Thermal Physics

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Lecture –5
Maxwell's Law for Energy Distribution Of Gas Molecules

Hello and welcome back. So, in this class we will start the discussion with energy equivalent of temperature then we will look into the energy distribution of Maxwell gases right.

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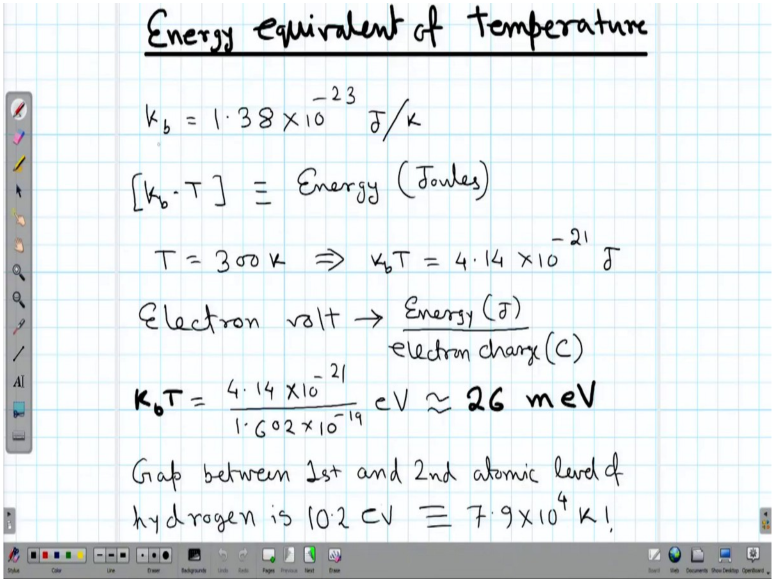

Energy equivalent of temperature

$k_b = 1.38 \times 10^{-23}$ J/K

$[k_b \cdot T] \equiv$ Energy (Joules)

$T = 300\text{ K} \Rightarrow k_b T = 4.14 \times 10^{-21}$ J

Electron volt → $\frac{\text{Energy (J)}}{\text{electron charge (C)}}$

$k_b T = \frac{4.14 \times 10^{-21}}{1.602 \times 10^{-19}}$ eV $\approx$ **26 meV**

Gap between 1st and 2nd atomic level of hydrogen is 10.2 eV $\equiv 7.9 \times 10^{4}$ K!

So, let us start we have already defined the Boltzmann constant. Now what is Boltzmann constant Boltzmann constant is k B is equal to 1.38 into 10 to the power minus 23 joules per Kelvin. Now you see look at the units here this is joules per Kelvin. So, if I multiply k B with temperature then the units will be of energy that is in SI units it is it will be expressed in joules. So, just to put things in perspective let us take T is equal to 300 Kelvin that means k b T will be equal to 4.14.

So, if I just multiply 1.38 into 300 we will get 4.14 into 10 to the power minus 21 of joules. Now this is a tiny bit of energy we see the see the number here this is minus 21. So, in order to represent this tiny energy in a better manner we have to introduce a new unit that is the electron volts or we sometimes call it the electron e V okay. What is electron volt electron volt is an unit in which the energy in joules is divided by the electron charge in coulomb right.

So, if we introduce if we take this tiny bit of energy which is 4.14 divided into 10 to the power minus 21 and divided by electron charge which is once again a tiny number what is that this is 1.602 into 10 to the power minus 19 coulomb then we get a number which is again small but at least understandable we can have a part we can get a field for this number that will be approximately 26 milli electron volt that means 26 into 10 to the power minus 3 electron volt.

Now this is the temperature scale or this is the energy scale to work with when we are talking about very small amount of energy. Now what is this energy? So, let us quickly look into it what this energy means to us. If we just you know try to compute the gap between the first and the second atomic level of hydrogen that will be 10.2 electron volts.

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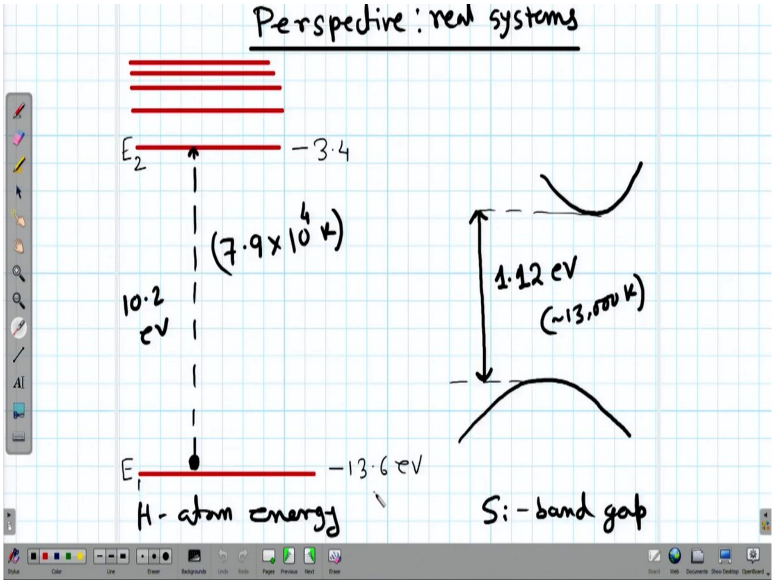

So, what does it mean that means. So, this is the energy levels of hydrogen the first energy level as we all know is at minus 13.6 electron volt and the second level is minus 3.4 electron volt. So, the unit in this case will be electron volt right. So the gap between the first and the second excited level is 10.2 electron volt. Now this 10.2 electron volt if I Now do a reverse transformation I put this use this formula k B T is equal to in electron volt is equal to the energy divided by coulomb the electric electron charge in Coulomb.

So, if I just do a reverse conversion of this energy scale 10.2 electron volt into temperature we get a huge temperature of 7.9 into 10 to the power 4 Kelvin right. Now what does it mean, that means a electron staying in the ground state of hydrogen goes up to the first excited state if and only if the temperature of the hydrogen atom becomes 7.9 into 10 to the power 4 Kelvin. Now this is a huge temperature and we generally do not experience such temperatures in our lab, lab environment okay in normal circumstances.

But if we go to the solar system for example or any star in which the you know the burning of hydrogen fuel is taking place hydrogen is being converted into helium. So, that is where this temperature is realized and the energy of the or the spectrum of the atomic spectrum of atomic hydrogen present in the solar systems or sorry in the sun or any of the star clearly shows that the electron is at a higher energy level could be 2 could be 3 and higher.

And that is because the temperature there is huge actually that is how we measure the temperature of a star looking at the spectrum of hydrogen and other some other elements okay. Now this is something that is almost once again that is not very intuitive towards us but there is another thing that is band gap of Silicon. Silicon we all know that that it is an indirect band gap semiconductor with a band gap of 1.12 electron volt okay.

Now once again if we convert this into temperature scale it is approximately 13000 Kelvin. Now that is once again is a very high temperature and we usually do not realize such high temperature in our normal in our labs or in under normal circumstances okay. So, that is why the any electron that will be residing in the ground state let us say this is an electron will stay in the ground state unless and until there is a voltage bias applied across the junction heterojunction and there is no conduction.

So, that is why the band gap is plays an important that is why silicon is a semiconductor and not a conductor. Now in a conductor what happens in a conductor the band gap is of the order of electron milli electron volts which is realized 20 room temperature is 26 milli electron volts. Now for a semiconductor for a semiconductor the band gap is of the order of one electron volt which we see is a huge temperature. So, an electron cannot normally go from the you know valence band to the conduction band at room temperature.

But in a metal what happens the band gap becomes of the order of few or some milli electron volt and the electron can freely grow go from for from the via valence band to the conduction band at even at room temperature and that is why we have free conduction of electron. Now in the last class you remember we have discussed about hydrogen spectrum. Now in hydrogen spectrum sorry the C V of hydrogen and what happens was see a C V of hydrogen gas.

When we calculated we when we looked at the data we have seen that at very low temperature we have translational only the translational modes are active and it behaves like a monoatomic gas that is because the vibrational energy levels are so spaced that at very low temperature the available thermal energy is less than that band gap. So, the vibrational modes are not activated okay. So, the equipartition theorem whatever we have learned so far it is valid for only those gases or those solids, for solids we will discuss it later.

For which the available thermal energy is at room temperature is sufficient to excite the system to its you know what should I say; for example if we want to see the equipartition you know equi partition theorem at work in a diatomic molecule we have to have we have to take this diatomic molecule to a certain temperature at which the rotational energy levels are active below the temperature it will behave like a monoatomic gas ok.

So, that is exactly what we see in the atomic hydrogen or the hydrogen molecule C V the the specific heat.

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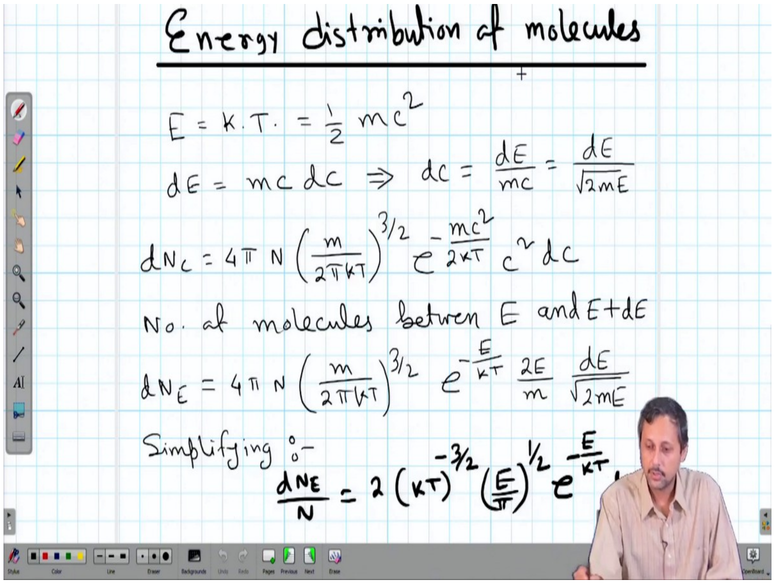

Energy distribution of molecules

$E = k.T. = \frac{1}{2} mc^2$

$dE = mc\,dc \Rightarrow dc = \frac{dE}{mc} = \frac{dE}{\sqrt{2mE}}$

$dN_c = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mc^2}{2kT}} c^2 dc$

No. of molecules betwen E and E+dE

$dN_E = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{E}{kT}} \frac{2E}{m} \frac{dE}{\sqrt{2mE}}$

Simplifying :-

$\frac{dN_E}{N} = 2 (kT)^{-3/2} \left(\frac{E}{\pi}\right)^{1/2} e^{-\frac{E}{kT}}$

Now let us look into the energy distribution of gas molecules in a Maxwell's Boltzmann or in a Maxwell velocity distribution. We see that energy e is equal to k T which is half m c square okay. Now if we take a derivative of this we get dE is equal to m c dc then we can write dc is equal to dE by m c which is dE by root over 2 mE. So, now we look at the Maxwell velocity distribution function dN c which is equal to 4 pi NA cubed I am just writing the a explicitly e to the power -m c square by 2 k d dc square dc.

Now if we substitute for c square here and here and if we substitute dc with dE by using this relation what we can get is a number of molecules. So, okay what is dN c? dN c is the number of molecules in the range of c 2 c plus dc. Now if we do this substitution with basically replace c with energy and dc with de we get number of molecules between E and E plus dE. Now in order to do this substitution we have to write dN E is equal to 4 pi NA stays the same.

Now this quantity to the power m c square by 2 k T is simply e to the power minus e by k T c square is 2 E by m dE is equal to root over 2 m dc is equal to dE by root over 2 mE and we do the simplification for example there is an m to the power 3 half here there is a 1 by m here there is a root m here. So, all these m's are cancelling out nicely. Similarly you know there is a pi to the power 3 half here there is a pi here.

So, it all together we if we simplify we get dN E by n is equal to 2 into k T whole to the power minus 3 by 2 actually I should write this as 1 by kT here 1 by k b T whole to the power 3 by 2 E by pi whole to the power half e to the power -E by k T dE. Now this gives you the number of molecules gas molecules in the energy range of E to E plus dE okay. So, now we have the Maxwell's energy distribution function and we see that there are 2 parts once again it varies with e to the power half the this function has 2 parts one part varies with e to the power half here.

And the second part varies with e to the power minus E by k T and as E increases this part falls off exponentially. So, at very high values of e this part will be dominating for very low values of E this part will be dominating. So, we try to plot this function dN E by E dN E by N or rather we just define this as you know define this function as F of E. So, basically dN E by N is equal to F of E dE.

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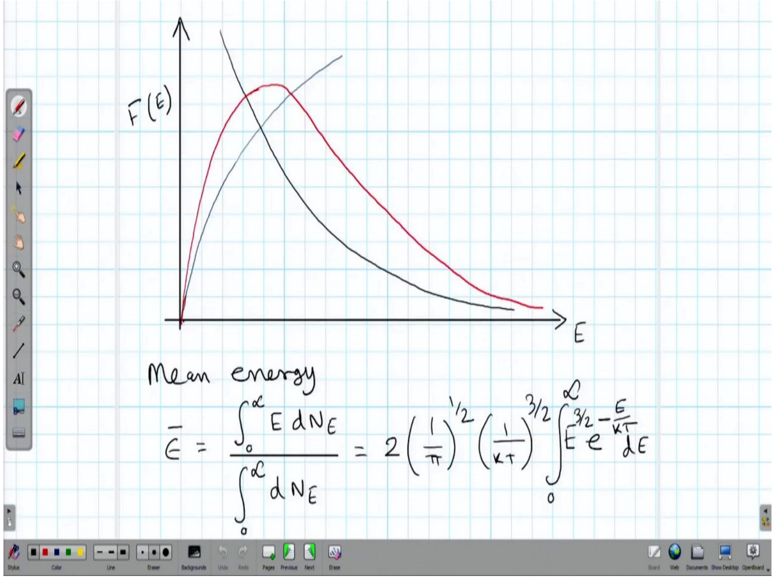

Mean energy

$$\bar{E} = \frac{\int_0^\infty E\, dN_E}{\int_0^\infty dN_E} = 2\left(\frac{1}{\pi}\right)^{1/2}\left(\frac{1}{kT}\right)^{3/2}\int_0^\infty E^{3/2} e^{-\frac{E}{kT}}\, dE$$

And we plot F of E as a function of energy E. So, we see that there are 2 parts the first part is e to the power it is going up with e to the power half and we have okay I should use a separate color. So, that it is easy for you to understand. So, it is e to the power half and it looks something like this and then we have another part which is e to the power minus E by k T at very low values this part falls off exponentially.

So, we have e to the power minus E by k T once again we are just drawing it for a fixed temperature this is the one. So, overall by adding this blue line and this black line we get this red line which looks like this right. So, we get the energy distribution curve for Maxwell gases which is given by this function. Now just like in the previous case we can compute mean energy which is E bar or in this case okay I should actually write E bar not epsilon.

E bar is equal to integration 0 to infinity E dN E divided by integration 0 to infinity dN E and once again integration the denominator 0 to infinity dN E will simply give you N. So, this one is nothing but N the total number of molecules and it will cancel out with the N factor here because if we write out dN E. So, it will be right where is it yeah. So, dN E is equal to N times this function right.

So, N will come out from here and N and N will nicely cancel. So, what will be left it will be 2 2 into 1 over k B T whole to the power 3 half and there will be a factor of 1 over root pi will come out from here and then we have 0 to infinity e to the power 3 half e to the power minus e by k T.

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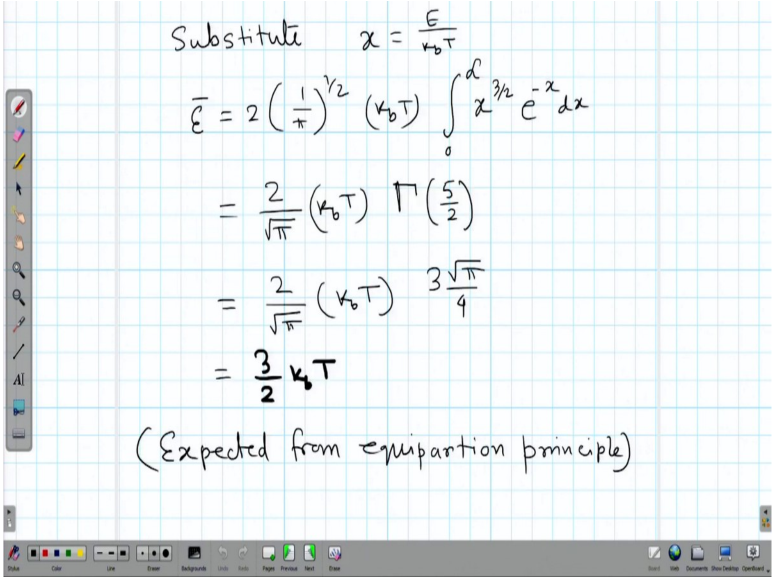

Substitute $x = \frac{E}{k_b T}$

$$\bar{E} = 2\left(\frac{1}{\pi}\right)^{1/2} (k_b T) \int_0^\infty x^{3/2} e^{-x} dx$$

$$= \frac{2}{\sqrt{\pi}} (k_b T)\ \Gamma\left(\frac{5}{2}\right)$$

$$= \frac{2}{\sqrt{\pi}} (k_b T)\ \frac{3\sqrt{\pi}}{4}$$

$$= \frac{3}{2} k_b T$$

(Expected from equipartion principle)

Now this integration we have to substitute x is equal to e by k B T and then this integration takes the form of course there are some factors here and. So, this cavity will be adjusted and finally okay. So, this k B T whole to the power 3 half will be adjusted with the factors and finally we have 0 to infinity x to the power 3 half e to the power minus x dx. Now this one is nothing but your gamma 5 by 2 and gamma 5 by 2 has a value of 3 root pi by 4 and after simplification we have E bar once again I should write E here E bar and finally the result is E bar is equal to 3 half k T.

So, the mean energy for as obtained from this energy distribution function is 3 half k T which is exactly what we expect from the equipotential principle. But please remember once again that equipartition principle is valid if and only if the temperature is sufficient to you know to excite all possible degrees of freedom of the system. For example hydrogen gas at molecular hydrogen gas at very low temperature behaves like a monoatomic gas because why rotational degrees of freedoms are not excited at that temperature.

Similarly at moderate temperature between 200 to 500 degree 500 Kelvin it behaves like a rigid diatomic molecule because the vibrational normal modes are not excited. And at very high temperature when the vibrational normal modes become prominent the dissociation takes over and we cannot really measure all the way up to very high temperature. So, we have to remember that equipartition theorem although if you or equipartition principle although it is a very nice tool to work with it has its own limitations in on range of validity.

And we will see that more of that in when we will be discussing the specific heats of specific heat of solids and we will see that the Dulong Petite law which is valid for some solids at room temperature are not valid for other solids and there are reasons for it. Then there are theories which takes into account all the other factors we will see that later on okay. So, now to end this class we will go back to the problem set week 1 problem set and as promised I have added few more problems in this problem set after problem 4 I have 5, 6, 7 and 8.

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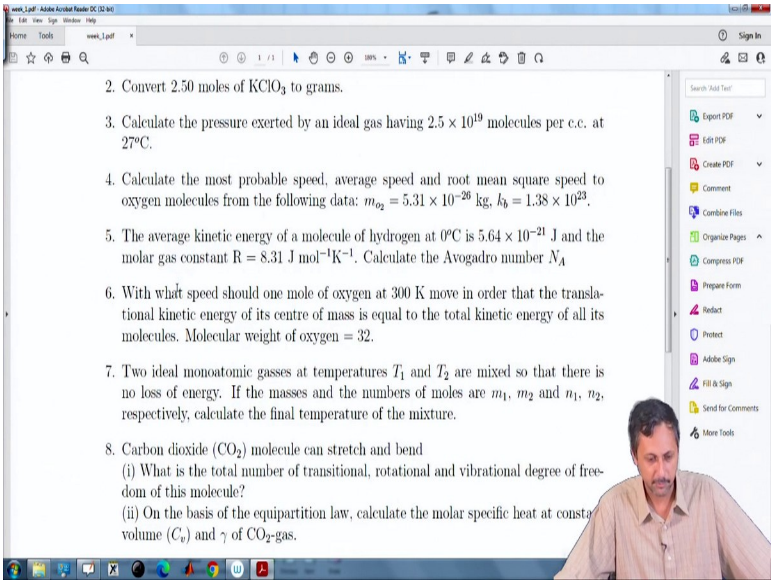

2. Convert 2.50 moles of $KClO_3$ to grams.
3. Calculate the pressure exerted by an ideal gas having 2.5×10^{19} molecules per c.c. at 27°C.
4. Calculate the most probable speed, average speed and root mean square speed to oxygen molecules from the following data: $m_{o_2} = 5.31 \times 10^{-26}$ kg, $k_b = 1.38 \times 10^{23}$.
5. The average kinetic energy of a molecule of hydrogen at 0°C is 5.64×10^{-21} J and the molar gas constant R = 8.31 J $mol^{-1}K^{-1}$. Calculate the Avogadro number N_A
6. With what speed should one mole of oxygen at 300 K move in order that the translational kinetic energy of its centre of mass is equal to the total kinetic energy of all its molecules. Molecular weight of oxygen = 32.
7. Two ideal monoatomic gasses at temperatures T_1 and T_2 are mixed so that there is no loss of energy. If the masses and the numbers of moles are m_1, m_2 and n_1, n_2, respectively, calculate the final temperature of the mixture.
8. Carbon dioxide (CO_2) molecule can stretch and bend
   (i) What is the total number of transitional, rotational and vibrational degree of freedom of this molecule?
   (ii) On the basis of the equipartition law, calculate the molar specific heat at consta volume (C_v) and γ of CO_2-gas.

So, for the rest of the class we will be solving this 4 problems here okay. So, before we begin let me quickly tell you there was a confusion in the last class regarding this units of moles and gram moles actually moles by definition is gram moles okay. So, I got bit confused in between. So, if we have one moles of water that means 18 grams of water actually and there is an unit called kg mole which means the mole in kgs.

So, that is a different unit I mean it is just that instead of 20, 18 grams of water we will have 18 kgs of water. So, gram mole and moles are essentially the same thing okay. So, let us start our discussion for this problems the first problem or rather the first problem of today's class is problem number 5 which says the average kinetic energy of a molecule of hydrogen at zero degree centigrade is 5.64 into 10 to the power minus 21 joules and the molar gas constant R is equal to 8.31 joules per mole inverse per calorie inverse calculate the Avogadro number NA right.

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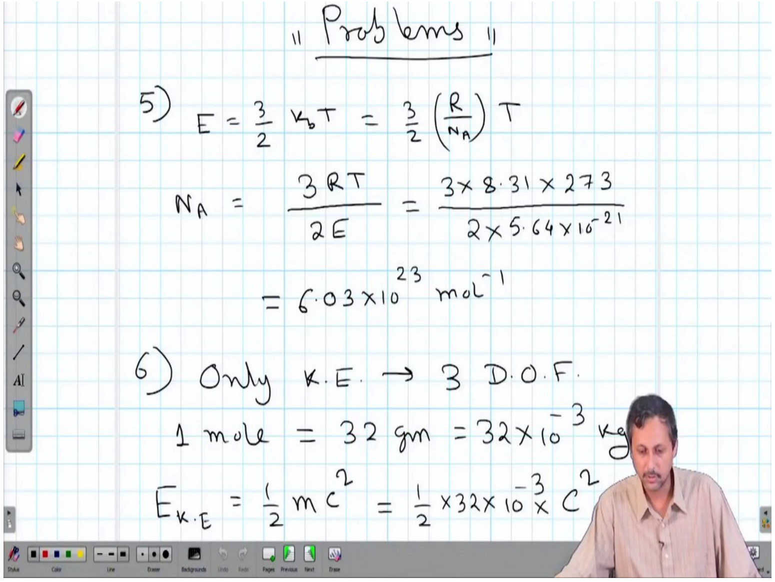

" Problems "

5) $E = \frac{3}{2} k_b T = \frac{3}{2}\left(\frac{R}{N_A}\right) T$

$$N_A = \frac{3RT}{2E} = \frac{3\times 8.31\times 273}{2\times 5.64\times 10^{-21}}$$

$$= 6.03\times 10^{23}\ mol^{-1}$$

6) Only K.E. → 3 D.O.F.

1 mole = 32 gm = 32×10^{-3} kg

$$E_{K.E} = \frac{1}{2} m c^2 = \frac{1}{2}\times 32\times 10^{-3}\times C^2$$

Now to in order to solve this problem we see that at 0 degree centigrade we assume that only the translational modes are active in a hydrogen molecule okay. So, we have e is equal to 3 half k T although we know that it is not exactly true but for simplicity we just assume that this is only the hydro the translational modes. So, we have only e T here which is 3 half k T which is for one mole it will be or I can just manipulate it by multiplying with NA and divide it with NA and we can write 3 by 2R by NA times T NA.

Then will be equal to 3 RT divided by 2E. So, just by putting these numbers in we get the value of the Avogadro number as 6.03 into 10 to the power 23 mole inverse. Of course this value is not very accurate because the energy itself is not very accurate accurately taken but you can try it yourself if you take the vibrational modes into consideration for example instead of 3 half kT if you put 5 of kT you will not get any anything close to this number.

So, that itself tells you if that at room temperature the vibrational or the sorry rotation rotational modes are not fully active as of even at room temperature or at zero degree Centigrades ok. So, for temperature we have put 273 right now. So, for the problem number six we have with what speed should one mole of oxygen at 300 Kelvin move in order that the translational kinetic energy of the center of mass is equal to the total kinetic energy of all its molecules given that molecular weight of oxygen is 32.

So, when we are talking about one mole of oxygen we are talking about 32 grams of oxygen. Now and also there is a hint given that considering only the. So, here we have to consider only the translational kinetic energy of all its molecule okay. So, the kinetic energy is has 3 degrees of freedom. So, 1 mole is 32 grams which is 32 into 10 to the power minus 3 kg. So, the kinetic when we calculate the kinetic energy of the center of mass it is E times E k E kinetic energy is equal to half m c square is equal to half 32 into 10 to the power minus 5 c square c being the speed at which the gas assembly moving through space.

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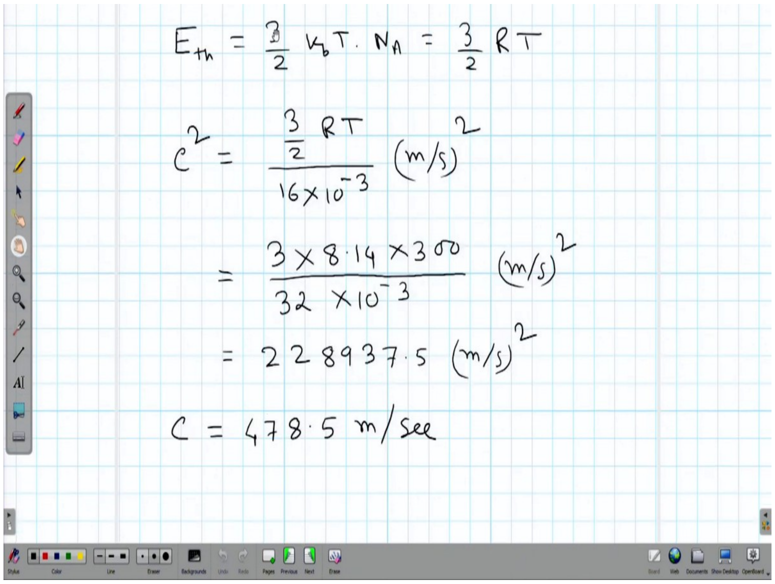

$$E_{th} = \frac{3}{2} k_b T \cdot N_A = \frac{3}{2} RT$$

$$c^2 = \frac{\frac{3}{2} RT}{16\times 10^{-3}} \, (m/s)^2$$

$$= \frac{3\times 8.14 \times 300}{32 \times 10^{-3}} \, (m/s)^2$$

$$= 228937.5 \, (m/s)^2$$

$$c = 478.5 \text{ m/sec}$$

And thermal energy is once again 3 half kT times NA which is 3 half RT. So, by equating this 2 E of k E is equal to E of th we get this relation that c squared is equal to 3 half RT divided by 16. So, we have 32 half into 32 into 10 to the power -3 grams okay 3 -3 here because 32 grams is 1 10 to the power minus 3 kg. So after simplification we get c squared is equal to 228937.5 meters per second square velocity square and then c will be simply 478.5 meters per second right.

Now for the third problem two ideal monoatomic gases at temperature n 1 and n 2 are mixed. So, that there is no loss of energy if the masses and the number of moles are m 1 m 2 n 1 n 2 respectively calculate the final temperature of the mixture right okay.

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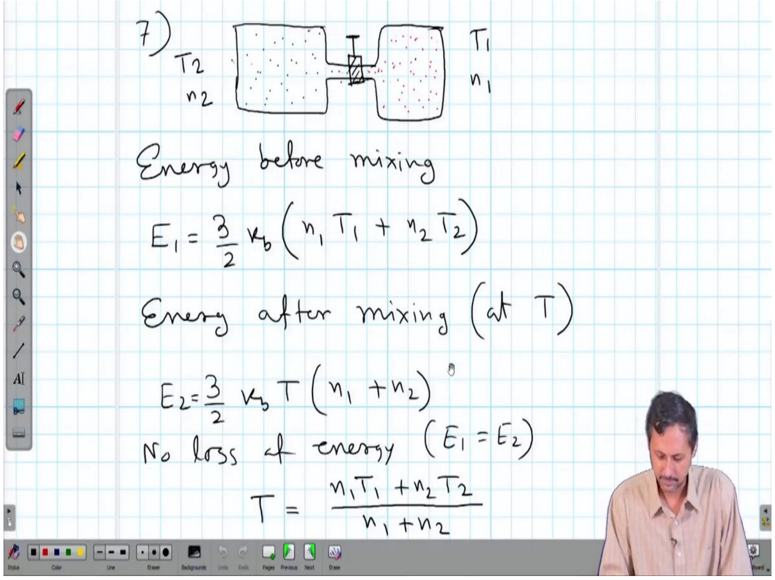

7)

Energy before mixing

$$E_1 = \frac{3}{2} k_b (n_1 T_1 + n_2 T_2)$$

Energy after mixing (at T)

$$E_2 = \frac{3}{2} k_b T (n_1 + n_2)$$

No loss of energy $(E_1 = E_2)$

$$T = \frac{n_1 T_1 + n_2 T_2}{n_1 + n_2}$$

So, we have the situation here we have n 1 moles of this red molecules at a temperature T 1 n 2 moles of this bloom or black molecules at a temperature T 2 and let us say they are capable kept at two separate chambers and we have a stock arrangement in the middle. So, the problem the so basically for mixing what we have to do is we have to remove this top here and then we have to allow it enough time to equilibrate.

So, once this equilibriation takes place or before this mixing we have E is equal to 3 half k T which is equal to n 1 T n 1 or or rather e is equal to rather I should write in this part it will be 3 half k b T because its ideal monoatomic gas times n 1 that is the total kinetic total available thermal energy. Similarly in this part it will be 3 half k B T times n k B T 1 sorry it will be 3 of k b T 2 times n 2. So, after mixing it will or rather before mixing the total energy is 3 half k B T times n 1 T 1 plus n 2 T 2.

After mixing the temperature becomes T the equilibrium temperature. Now if the equilibrium temperature becomes T then we have E 2 is equal to 3 half k B T times n 1 plus n 2 we have both the gases at same temperature. So, n 1 moles of the first gas and then 2 moles of the second gas they are at exactly the same temperature right. So, by equating E 1 and E 2 because there is no loss of energy in this mixing we can write T is equal to n 1 T 1 plus n 2 T 2 divided by n 1 plus n 2. Now what in interesting point to note that although the masses are given m 1 and m 2 there is no function of these masses in this in this problem.

And this is obvious because in equipartition theorem we do not go by the energy part or energy of the individual masses but we consider that there are degrees of freedom and each degree of freedom contributes half k B T irrespective of the mass of this molecule. So, one mole of gas one and one mole of gas 2 both at same temperature both will have equal amount of energy thermal energy available to them irrespective of the masses.

So, that is why the final expression for temperature has no mass term associated with it okay. The last problem once again it is about this equipartition partition theorem carbon dioxide molecule can stretch and paint we have discussed it briefly in the last class okay we will do it once again here. What is the total number of translational rotational and vibrational degrees of freedom of this molecule. And then on the basis of the equipartition law calculate the molar specific heat and constant volume at constant volume C v and gamma for CO 2 gas.

The second part I will just leave, leave it to you to calculate because once you know the degrees of freedom it is absolutely easy to compute C v and gamma because gamma is nothing but C p by C v C p is equal to C v plus R as we all know at least for ideal gases we have to consider ideal gas in this case right.

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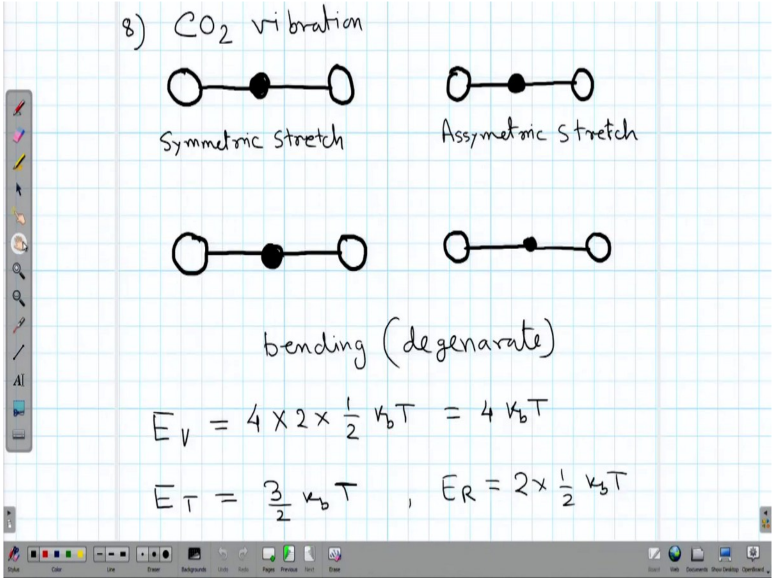

8) CO_2 vibration

$$E_V = 4 \times 2 \times \frac{1}{2} k_b T = 4 k_b T$$

$$E_T = \frac{3}{2} k_b T \quad , \quad E_R = 2 \times \frac{1}{2} k_b T$$

So, what are the possible modes of carbon dioxide vibration as I have said there are symmetric stretching in which these two molecules goes in or out simultaneously whereas the carbon molecule stays which is at the center does not move. So, this is the symmetric stretch then we have the asymmetric stretch in which these two molecules goes in phase and this one goes in the opposite direction. And in the next cycle this is going sorry yeah this one these two are going in this direction whereas this one is moving in the right side.

And what happens in this vibration overall the center of mass of this molecule does not move. So, vibration the definition of vibration is in which the center of mass does not change and once again we have two degenerate bendings we have discussed because carbon dioxide is a linear molecule. So, it is a linear molecule right. So, in a linear molecule we can have two symmetric and anti symmetric stretching and we can have bending which is in-plane or out of the plane.

So, when this one is going up these two are going down right this and these are going down when this one is going down yeah inside the board then these 2 are coming out of the board. So, this is called the bending modes which are degenerate in nature but all in all total vibrational degrees of freedom there are 1, 2, 3 and 4 different modes of vibration each will contribute 2 degrees of freedom which will contribute half k T of energy each. So, all together there are 4 k B T of energy from vibration given that all the vibrational modes are active.

Next we have E T which is the translational kinetic energy which is T half k B T we have 3 translation and we have 2 rotation because finally it is a linear molecule also please keep in mind if it is a non-linear molecule instead of 2 rotations we have all 3 rotations okay. So, for example if we are talking about water molecule which is a non-linear molecule we can have 3 rotations and 3 translations. Translations on we understand but rotation also we have to realize that because it is a non-linear molecule we can have all 3 rotations independent rotations around 3 axis okay.

So, but once again for a carbon dioxide molecule it is a linear molecule. So, we can have only 2 rotational normal modes. So, all together we have 4 k B T from here 3 half cavity from here and half into 2 which is k b t from here. So, the altogether energy possible is 4 plus 1, 5 plus 3 half which will be 13 by 2 k B T of energy. So, your C v which you can very easily compute will be

13 by 2 R and that the C p will be that div plus R simply and then you can compute the value of gamma right.

So, that part I will just leave it to you and this is the end of the discussion about kinetic theory or the simple kinetic theory of kinetic theory of Maxwell gases. Next lecture onwards we will be talking about the collision because what happens is we in this part we have only discussed about the mean translational velocity or rms translational velocity of the gas assembly or we have assumed that the system is in thermal equilibrium with all the possible you know movements taking place that means all the degrees of freedom in action and we have computed the the parameters like C v or kinetic energy whatever.

In the next section what we are going to do is we are talk we will consider the inter molecular collision into account and we will define something called the mean free path of a molecule, thank you.