocity it is the average speed or the square of average speed which we know or which we call as a mean square speed. that is connected to temperature of the gas.

So, and that is known as basically that is the one of the greatest I mean discovery which I mean laid the foundations of a kinetic theory of gases. So, we will be frequently using this relation and we will see that how using this relation one can calculate the parameters in the Maxwell Boltzmann distribution.

Now, we will start our so far what we have discussed is that we just discussed the essence of the kinetic theory of gases. And how we said that how pressure can be formulated by assuming that the gas molecules are basically composed of a number of gas is composed of as number of molecules which are constantly moving around. And they will strike the wall of the container there in and that striking at the wall will cause the moment change which is related to pressure. And that is a molecular interpretation you can say of the pressure.

But, when I say molecular interpretation this is actually a these molecules and now we have been classically they are all being classical mechanics the Newtonian law remember that. There is no quantum mechanics here, but still there is an idea that the molecules exist and this because this mass you can see is actually mass of a particular gas molecule.

Now and they are striking the wall and then after the after they strike the wall it was a pressure and, but pressure we could have also got from a macroscopic experiment by combining Boyle's law and chance law and also the concept of Avogadro. And then you get the ideal gas equation and we are arguing that if the gas obeys the ideal gas law then we can get this expression.

Now, one crucial point even if the gas does not obey the ideal gas equation this expression will still be correct. The reason is we are only suppose there is a non ideal gas, but the distribution of the pressure of course, we have to use the Vander wall’s gas equation. Then the pressure will be slightly different, but we will we will argue that the distribution of the speed or in Maxwell Boltzmann distribution we will still hold.

Ah the reason is this distribution is over only kinetic energy of the gases and even if there is an interaction present that interaction comes into the potential energy of the gas. But, we are only interested right now how the molecules are moving around, we do we are not imposing any condition that what is the internal energy like internal or better I should say that what are the energy of the internal degrees of freedom? Like for example, vibration rotation translation now how those degrees of freedom are affected if there are intermolecular potential.

Those who are not considering, we are only considering the molecular speed distribution and that will be at the whatever expression we will get using this ideal gas using the velocity expression which we derived using the ideal gas expression will also be correct for a real gases.

That will just argue, but we want to be proving it here because this needs a understanding of the that is called actually a configuration integral in the statistical mechanics that will not discuss here. Now, to begin with what Maxwell Boltzmann distribution says which is basically.

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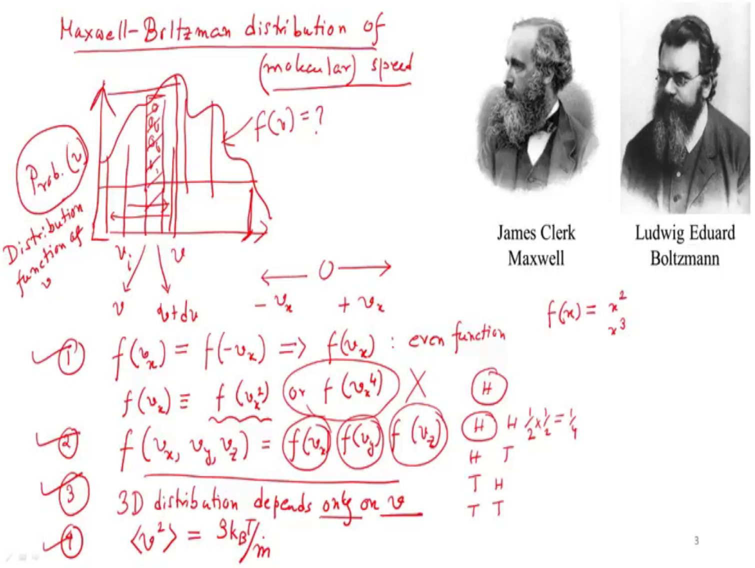

Developed by James clerk Maxwell and then Ludwig Boltzmann extended it to find the statistical interpretation of the Maxwell Boltzmann distribution and. So, what it says is that there will be when we have a collection of molecules so, not all molecules are moving at the same speed at a time.

So, what is happening here the molecule suppose is moving say just take a number say 1 kilometer per second and then it collides another molecule which was moving in some other direction with some other speed. And then due to this collision they exchange their kinetic energy and then maybe the faster molecule becomes slower and the slower molecules become faster. And then what will happen is that their molecules are not only moving around, they are also at different velocities.

Every molecule is also constantly changing it is velocity. But, on statistically what you can say is that I have many molecules and then there is a distribution of velocity suppose this is the value of the velocity or say speed I in I should always there the speed because we just considered in the magnitude of it.

So, it is independent of it is direction that what is that is exactly what we are going to are going to evaluate. Now, suppose a molecule has a particular velocity in this which is suppose there is very specific velocity which is suppose this v initial, but after collision it just it is velocity is changed to here, but then in the next collision into velocity is changed to here.

So, the velocity is randomly changing, but what we can always say is that other molecules of velocity are also changing. So, if you consider a narrow range of velocity which is say for example, or narrow range of speed which is v to v plus dv. Within this narrow range the number of molecules which are basically if I just on this axis if I just brought the probability of these molecules of having some speed say v.

So, that will be kind of a constant within this range. why because some molecules are changing every molecule is changing the speed due to collision. But, if you have a large number of molecules so, on statistically you can say that within v and dv the total number of molecules or the probability of having the molecules in the that narrow velocity range v to v plus dv will always be independent of time.

Now ah; that means, actually it does not mean that all the molecules if I take a snapshot and if I find that some say 1000 molecules are having speed in this particular range. But in the next instant I will also have 1000 molecules, but those thousand molecules are not the same 1000 molecules. Because, some molecules due to collision have changed their speed and they have moved out of that velocity range. But, a statistically similar number of molecules same number of molecules also entered in that speed zone due to collision.

So, on average this number does not change and we are just going to calculate that average. Now, if make some assumption to begin with I mean there are many ways to derive this Maxwell Boltzmann distribution of molecular speed. But, the way we are going to do is slightly I would say less rigorous in the sense that it will mostly I mean do it on a conceptual basis. But, you can do it on a very rigorous way by calculating the energy levels a kind of Boltzmann's approach.

And then calculating the statistical probability of finding some molecule in some energy state and then you can solve this equation based on constraint using Lagrange's method all these things we are skipping.

And then you can get an energy distribution and then you can convert it into velocity distribution that is one of the standard ways of doing it. But, right now what we are doing is we are first doing the velocity or the speed distribution and then we will derive the energy distribution, it is the other way.

Ah so, it is basically the kind of Maxwell's way of doing it, although it is not exactly the same way which Maxwell derived. Now, the logic behind it is that in this maximal Boltzmann distribution we call it as a Maxwell Boltzmann distribution of molecular speed. But, it can also be the atomic speed suppose if I have an atomic vapor then also it follows the Maxwell Boltzmann distribution.

So, now the assumptions are think about it a molecules are moving around and then and the first assumption we are making that the molecule has an equal probability of going into the right or going into the left.

Now, what we are going to formulate is some kind of probability function which is known as a distribution function. Because actually tells us a particular distribution or probability of the molecular speed distribution function of v. And suppose I am just drawing arbitrary so, this is suppose the distribution function which means this particular velocity is very less probable.

However, this particular velocity is very very high probable something like that. So, that function what is the nature of this function that we want to calculate. So, that function I am just writing as some f now; that function when first we will calculate the velocity suppose the velocity function and then we will go to the speed function.

We will basically make sure that we are calculating the sum distribution which is independent of the direction that will give us the speed distribution. So, so what I had right now I am saying is that the molecule should have equal probability of going into this direction versus this direction. So, it speed a distribution or the sorry velocity distribution in either direction should be same.

Now, if you can think about it like if it has a biased distribution meaning in one direction the molecules have a higher probability of going which means the all the gas molecules will have a net velocity in some particular direction. So, that is useful when you are considering a flow of molecules. But, here we are not considering any flow where we were considering the molecules are all content in a cont I mean kept in a container and there is no met or in there is no biased flow in one particular direction.

So, this function f of v then whatever function it is will be independent of the direction right now we are again considering first the velocity distribution. So, because we are concentrating right now telling about right or left which means it has a directionality, which means it is a velocity distribution.

Now, we are saying that that has to be identical to minus v x. Which means if I calculate the probability of having as velocity with plus 10 kilometer per second that will be exactly in x direction that will be exactly equivalent to up the probability of the molecule going in to minus x direction with plus 10 kilometer or minus 10 kilometer per second velocity. So, that is the meaning of that.

So, that immediately tells me that f of v x should be an even function. So, you know what is an even function. So, for example, if f of x is suppose x square that is an even function because if I choose x to be plus 1 or minus 1 the value of f of x is the same.

However, if it is a x cubed something like that it is an odd function f of x will be minus of f of minus x.

Ah so, this even function set the functional form will be something like f of v x will be something like f of v x square just like we saw. It can be also higher order term like it can be f of v xs v x to the power 4 that is also an even function. So, it is it is not only a function of v x it is a function of v x squared that is why it is say even function or v x to the power 4 or maybe a combination of many other things. But, we will first see what happens with v x squared and we will argue that all these things actually are not correct, all these higher order even functions.

Now, second thing is very interesting that when a molecule is moving it it is moving in the arbitrary it is it always moves in arbitrary direction. now, that arbitrary direction or the component of the velocity is along that arbitrary direction we are resolved that into the laboratory frame or or. And ask this question that what is the component x component of the velocity? What is the y component of velocity? What is the z component of velocity?.

Now, when the molecule is moving this components xyz the these are basically independent quantities because these are as you know that this velocity along x does not depend on the velocity of y. If it does, then it will be very different; So, the x component velocity and the y component velocity, a z component velocity that is independent component of the velocities.

So, what does it mean is that the distribution function the or the entire distribution function which basically says find what is the probability of a molecule having velocity v x v y velocity components as vx vy vz. That will be just multiplication of the probabilities along v x, along v y, along vz.

Now, what is this? Where this is coming from? Suppose you have 2 coins and each coin has a head side and a and a tail side. And suppose we have 2 coins and then you toss the coin suppose you toss the first coin I mean then you just do some huge number of experiments. And then suppose you do it 1000 times, you toss it and there you will see that on a statistical way. Now, you will see more or less that there is a half probability of having outcome as head and there is a half probability of having an outcome as the tail.

Now, suppose you bring 2 coins together. So, each one has a head and tail side 2 sides and other and both of them has one head side and one tail side. Now you toss the 2 coins simultaneously and ask this question what is the probability of having head head, head tail, tail head and tail tail? Now, that you will see that those probabilities will be nothing but one fourth.

And because there is a half probability of having the first coin in a head with a head outcome and similarly there is a half probability of having the coin in the second coin in to have the head outcome. So, the total probability will be one forth. Now this will happen where this is happening because the outcome of the first coin is totally independent of the outcome of the second coin. So, if you because they are not talking to each other, they are just independent measurements.

So, exactly similar thing we are using here. So, since these are probabilistic distribution which are independent of each other. The joint probability of having head and tail together or joint probability of having the molecule with simultaneously with speed x axis component of velocity as v x, y axis component as v y, z axis component as z v z will be just multiplication of the individual probabilities.

Now the third thing which is a very interesting is that if this is correct that I have a joint probability and also now we see that this thing. This velocity distributions are basically the joint probability we will you can explain it I mean more, let us discuss the third point first.

So, the third point says that we have ultimately we are going to calculate a 3D distribution. In the sense that the molecule is moving in this direction or this direction that we are not going to calculate which direction it is moving because, it is a isotropic in nature.

What we are interested is to find the speed of the molecule in any arbitrary direction. The reason is since there is no preferential direction; the you can always argue the what is the probability; The probability of having the molecule or having the number of molecules in with a say velocity from say 10 kilometer per second to say 10.1 kilometer per second.

All because, always probability means you have to consider a range because you are considering a number probability is just the total number divided by. So, that those number of molecules divided by the total number so, you have to always consider at some weight.

Now, if you ask this question that fine if I have this molecule going in fact some particular direction, then what is the probability of having the molecule having speed say 10 kilometer per second to 10.1 kilometer per second in this direction.

But, those two probabilities will be identical because if it is not identical then again the molecule have a net flow in some other direction, which is not true. Which means actually these what we are going to calculate is these only this magnitude 10 kilometer to 10.1 kilometer per second independent of the direction; If we really want to calculate that 3 dimensional distribution. So, what we are going to calculate is a speed distribution finally, not a velocity distribution. We will start with a velocity distribution, but we will end up in a speed distribution.

So, this 3D distribution depends only on v. v means actually I am writing v for speed, the magnitude of the velocities so, it is only on the v. And then this is just a logical foundation and the fourth thing is that whichever way I calculate v, I know that this average value of this v square should be equal to 3 k B T by m. That we have already shown for kinetic theory of gases.

So, these are the main 4 main assumptions or axioms that we are going to use, but we we give a logical explanation for each of them why and we are applying it. So, the first thing is that it has to be an even function because there is no preferential direction of movement for any velocity component. Second thing is that each velocity component is independent of each other because, they are just probability distribution. So, the joint probability will be just the product of individual probabilities. The third point is that what we are going to calculate is independent of direction.

So, we are only going to calculate the magnitude of that because, if I ask you the magnitude in this direction and magnitude in some other direction this two will be just equal. So, a a 3 dimensional distributional depends only on the speed not the velocities. And the fourth thing will be these average value of these square of the speed should be equal to 3 k B T by m as we saw as we derived from the kinetic theory gas.

So, in the next part we are going to discuss we are going to use all these 4 assumptions and we are going to basically based on these assumptions it is not assumption is that all logical reasoning. Based on these 4 reasoning's we are going to derive the Maxwell distribution of molecular speed.