Chemical Principles 2
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Microscopic Definition of Temperature Part 1

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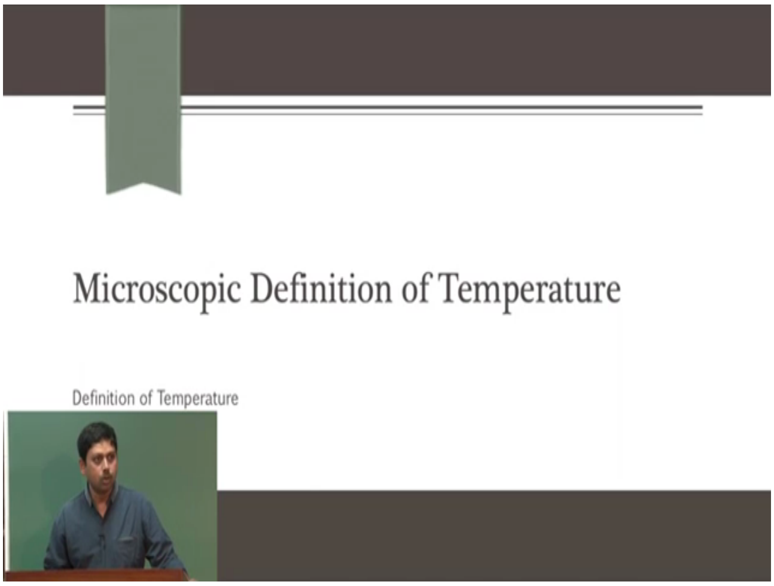

Microscopic Definition of Temperature

Definition of Temperature

So last lecture we have discussed about zeroth law of thermodynamics and implications of heat and temperature, how zeroth law can give us a sense of temperature. So today we are going to understand what is the microscopic basis of this temperature.

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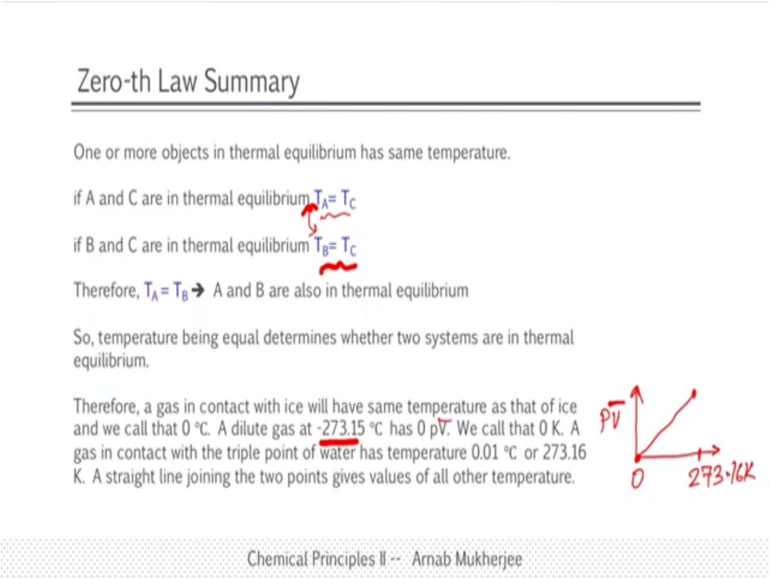

Zero-th Law Summary

One or more objects in thermal equilibrium has same temperature.

if A and C are in thermal equilibrium $T_A = T_C$

if B and C are in thermal equilibrium $T_B = T_C$

Therefore, $T_A = T_B$ → A and B are also in thermal equilibrium

So, temperature being equal determines whether two systems are in thermal equilibrium.

Therefore, a gas in contact with ice will have same temperature as that of ice and we call that 0 °C. A dilute gas at -273.15 °C has 0 $p\bar{V}$. We call that 0 K. A gas in contact with the triple point of water has temperature 0.01 °C or 273.16 K. A straight line joining the two points gives values of all other temperature.

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So before that we will just do a summary of zeroth law, so one or more objects in thermal equilibrium has same temperature. So we discussed that if C is in contact with A, so let us say

A and C are in thermal equilibrium so temperature of A and temperature of C will be equal and let us say B and C are in thermal equilibrium so temperature of B and temperature of C will be equal and therefore temperature of A and temperature of B are also equal because T A equal to T C equal to T B. However, we did not specify that A and B are in thermal equilibrium.

So therefore zeroth law says that once thermal equilibrium is established then a quantity which is defined to be temperature is going to be same between two objects in equilibrium with each other. Now temperature being equal determines whether two systems are in thermal equilibrium or not so that is the definition again, so alternatively we can say that if temperature is equal then two bodies are in thermal equilibrium with each other.

So just to summarize so therefore, a gas in contact with eyes will have same temperature of that of eyes and we call that 0 degree centigrade that is our definition. A dilute gas at minus 273.15 degree centigrade has 0 pV, pV bar is 0 we call that 0 kelvin. A gas in contact with triple point of water has a temperature of 0.1 degree centigrade or 273.16 kelvin. So now once we define these two points and plot pV one point is 0 kelvin, another point is 273.16 kelvin, once we define that we get temperature for all the rest of the temperatures in between because we know that it follows a straight line dilute gas.

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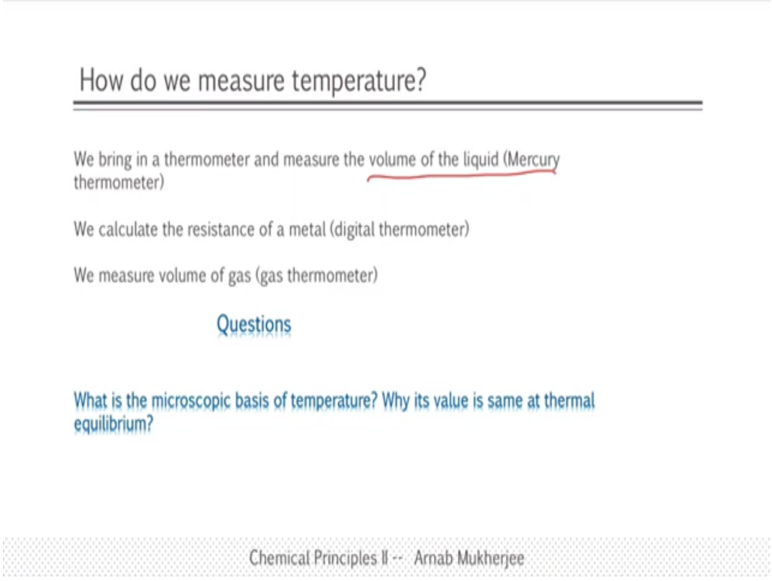

How do we measure temperature?

We bring in a thermometer and measure the volume of the liquid (Mercury thermometer)

We calculate the resistance of a metal (digital thermometer)

We measure volume of gas (gas thermometer)

Questions

What is the microscopic basis of temperature? Why its value is same at thermal equilibrium?

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Now how do we measure the temperature, so in order to measure the temperature we bring a thermometer, thermometer is typically of can be of different types we will discuss that and either we measure the volume of liquid mercury that we you know commonly use at home for measuring the temperature because volume will expand or we calculate the resistance of a metal so that is a digital thermometer that we discussed last time that it actually calculates the resistance which changes with temperature.

And we can also measure the volume of a gas that is a gas thermometer that we discussed. However, you know still leaves us with some questions that what is the microscopic basis of this temperature? Why two bodies are in contact with each other will have thermal equilibration?

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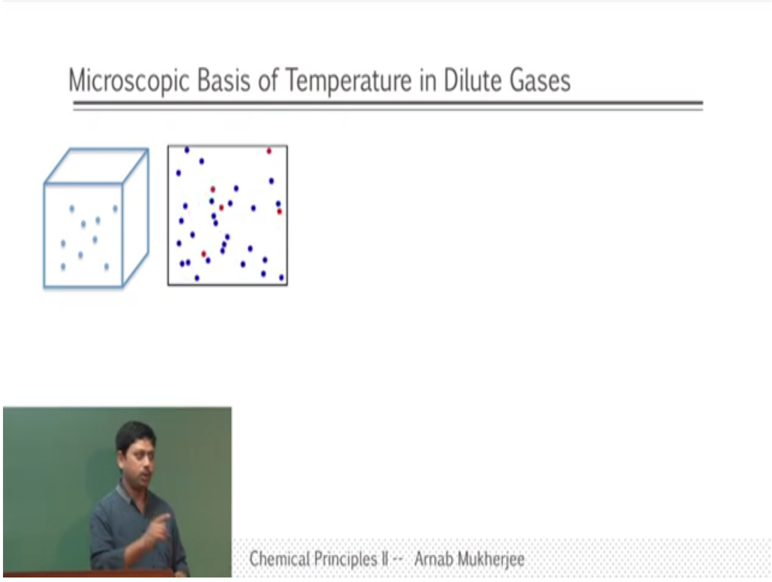

Microscopic Basis of Temperature in Dilute Gases

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And so that question we have to understand and in order to understand that particular question we will first take a gaseous system a system in which the gas particles are there in a dilute limit let us say take the pressure to be very low and the gas molecules are randomly distributed within that. So when the gas particles are inside that particular box of some volumes, what do you think should happen?

The particles will move around at that particular temperature, right. So this kind of situation will arise, where different particles will randomly move around within a particular closed volume. Now we cannot really see a gas molecule because they are too tiny for us to see. However, we can mimic the situation by a similar thing. So we have a demonstration setup early for you to mimic a situation in which gas like random particles will move around.

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So we are going to show that, so you see this is a box you can think of that as a particular box of gas molecules and in order to mimic the gas molecules we have used thermocol balls of different colours, so these thermocol balls at normal temperature or you know right now the temperature will be 300 kelvin 27 degree centigrade it will not oscillate it will not move, you know tiny particles will move with this mass of these particles are too high for it.

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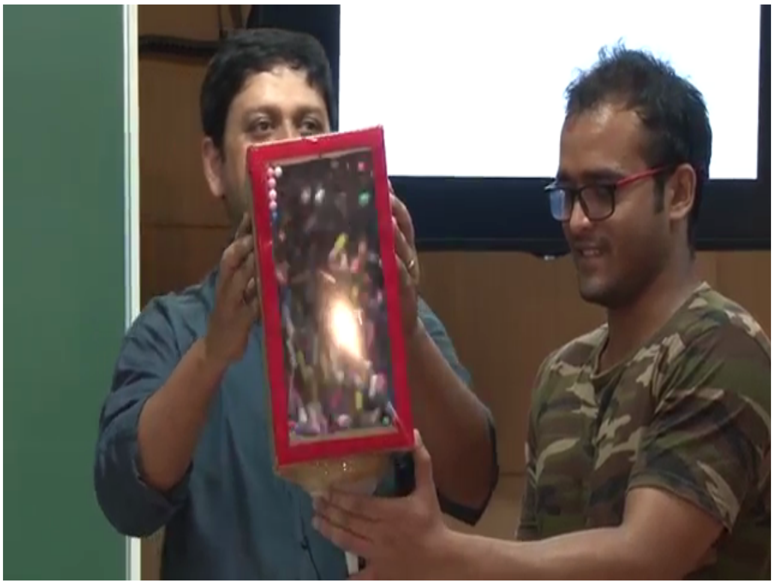

So therefore we are going to induce flow of air inside this chamber and mimic a situation how these things would have moved if they were very tiny particles in a particular box so it will replace it, okay. So we are going to place it, okay so now we are going to flow air through this, are they moving randomly? (So okay) So now if we change the force of air flow then the motions will be faster and more you know random it will be always but it will be much faster and hitting the wall of the chamber much faster.

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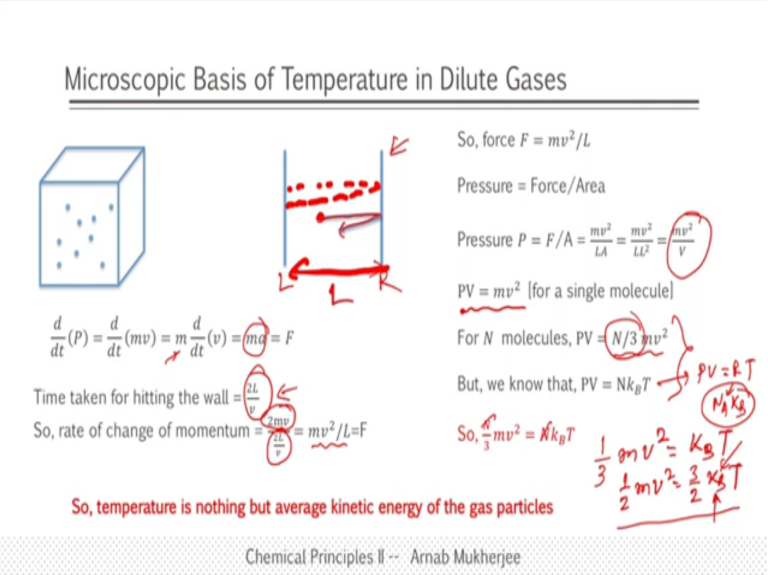

Microscopic Basis of Temperature in Dilute Gases

$\frac{d}{dt}(P) = \frac{d}{dt}(mv) = m\frac{d}{dt}(v) = ma = F$

Time taken for hitting the wall = $\frac{2L}{v}$

So, rate of change of momentum = $\frac{2mv}{\frac{2L}{v}} = mv^2/L$=F

So, force $F = mv^2/L$

Pressure = Force/Area

Pressure $P = F/A = \frac{mv^2}{LA} = \frac{mv^2}{LL^2} = \frac{mv^2}{V}$

PV = mv^2 [for a single molecule]

For N molecules, PV = $N/3\, mv^2$

But, we know that, PV = Nk_BT

$PV = RT$

$N_A k_B$

So, $\frac{\cancel{N}}{3}mv^2 = \cancel{N}k_BT$

$\frac{1}{3} mv^2 = k_B T$

$\frac{1}{2} mv^2 = \frac{3}{2} k_B T$

So, temperature is nothing but average kinetic energy of the gas particles

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So here in these situations in order to understand that what actually happens when it does that let us say we are going to now consider two opposite side of that particular wall. So this is mimicing the left wall and this is mimicing the right side of the wall. A particle that moves will go hit the wall and come back, right. So we can calculate the force acting on this particular wall and then we can calculate the pressure we know that pressure is force per unit area. So once we calculate the force we will be able to calculate the pressure that is acting on this particular wall.

So what do we know about force, force is something is change of momentum, so let us say d dt of P, P is nothing but mass into velocity so then we take the mass out and d dt of v which will give us ma and we know that force is equal to mass into acceleration. So change of momentum is basically force that is what we have shown in this particular line. Now also we can calculate that how much time it will take for the particle to change its momentum.

Now if the length of the particular box is L and if the velocity let us say take all the velocities to be same, the velocity of the particle is V then the time taken to hit the wall will be 2L by v, so because a particle will have to go let us say it starts from here, it will have to go till this much L, come back L and then only it will again reverse back its momentum. So therefore in order to change the momentum it has to travel 2L distance and assuming the velocity of the particle as v we can calculate the time to be distance by velocity, so that is 2L by v.

Therefore, the rate of change of momentum will be 2mv divide by 2L by v, which comes out to be mv square by L. So now we know how much force is acting on one side of the wall. However, remember that in a particular cubic box there are six sides so this force that we have calculated right now is for only two sides or one direction. So therefore, on an average only one third of the molecule will actually hit one side of the wall because there are three different directions.

So force that is acting is mv square by L, so a pressure we know to be force per unit area and pressure will be force per unit area which is mv square by L into A and A is nothing but it is a cubic phase so L square giving rise to mv square by v. So mv square by v is the pressure that is acting on one side of the wall in one direction. Given n number of molecules one third of the molecule will actually go along x direction, one third of the molecule will go along y direction and one third will go along z direction. The reason being since the particle motion is random there is no preferred choice of the particle to go to one side.

Therefore, in order to calculate that so now before we say that PV equal to mv square because we can multiply V with P and then for N molecules PV equal to N by 3 mv square. See this 1 by 3 factor is taking into account that we are only taking on an average one third of the molecules if there are N molecules present then the force that is going to be acted on the wall on one side of the wall will be one third of mv square.

So now we have this equation which is PV equal to N by 3 mv square and we already know from our previous discussions of a dilute gas or ideal gas situation is that PV equal to N k B T that we have already stabilised. So therefore equating these two equation we are going to get N by 3 mv square equal to N k B T, which means now if I cancel our N which is 1 by 3 mv square equal to k b T.

So therefore temperature is nothing but average kinetic energy of the molecule. So here 1 by 3 mv square equal to k b T, so therefore half mv square is equal to 3 by 2 k b T. So we see that k b is Boltzmann constant that we know already, one thing I just wanted to mention here is that we have studied PV equal to RT so that is true when you are talking in terms of moles however we need to talk in terms of molecules then R is nothing but Avogadro number of molecules multiplied by K B.

So what we get here is that 3 by 2 K B, K B is a constant so therefore T is proportional to half mv square or kinetic energy. So temperature is nothing but kinetic energy for atleast for the gas molecules.

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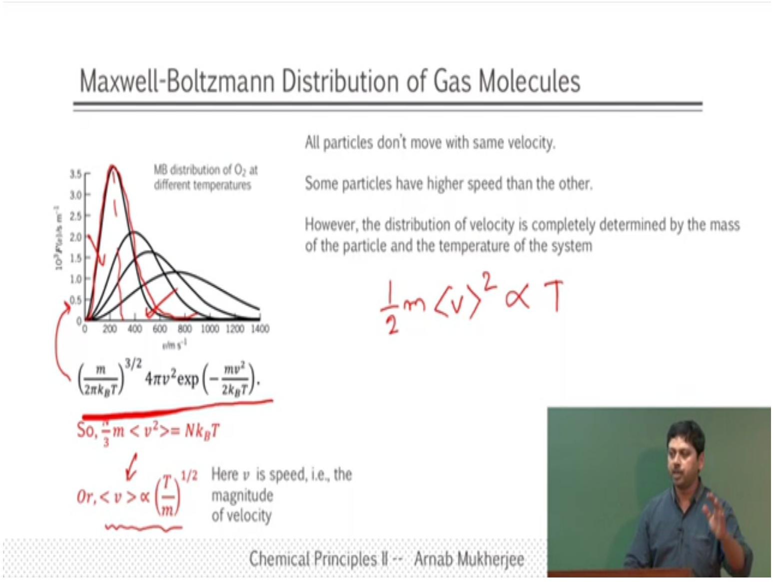

Maxwell-Boltzmann Distribution of Gas Molecules

All particles don't move with same velocity.

Some particles have higher speed than the other.

However, the distribution of velocity is completely determined by the mass of the particle and the temperature of the system

$$\frac{1}{2}m\langle v\rangle^2 \propto T$$

$$\left(\frac{m}{2\pi k_BT}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_BT}\right).$$

$\text{So, } \frac{1}{3}m < v^2 >= Nk_BT$

$\text{Or, } < v > \propto \left(\frac{T}{m}\right)^{1/2}$ Here v is speed, i.e., the magnitude of velocity

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Now does it mean that all the particles are moving with velocity V? Because we have what we have considered here, we have considered that particle velocity is V, just one value of V and we have done our calculations and it turns out that all the particles will not have the same velocity V, it is very improbable to have all particles velocity V. So that is the work of first Bernoulli and then Maxwell and Boltzmann, Maxwell-Boltzmann distribution that shows that there will be a distribution of velocities at a given temperature.

So here we are showing that Maxwell-Boltzmann distribution of oxygen at different temperature and at one particular temperature the curve is like this which indicates that there are particles with smaller velocities, there are particles with much larger velocities and there is some most probable velocity also is present. (So what) if you do a very sophisticated calculation in which we consider all possible velocities of those particles, then we can arrive at this particular equation of Maxwell-Boltzmann velocity distribution, where this equation if you plot it will look like this which says that there are few particles with smaller velocities, there are few particles with much larger velocities and most of the particles we will have a velocity which we call as most probable velocity.

So distribution of velocities is determined completely by mass of the particle and if we calculate the average velocity then we can show that we can write that average velocity of the particle as root over T by m, just to clarify the velocity here is actually nothing but the speed of the molecules which does not have any directions, it has only the magnitude. So it is obtained by taking the average of square velocities and then taking the square root of that. So subsequent discussions when we mean velocities actually we mean speed of the particles.

Individual velocities we cannot really consider but the formula that we are going to ultimately use considering all positive velocities is that it is the half m v average square so if I use this then it is half m v average square is proportional to the temperature. So it is not one particular velocity that all the gas particles will have, we are going to consider the average of the particle and still the equation will remain true and also it indicates that if the temperature is higher the velocity of the particle will also be higher.

So temperature is nothing but then average velocity of the particle when we are talking about gas molecules atleast because all the derivations that we use we assumed that is a random motions and it is hitting the walls and creating the pressure on the walls.

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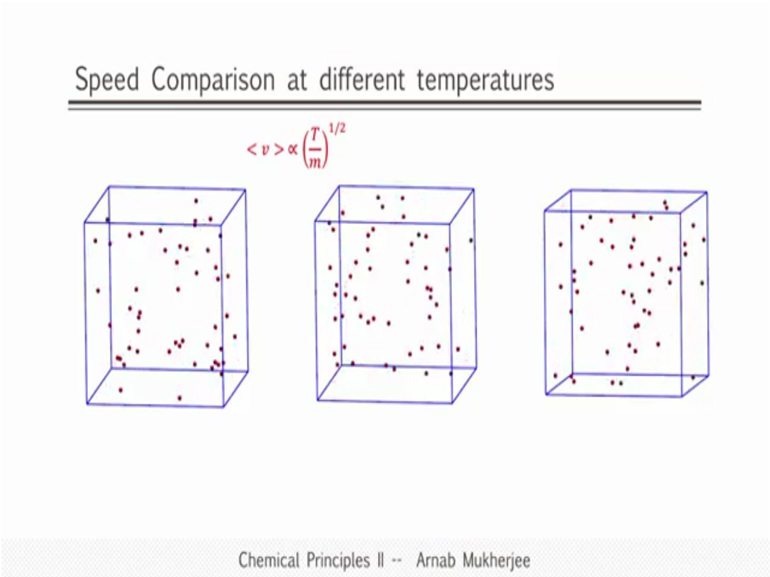

Speed Comparison at different temperatures

$$< v > \propto \left(\frac{T}{m}\right)^{1/2}$$

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So in order to show that velocity is indeed going to be proportional to root over of temperature, we have carried out the simulations of gas particles at different temperatures so we are going to show you that. So the left hand side the gas molecules are at 300 kelvin, this system is at 500 kelvin and this system is at 700 kelvin. So we can see from this movie that as the temperature increases average velocities of the particles are increasing, there is a change in the speed of the particles as such, although it may not be very apparent looking at this however, if you just compare the lower and the higher one then you can see that there is a big difference.

So that indicates that all these particles if you actually really go and calculate the velocities of the individual particles, all of them will not be having the same velocity and all of them will not be moving with the you know same of course same velocity. However, if we now calculate the average velocity we will see that as the temperature increases the average velocity of the system increases.

So this we have understood that when we have an object closed to another object we can measure the temperature, we have understood that, okay. So the question is that if you give heat and then for enough long time from all sides whether the distribution will be same or not, okay. So to clarify that question is that all that we are talking about is when the system is equilibrated properly when you give heat from all different directions and let it be in contact with a reservoir of a particular temperature and when the system comes in thermal equilibrium with that system then only we will get the Maxwell-Boltzmann velocity distribution.

So the distribution of velocities in which you have several possible velocities is in fact when the system is in equilibrium. So it is the property of the equilibrium that all the particles will not have the same velocity. So that is what it is not possible to have same velocity for all the particles. So the nature of equilibrium is such that it will have the Maxwell-Boltzmann velocity distribution, it cannot have all particles having same velocity, okay so that is the property of the equilibrium itself.

So all the thing that we are talking about in this particular class in thermodynamics they all pertain to system in equilibrium we cannot really talk about anything that is out of equilibrium. So the fact that the with temperature the velocities are higher will have its own consequences. For example when we have a mixture of two different gases or liquids at two different temperature the mixing rate will be of course different because molecule will move faster or slower depending on the temperature.

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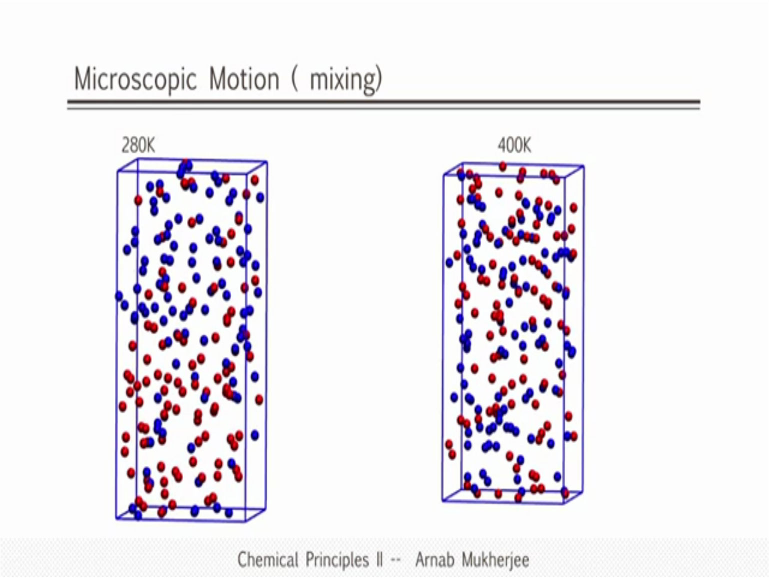

Microscopic Motion (mixing)

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So here we are going to show you animations that when there is a mixture of two systems, one is let us say at 280 kelvin and another is at let us say 400 kelvin, initially they are separated this blue and red particles, you see as the time progresses 400 kelvin system is mixing much faster than the 280 kelvin, 280 is pretty close to the ice like situation and 400 is almost little bit higher than the boiling point.

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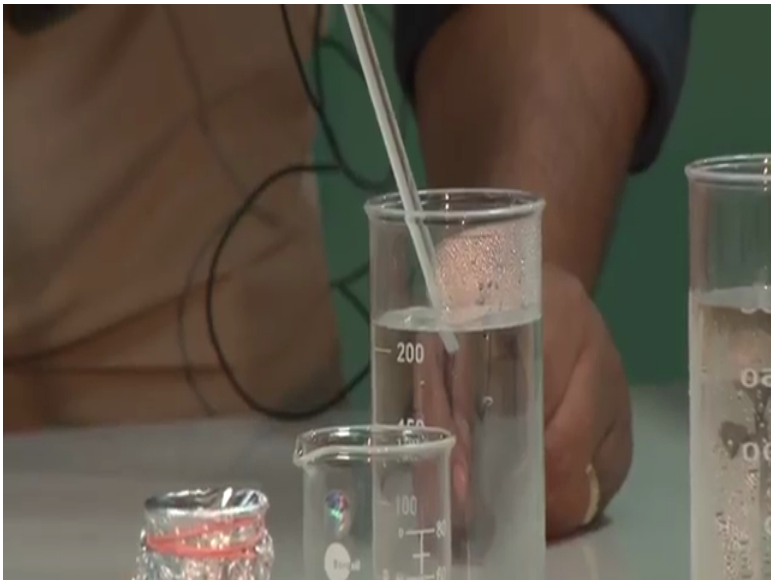

So we are going to also show that through a demonstration here. So this is ice cold water and this is warm water, it is not very hot. So what is the temperature of that, can we just measure it? 40 degree just 40 degree enough and this will be okay 20 degree. So not much of a difference but we are going to whether it works or not.

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So without shaking we want to take it here, this is a cool water, this is hot water and the ink particles are actually going to be distributed. In order for it to be distributed ink has now become in thermal equilibrium ink has come to thermal equilibrium with the water. Now it is going to have similar distribution of velocities that is there in water for the ink particle as well. You see here the spread of the ink indicates that the motion is higher when the temperature is higher compared to when the temperature is lower (correct). So the question is that if now the particles will have different size, how does that effects?

So the thing is that when we are talking about very dilute gases which is also very equivalently we can say ideal gas, then size will not matter because size only matter when you have interaction with the particles. But if you said that mass is different than obviously there will be a difference because our velocities will be proportional to mass and temperature, so if the mass is heavier than the velocities will be smaller for a given temperature, it will move slowly at even the same temperature.

So hydrogen and oxygen when mixing together hydrogen of course will move faster at that same temperature because it goes inversely proportional to the velocity, was that your question? Okay, so Boltzmann distribution or Maxwell-Boltzmann distribution is (it is okay) I have to be very clear now Maxwell-Boltzmann distribution for a given temperature so let us say you bring a gas bring a chamber full of gas molecules in contact with a reservoir having certain temperature.

Let us say our room is a reservoir you keep a box, when you keep a box full of gas molecules at so the system will now come in equilibrium with the surrounding having same temperature so system temperature is same as the outside temperature because it has come in thermal equilibrium. Now if you pick individual gas molecules and calculate its velocity, you will see that their velocities are different and now you are going to plot all the velocities, you are going to find Maxwell-Boltzmann distribution.

So when their microscopic variables so we talk about microscopic and microscopic variables, right volume, temperature, pressure are microscopic variables. So given a fixed microscopic variables T same the microscopic variables like velocities going to have the distribution not one value, okay. So similarly when you talk about this particular hot water, so the temperature is fixed right now let us say at 40 degree. However, the velocities of these water molecules are all different having a distribution, they will not have all the water molecules will not have the same velocity, there will be a distribution.

So the equilibrium enforces that there will be a distribution of velocities and it will be clear later on when we talk about entropy that why that happens, why not all of them will have the same velocity, why by nature itself we will choose to have all different possible velocities. So the question is that whether a mixture of gases will have Maxwell-Boltzmann distribution or not. So as long as the gases can be treated ideally which means the interaction is very less or you can say dilute gases it will follow Maxwell-Boltzmann distribution.

Student is questioning: Nature does not matter as long as there is chemical (())(22:36).

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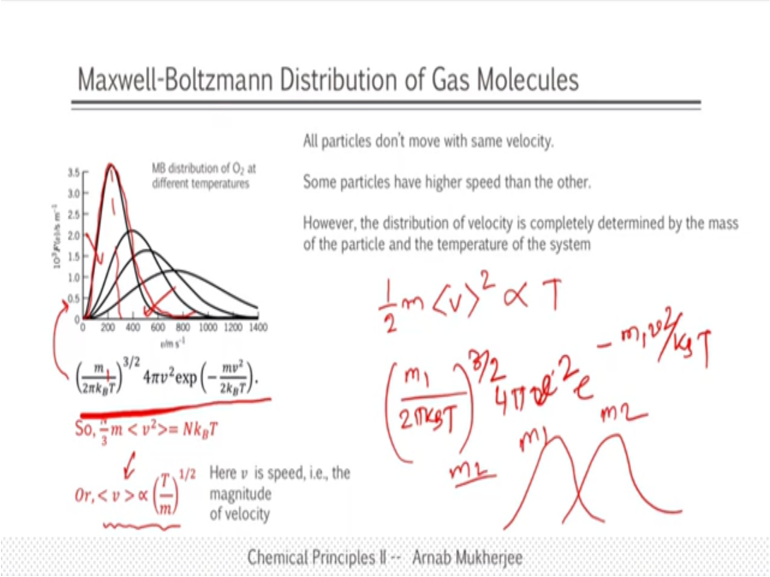

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$$\left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right).$$

So, $\frac{1}{3} m < v^2 >= N k_B T$

Or, $< v > \propto \left(\frac{T}{m}\right)^{1/2}$ Here v is speed, i.e., the magnitude of velocity

$\frac{1}{2} m \langle v \rangle^2 \propto T$

$\left(\frac{m_1}{2\pi k_B T}\right)^{3/2} 4\pi v^2 e^{-m_1 v^2 / k_B T}$

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Nature does not matter as long as the interaction is or it is a very dilute gas. If three are different masses present then as you see that in the equation there is a mass here, right. So you are asking that what will happen to mixture of that distribution, right. So it will be a mixture of these two equations, so it will be a mixture of two Maxwell-Boltzmann distributions, so one Maxwell-Boltzmann distribution will have.

So for example I can write m 1 by 2 Pi K B T to the power 3 by 2 4 Pi v square exponential minus m 1 v square by K B T and let us say you have another one let us say the m 2 is very very large compared to m 1, so what is going to happen is that, you are going to get two distributions, one corresponding to m 1 and another corresponding to m 2. So individually so if the masses are equal then it will fall on top of each other if the temperature is also equal.

However, if masses are different then it will be shifted so it will be a mixture of two Maxwell-Boltzmann distribution that is a very good point.

Student is questioning: (())(24:00).

Right, so the question is that why we took very simplistic assumption that the length is too well, the particle can zigzag have a zigzag motions and the length can be this thing. So as I said that it is a very simplistic approximation, so the simplistic approximations are in you know two forms, one is that we have taken a straight line and then we have consider also same velocities for all the particles, it turns out even if we did not do that result would be still same, although you have taken a very simplistic description here, if you took a complicated descriptions of all possible random velocities and all possible path ways it would still give you the same answer.

So now another question is that particle will interact with each other and therefore it may not even reach the wall, that assumption we have already taken into account by saying that we are talking about extremely dilute gas system or ideal gas in which there is no interaction among the particles.