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Last time, we went through the same arguments that Maxwell and Boltzmann did to understand the microscopic origin of the ideal gas law, $PV = nRT$.

And we saw how Maxwell had hypothesized that the pressure of a gas on the walls of some container, if the molecules were moving and they collided onto the walls, that pressure must be due to the individual impacts of the molecules on the wall.

That must be due to the change in the momentum of the wall when the molecules slammed right into it.

And that change in momentum over some change in time is this force. That force divided by the total area is the pressure. And it was using that argument that we came up with an expression, just like Maxwell did for the pressure times the volume.

And we see that we were able to write it in terms of the velocity of the molecules that were moving in this gas.

Well, that is very nice because if we have this theoretical expression P times V , and we know experimentally that P times $V = nRT$, if this theory is correct, then this quantity nM , average of the velocity squared, over three, that better be equal to nRT .

Or, solving for what we call the root mean square velocity, that better be equal to the square root of $3RT$ over M .

That kinetic theory made a prediction for what the velocity ought to be. It took, of course, another hundred years before somebody could measure that.

And, of course, it is correct.

But what is interesting here is that this model gave us an understanding for what temperature is.

Temperature is a measure of the speed of the molecules in the gas. It is also, as we saw last time, a measure of their kinetic energy.

We saw that the kinetic energy is one-half M average of the velocity squared. We put in our result from kinetic theory.

That shows us that the average energy is three-halves RT .

Temperature is the measure of the kinetic energy of these molecules in the gas.

For the first time, there was a microscopic understanding of what temperature was.

Now, what we looked at also, last time, was the Maxwell-Boltzmann distribution of velocities or speeds and talked about this particular functional form.

How there was this quadratic dependence right here, a low v because of the v squared here and then an exponentially decaying tail. There were two parameters, the mass and the temperature. We talked about that last time.

But, of course, if there is a distribution here of speeds where this distribution is a probability of finding a molecule with a particular speed between v and v plus dv , -- -- then there also has to be a distribution of energies because the velocity is related to the energy. What do we have to do?

We have to take that Maxwell-Boltzmann speed distribution and change the variable to energy.

We know how to do that. We know how to equate those two distribution functions. And, using the Jacobean of the transformation that we talked about last time, we can calculate what the energy distribution is.

f of E is our Maxwell-Boltzmann energy distribution. It is the probability of finding a molecule with a kinetic energy E to E plus dE .

It also has a decaying exponential term, here, with the energy in the argument, and it is multiplied by E of the one-half. Let's take a look at what that distribution function looks like.

Here it is. Notice, as we learned last time, that the energy has nothing to do with the mass of the particle. The only parameter that is important is the temperature. At a given temperature, all particles, it doesn't matter what their mass is, have the same energy. So, all particles at degrees Kelvin have a Maxwell-Boltzmann energy distribution that looks like this.

There is a very rapid rise in that distribution function, unlike the velocity distribution, which increased as v squared.

It peaks rapidly, and then there is an exponentially decaying term in the energy.

At 1500 degrees Kelvin, the energy distribution looks like this. The energy of the molecules has increased. Since this is a probability, and the area under these curves has to equal to one, if the energy goes up, that is we have more molecules out here with higher energies, well, then this maximum value for the probabilities has got to go down because we have to keep the area under that curve equal to one, since this is a probability. What we see

here, as we raise the energy, is that we have more and more molecules with high energies. There are not a lot of them, but there are some. And they are going to be really important in the example I am going to show you in just a moment. Average energy at 600 Kelvin, just three-halves RT, is 7.5 kilojoules per mole.

Average energy at 1500 Kelvin is 18.7 kilojoules per mole.

But now, I want to show you an example of the importance of this Maxwell-Boltzmann distribution function for energies to chemical reactions, the importance of it in making some kinds of chemical reactions actually work.

And so the example is going to be this reaction.

This reaction is called steam reforming of natural gas.

It is the reaction of methane plus water.

Natural gas is mostly methane. But this reaction of methane and water makes CO and hydrogen. It turns out that this reaction does not work in the gas phase.

That is, if you have a methane molecule and water molecule collide, they are just going to collide, bounce apart and go in their opposite directions. They are not going to make CO and hydrogen. And so what you have to have in this reaction to make it go is a catalyst.

That catalyst is going to be a nickel surface.

A catalyst is something that will lower the activation energy barrier by changing the mechanism of a reaction so that the reaction can proceed. In this case, what happens is that the methane and the water impinge on this nickel metal catalyst. And the methane and the water decompose. They fall apart to their elements on that nickel surface. And then, once you have carbon, hydrogen and oxygen on that nickel surface, the atoms rearrange and come off as CO and molecular hydrogen. So, that nickel surface is a catalyst. We call this the catalytic reaction. In particular, we call it a heterogeneous catalytic reaction.

It is heterogeneous because the catalyst is in a different phase than the reactants. The catalyst here is a solid.

The reactants are gases. A homogeneous catalyst is one in which the phase of the catalyst and the reactants is the same. This is a heterogeneous catalytic reaction. It turns out that this reaction here is really an important reaction from the standpoint of the production of hydrogen. All of the hydrogen that you use, you know, if you are doing a laboratory experiment and you go get a tank of hydrogen, that hydrogen is made by this reaction, by reacting methane and water to form that hydrogen. All of our commercial sources of hydrogen come from carrying out this reaction.

For example, if you are in the business of ammonia synthesis, which is taking hydrogen and nitrogen to make ammonia, which is also carried out on an iron surface, another heterogeneous catalytic reaction. And ammonia, of course, is the starting material for lots of chemicals, in particular fertilizers. If you have an ammonia plant, right next to the ammonia plant you have a steamer-forming plant to make the hydrogen to feed into this reaction.

And another place where this is useful is in methanol synthesis.

That is, you can take hydrogen and CO on a copper zinc oxide heterogeneous catalyst and make methanol, the starting point for gasoline, which now is certainly economically feasible.

But it turns out that this reaction here is really a hard one to carry out. Despite the fact that nickel is a catalyst for the reaction and makes it go, the reaction still has to be carried out at very high temperatures.

1500 degrees kelvin is a very high temperature.

It also needs very high pressure.

And one of the reasons why we don't have a hydrogen economy is because it is so difficult to make.

Hydrogen can be done, and it is done in all of the commercial processes that I mentioned to you, but it is still hard. 1500 degrees kelvin, high pressures. The question is, why is it so hard? Why is there this barrier here?

Why do we need to raise the temperature of the gas in order to get this reaction to go? Well, let's take a look at that. What there exists here in this problem is what is called an activation energy barrier to making the reaction go. It turns out that this activation energy barrier is really in the very first step of the reaction, which is pulling the methane apart, pulling that first hydrogen atom off of the methane molecule. What I represent right here is the energy of the reaction as a function of the reaction, and the reaction here is just the first step.

It is taking methane gas, pulling the hydrogen off so that you have a methyl radical stuck to the surface and you have a hydrogen atom stuck to the surface.

It is just breaking that first C-H bond.

What you can see here is that you have to put 50 kilojoules of energy into that reaction in order to make it go.

You have to put that 50 kilocalories of energy in first, before you get any energy back. You can see that this is exothermic. But you have to put this energy in, in order to get that reaction to go.

Well, how do we know that? Let me back up a minute.

Here is where the Maxwell-Boltzmann energy distribution is important. What I did was I took those Boltzmann energy distributions that I plotted for you at Kelvin and 1500 Kelvin and turned them on their side.

This is essentially equal to the probability of finding a molecule at a particular energy versus the energy.

Here is the Maxwell-Boltzmann distribution at 600 degrees Kelvin. It is peaked to very low energies. And, if you look here in this Maxwell-Boltzmann tail, there are not very many molecules that have enough energy to get over that barrier.

However, if we raise the temperature of the gas to degrees Kelvin, then now you can see that there are more molecules here in the high energy part of this tail.

And it is these molecules at these high energies that actually can get over this barrier to dissociation of the methane molecule. They are not many of those molecules with high energy, but there are some.

And that is important, because what happens is when they have enough energy, they react and they leave.

And then this Boltzmann distribution re-equilibrates.

If the high energy molecules leave, then there are lots of collisions here that kick some more molecules up to the high energy part of the tail, and they react.

And so it works. That is why it is important.

How do we really know that there is this barrier here to the dissociation of methane, and why is there this barrier?

What is the physical origin of this barrier to pulling this C-H bond apart? Well, one way we could know that there was this barrier there for sure is to do the following. If we had a way to take methane gas and make it have just a single energy, not the Maxwell-Boltzmann distribution of energies that have lots of different energies, which have lots of different energies in them, and you saw how broad those curves were. But if we had a way to make methane gas with just say energy $E_{sub\ 1}$, whatever that is, we could then take those molecules with just those energies, aim them at this nickel surface, and see if the methane fell apart.

And, if it didn't, then we would prepare molecules at some higher energy and see if they fell apart.

If they didn't then we would go to higher energy.

We would keep going until we got to the top of the barrier.

Well, how do you do that? How do you make molecules with a particular energy? Because I just showed you a

Maxwell-Boltzmann energy distribution at 300 Kelvin, 600 Kelvin. There are a lot of energies present. How do we make molecules with just one energy? We have a way to do that by using some beam techniques and high pressure adiabatic expansions. Basically, the way it works is this. What we are going to do is take a tube here, which is going to have a high pressure of methane in it. Then we are going to punch a little hole in that tube. This tube is actually sitting in a vacuum, so we are going to expand the methane from that tube into the vacuum. We are going to squirt it out.

It is going to become a beam of molecules.

But when you expand a gas from high pressure to low pressure, this expansion is called an adiabatic expansion, which means the gas cools. I will explain that in a moment, but the adiabatic expansion you are going to talk a lot about in 5.60. And, if you are a chemical engineer, you will talk even more about it past 5.60.

Here is how it works. You take these molecules and squirt them out. Because the pressure right here is so high, what happens is there are lots and lots and lots of collisions. And so, you can imagine, if you have some slow molecule just kind of lumbering along and a fast one comes and hits you, what is going to happen is you are going to speed up, and the fast one is going to slow down. And, if you keep doing that again and again and again, all the molecules are going to end up with the same energy or the same velocity.

If you have so many collisions, after a while they are going to all have the same velocity or the same energy because one gets sped up, one gets slowed down. They are all going to end up with the same energy. That is what happens.

That is how we make a beam of molecules, a source of molecules with the same kinetic energy. And basically, what is happening then is that before the expansion, just look at this curve, here is an actual Boltzmann distribution of velocities. It is broad.

But after this expansion, here is the distribution.

It is really pretty narrow. If you put a temperature to that distribution, you might find that at one degree Kelvin, you can really make molecules with a single or very narrow distribution in energies.

That is what we do. We make those molecules with this energy $E_{sub 1}$. Then we have some more tricks for changing those energies in a controlled way.

And we just keep cranking those energies up and watch to see when the methane falls apart. And so, you get data that kind of looks like this. This is a dissociation probability of a methane as a function of its energy.

This is in kilocalories per mole.

At some point, say right about here, 15 kilocalories per mole, the dissociation probability skyrockets. All of a sudden, you are at a high enough energy to get that methane to fall apart. This tells you exactly where that barrier is. But now, the question is, why is there this barrier? Physically, why is there a barrier to pulling the hydrogen off of the carbon when that methane molecule comes close to the surface?

Well, the reason is this. In order to break the carbon-hydrogen bond in methane, in order to have enough energy to break that bond, what you need to do is you need to simultaneously form a nickel-carbon bond and a nickel-hydrogen bond. In other words, when this methane molecule here comes into some nickel surface very slowly, because that methane is tetrahedral and the carbon is kind of hidden in the center, the hydrogens interact with the nickel. But the carbon does not get in close enough to the nickel to start to form a nickel-carbon bond. Now, if you speed that methane molecule up and you really ram it into the surface, upon collision of the molecule with the surface, the hydrogens are pushed back, the carbon gets in close enough to the nickel to start to form, here, this nickel-carbon bond.

You form a nickel-hydrogen bond, and now you can break that C-H bond. We call this black chemistry.

The barrier, there, to that reaction physically is the amount of energy that you have to put into the molecule to push those hydrogens back, to bend those hydrogens back to distort this methane molecule.

Once you do that, the reaction goes.

You are on a roll there. It goes.

So, that is the physical origin of this barrier, here, to the dissociation of methane.

You need to put enough kinetic energy into those methane molecules in order to get over that barrier.

And we do that on a practical scale by raising the temperature of the gas. And on a microscopic scale, this is what is happening. You can imagine that my students and I did this experiment 15 years ago.

But then, we said if this barrier here is the energy required to deform that methane molecule, then we should be able to do this experiment. This experiment is the following. We are going to take our nickel surface, here, and lower the temperature of the surface to 47 kelvin. At that temperature, what we can do is we can freeze a layer of methane on the surface. We call it fizzy-sorb, a layer of methane on the surface.

It will just stick there. And then, if this barrier is the energy required to deform or to start the molecule, then in principle I could take a hammer and pound that molecule into the correct shape for the transition state that leads

to dissociation. It sounds like a simple idea, and it is, except that we cannot really take that hammer.

But we can take an argon atom. We can freeze the methane onto the surface, and now we come in with an argon atom.

That is just a big ball. Or, a xenon atom or a krypton atom. And we know how to accelerate xenon or krypton. We don't accelerate it too much, 50 kilocalories, 70 kilocalories per mole, something like that. And then we can bring it in.

What happens is that the impact of the collision on that methane causes that methane molecule to compress, distort, gets it into the configuration of the transition state that leads to the methane falling apart.

And so, you get the same result.

The question, there, is just getting the energy into the molecule to actually distort it, to deform it so that you can make the nickel-carbon bond and the nickel-hydrogen bond. That is the key.

My students and I, after we had spent many years doing this experiment and spent a lot of money on this experiment, said we have proven for sure that when a bug flies into the windshield of your car, you do get the same result as if you hit the bug on the windshield of your car with a bug swatter. That is what we get.

This is an example of one chemical reaction for which we know the physical origin of the barrier.

There are very few chemical reactions for which we know anything about the physical origin of a barrier to a reaction. Now, what I want to talk about is go back to kinetic theory, because the kinetic theory is going to allow us to calculate a couple of more quantities that are of interest to us. And one of those quantities is the collision frequency. And let me just write that on the board here. What I am going to want to calculate is something called Z_1 , or I am going to call it Z_1 .

It is the number of collisions that a molecule makes in a gas per unit time. And our unit time is going to be seconds. This is the collision frequency of a single molecule in a gas.

How am I going to calculate the quantity using the kinetic theory approach that we have been talking about?

What I am going to do is this. I am going to take some gas, and the molecules in that gas are represented by these blue circles right here. They have a diameter D .

And then, within that gas, I am going to imagine this lighter blue cylinder. That cylinder is an imaginary construct. We are going to use it to calculate this collision frequency.

What it is going to be is the collision volume.

I have set the diameter of that cylinder to be equal to two times the diameter of the molecule.

I have set this upright. And the bottom line is that all of the molecules that instantaneously happen to be in this cylinder when a molecule comes through, all of those molecules are actually going to be hit.

They are going to suffer a collision with another molecule.

And I am going to use that, the number of molecules in this volume, to calculate this collision frequency.

That is what I am going to do. Snapshot in time, those molecules are frozen there, except there is one smart-alecky molecule that comes cruising on through.

Here he comes. Bam, bam, bam.

Hits these three molecules, here, because they are more than halfway into that collision cylinder.

What I know is this smart-aleck was moving at some average velocity, which I am going to call v_{bar} .

In a time T , this molecule, since it is moving with an average velocity v_{bar} , in a time t , it is traveling a length v_{bar} times t .

Velocity times time, that is going to give you a length. And so, I am going to set, for convenience, this time equal to one second because that is going to be my unit of time.

I want to do this per second. I am going to set this equal to one second. Therefore, this molecule is going to travel a length v_{bar} in one second.

And that is the length that I am going to make the collision cylinder. I am going to make that collision cylinder be v_{bar} long. That is the distance traveled in one second by this smart-alecky molecule.

Now, all I have to do is I have got to take the volume of the collision cylinder and multiply it by all the molecules that happen to be at the volume at that particular time.

Because that volume represents the volume swept out in one second by this smart-alecky molecule.

What is the volume of the cylinder?

I set the diameter to be equal to $2d$.

The volume of the cylinder is the cross-sectional area times the length. That cross-sectional area, then, is πr^2 , but r here is equal to $d/2$, just to make it confusing. The area is $\pi d^2/4$.

The length is \bar{v} .

That is the volume of the cylinder, $\pi d^2/4 \bar{v}$.

So, we have the volume of the cylinder. Now what we are going to need to know is the density of the molecules in this cylinder, which is the density of the molecules in the gas.

The cylinder is not special. The cylinder is an imaginary construct that I put in there to help me calculate the collision frequency. I need the density of the molecules in the gas or in the cylinder.

The density of the molecules I am going to set as equal to N/V , the total number of molecules in this volume, divided by the volume of the gas.

I am going to call that ρ . N/V is going to be equal to ρ . That is the number of molecules per cubic meter. That is the density of the gas.

This is the symbol that I am going to use from now on for density defined as molecules per cubic meter.

Then the collision frequency is simply going to be the density of the molecules times the volume of the cylinder.

The collision frequency Z_1 , here, is this volume of the cylinder, $\pi d^2/4 \bar{v}$ times the density.

Why?

Because I set it up so that every molecule in that cylinder would suffer a collision. And that cylinder is the length that a molecule travels in one second.

There is the density times the volume.

The meters cubed disappears. What I have left is ρ , the density, $\pi d^2/4 \bar{v}$.

This is collisions per second.

So, I have my collision frequency.

This is the single-molecule collision frequency.

This is the frequency of collisions that one molecule makes with the other gas molecules.

That is important. We are going to do a different kind of collision frequency in just a moment.

But now, it turns out that there is another factor here that I had left out because I haven't done as sophisticated of an analysis as I could. And that is that I made the assumption in my picture before that all the other molecules were frozen in time and that there was only one smart-aleck that was moving around, cruising through.

The reality is they are all moving.

And what I really have to do is I have to take into account the relative velocities of the molecules, the relative speeds.

I can do that. There is a little more sophisticated analysis in doing that, but I could do that.

And, if we do that, this makes a difference of the square root of two. I am just going to put that square root of two in there right now, and later on you will be able to see where that comes from, in a later course.

That actually is the collision frequency of a single molecule in the gas.

I am also interested in another quantity, which is the total collision frequency. That was the single collision frequency, but I am also interested in knowing how many collisions are occurring in the entire gas per unit time, the total collision frequency. You know why I am interested in that number? I am interested in that number because that is going to be the upper limit to any reaction rate. A reaction in the gas phase or in solution cannot happen any faster than the molecules collide. They have to collide before a reaction is going to occur. The total collision frequency, the importance of that number is that it is the upper limit to a reaction rate. Let's calculate that.

Z is going to be equal to the collision frequency of one molecule, Z_1 , times the total number of molecules in the gas, N .

That is what N stands for. But since each collision involves two molecules, I am going to have to multiply this by one-half. Otherwise, I am going to over count the number of collisions because each collision involves two molecules. The total collision frequency here is one-half times N times Z_1 .

Therefore, if I go and plug in my expression for Z_1 and N and simplify things, my total collision frequency here is one over the square root of two times N times $\rho \pi d^2$ times the average speed.

That is my total collisions per second. This is not rocket science.

This is easy. What I want you to realize is that you do have to understand what N is, what ρ is, what d is, what \bar{v} is. And I am always surprised on an exam, when we are going to give you this equation, that students don't

actually know what ρ is, or N is, or v is, or d is.

This is easy. You do just have to understand, this is the total number of molecules in the gas, this is the density of the gas in molecules per cubic meter, the diameter of the molecule, the average speed.

That was just a helpful hint. This is the upper limit to the reaction rate. When somebody tells you, the rate of this reaction is so and so many molecules per cubic meter per second, what you can do is a back-of-the-envelope calculation to see whether or not they are telling you the reaction rate is greater than this number.

If it is, you can say ah-ha, got you, it cannot possibly be.

Really important. If a reaction has this rate, it will mean that the probability of the reaction occurring is one. If the reaction has that rate, we call that the gas kinetic rate.

That is a term that we also use.

Then, finally, one other quantity from the gas kinetic theory. Yes?

She asked, what velocity, here, would you use?

You actually are going to, in that particular case, have to take the average of the average velocities.

In other words, if you had two different molecules that were reacting for this average velocity here, you are going to have to use the average of the average velocity. And then your error bars on the experiment will always be large enough to take that into consideration. Good question.

One other quantity, something called the mean free path. What I want to know, here, is on the average, how far does the molecule travel in the gas before it suffers a collision?

That is what a mean free path is.

A mean free path in solution. Sometimes you will do a solid state physics course and will hear about the electron mean free path. A mean free path is always the distance traveled between collisions.

That is what that is. And we are going to call it λ . This is not wavelength anymore.

We just changed our definition of λ .

λ , here, is the average distance between collisions. How are we going to calculate that? What we are going to do is take the average distance that a molecule travels per unit time, per second, and are going to divide it by the number of collisions that occur per second.

And you are going to see that the per seconds are going to cancel here. We are going to have the average distance per collision. That is what we are after.

This is easy to do because the average distance traveled per second is simply the average velocity.

It is meters per second. The average distance traveled per second. The number of collisions per second that happened, we just calculated that.

That was Z_1 . We can substitute in $Z_1 \bar{v}$, \bar{v} cancels, and what we are left with is one over the square root of $2 \rho \pi d^2$.

That is meters.

That is the average distance the molecule traveled per collision. This is another general generic quantity useful in many cases, also in other kinds of cases that I just mentioned in solid state physics.

What I want to do now is that we said we were going to start talking about the motions of molecules.

We have taken care of, now, the translational motion.

Now I want to start talking about the internal degrees of freedom. And let's do that.

Let me just see if I have something, here.

Let me raise the board, here.

We have talked about this molecule, which is a set of atoms that are bonded together. And, as we always say, they are bonded together for the mutual comfort of their electrons. And we saw that it is not frozen. It moves.

It has kinetic energy. It has velocity.

The velocity generates this macroscopic property of pressure. But molecules also jiggle.

For example, we are going to take here nitrogen, triple bond. That triple bond actually functions like a spring. We can think of that bond as a spring between the two atoms. That spring can stretch, and that spring can compress. When we tell you the equilibrium bond length of some molecule is some number, it is the equilibrium bond length.

It is not the bond length when the molecule is stretched.

It is not the bond length when the molecule is compressed.

This motion is the vibrational motion of the molecule.

So, we have that kind of internal motion in a molecule.

Molecules also tumble. For example, let's take our nitrogen molecule, again.

It rotates around an axis. Going through the center of the mass, it rotates around this axis.

This nitrogen molecule also rotates around an axis, here, perpendicular to the board.

It rotates in that direction. This is the rotational motion of the molecule. The different ways in which we can have this motion are called modes.

This is a rotational mode. This is vibrational mode.

We did not use the word before in talking about translation, but those are translational modes.

Sometimes, we also call these modes degrees of freedom.

A molecule has translational modes or degrees of freedom, vibrational degrees of freedom, and rotational degrees of freedom. Now, in general, if you have an N -atom molecule, you have $3N$ total modes.

When I say total modes that means the sum of translation, rotation and vibration. Of those $3N$ total modes, three of them are translational modes.

Why do we have three translational modes?

We have three translational modes because we are operating in a three-dimensional space. If we have a molecule here, that molecule has motion in the x direction, in the y direction, and also in the z direction. Those are the three translational modes of the molecule.

What that means then, if three of the modes are used up for translation, then we must have $3N$ minus 3 internal modes. $3N$ minus 3 must be the number of modes that is leftover for the internal degrees of freedom for rotation and also for vibration.

And what we are going to see, next time, is that these internal degrees of freedom, these internal modes are going to be quantized. That is, this molecule is going to be able to vibrate with only certain amounts of energy.

There is going to be a ground vibrational state.

There is going to be a first excited vibrational state.

A second excited vibrational state, just like we talked about the energy levels of a hydrogen atom, where the electron was bound with different amounts of energy dictated by a principle quantum number. The vibrational degree of freedom is also going to be dictated by a vibrational quantum number. In addition, the rotations of the molecules, they are also quantized.

A molecule is going to be able to rotate with only one energy, or another energy, or another energy, but not any energies in between.

There are discrete rotational states.

We are going to be talking about another kind of quantum number. In that case, a rotational quantum number. That is where we are going to pick up on Monday. See you then.