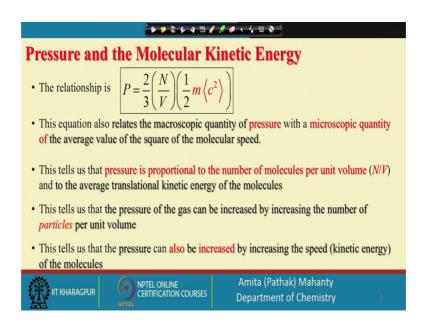
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Lecture – 03 Kinetic theory of gases (Contd.)

Welcome, to the 3rd lecture on Kinetic theory of gases. Today, we will recapitulate what we had talked about in the last class. I had asked you to verify the kinetic has whatever we our information we obtained from the kinetic theory of gases and I hope you were able to do so.

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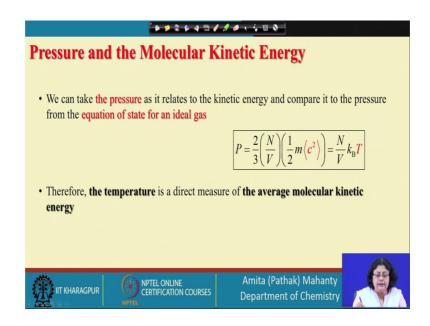
So, anyway we are going to proceed and see what we have gathered till now and proceed a little further. So, what we have got from the kinetic theory of gases; we have derived a relationship of pressure. And from this equation we can see that pressure which is a macroscopic property of a gas can be related to one of the microscopic properties of the gas which is derived from the kinetic theory of gases and that is the average value of the square of the molecular speed.

So, the what we can see from here the pressure is proportional to the number of molecules present in the system per unit volume and it is also equal to the average translational kinetic energy of the molecule. This tells us the pressure of the gas can be increased by increasing the number of particles per unit volume; that means, if you

increasing the number of particles the number of particles striking the walls will be increasing and hence the pressure exerted by the gas will be increasing.

This also tells us that pressure also can be increased by increasing the molecular speed or the kinetic energy of the molecule. What does that mean? That means, if I increase the number of the speed of the molecule the number of striking with the wall also increases. So, number of collisions increases with the wall and that also increases the pressure of the gas.

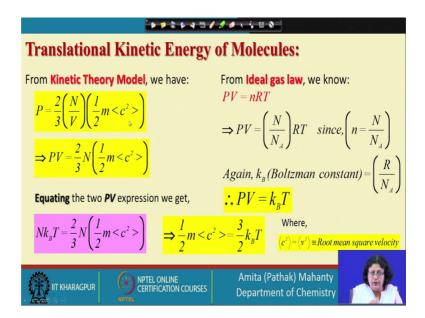
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So, the next one, this is the next relation which we have. Pressure we have related to the kinetic energy of the molecule and compare it with the pressure from the equation with that of the equation of the ideal gas law. Now, what is the it relation which we have this is the pressure relation which we had and now we have related that to the temperature of the system.

So, that temperature is a direct measure of the average kinetic energy of the molecule that we have seen.

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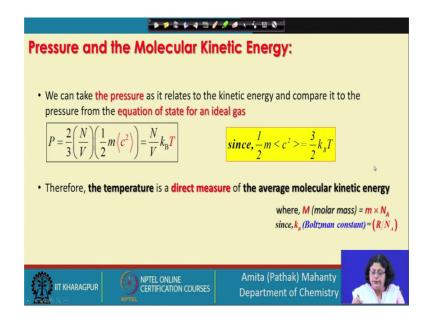
How we have seen? We have seen by the following equations which we had derived in the last class. What we had seen we have derived what the what the pressure is and after the derivation of pressure which is in terms of the root mean square velocity of the molecules and then we had this ideal gas law which where you have PV equal to nRT.

Here we have the definite molecules of gas with a definite mass and occupying a definite fixed volume, ok. So, the volume of the gas is fixed. So, if the volume of the gas is fixed depending on the number of molecules which are present in that for the definite volume we get the pressure relationship in terms of the root mean square velocity of the particles.

Now, from the ideal gas law we derive another expression for the PV which is we are manipulating the term n, the number of moles, number of moles is nothing, but the total number of molecules present divided by the Avogadro number. And again we have a relationship between R and the Boltzmann's constant which is R is the gas constant gas constant divided by the Avogadro's number gives you a new parameter known as the Boltzmann constant. This is how we can put the PV equation from the ideal gas law.

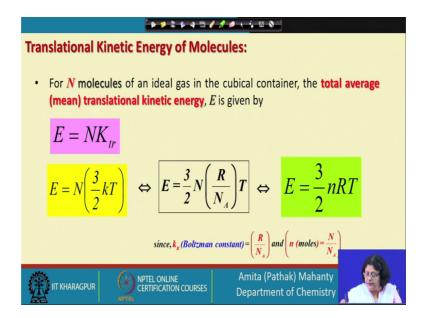
So, from ideal gas law we have got this PV from the kinetic model we have got this PV. So, if we equate these two PVs, if we equate these two PVs what do we get; we get the half m c squared equal to 3 by 2 kT. Where, what is this c or we can sometimes we write v also this is the root mean square velocity of the particles.

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So, what we have just now got is the expression of the half mv square or an mc square equal to 3 by 2 kT and kT is kT, where k is the Boltzmann constant, T is the temperature in absolute temperatures scale, in Kelvin scale.

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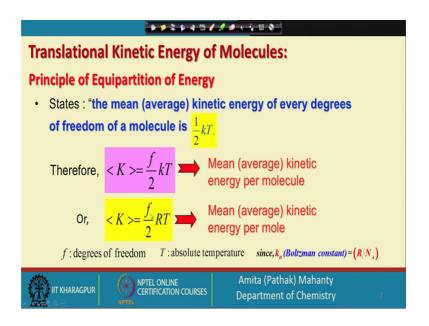


So, what we have got from here? We have got for N number of molecules in a cubic container of volume v we can write for if K is the average kinetic energy of 1 molecule then for N molecules the total energy will be N into K and this K expression we are replacing by 3 by 2 kT, k is the Boltzmann constant. This we can rewrite in terms of k

being equal to R by NA. So, we can replace this and rewrite in terms of the expression of RT.

So, I hope you can understand this what I have substituted here this is R by N. So, R by N is this and then N by N A is nothing, but the number of moles. So, I get R and number of moles. So, this is the another expression of the kinetic the translational energy of a molecule from the kinetic theory of gases.

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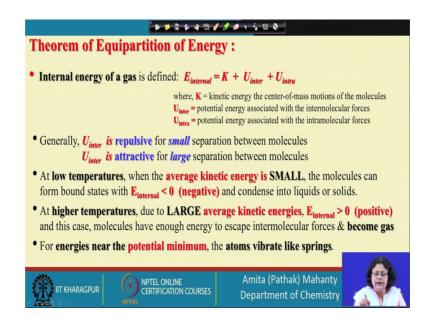
Now, what I today wanted to discuss is about the equipartition of energy. What is the mean energy or the of kinetic energy of the particles? It states the equipartition states that mean I mean or the average kinetic energy of every degree of freedom of molecule can be given by half kT. kT is nothing, but the kB T what is kB is the Boltzmann's constant.

So, if I have say the number of degrees of freedom is f, then the translational energy of the molecule will be nothing, but the number of degrees of freedom into half kT. So, the mean and kinetic energy per molecule can be given by this and the mean kinetic energy per mole can be given by the same degree of freedom multiply by the R.

So, this is what we have, but what do we really understand by the equipartition of energy is what I am going to discuss today and for that what we need to understand when we are talking about the translational kinetic energy out here, the average kinetic translational

kinetic energy what is it that is contributing to the total internal energy of a gas. Let us see what it is will come to this later.

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So, what we are seeing is the total kinetic energy is the sum of the kinetic total internal energy of a gas. This is what we are going to be discussing right now is the equipartition of energy, right from the beginning of the concept of internal energy of a gas, right.

So, the internal energy of the gas is nothing, but the summation of the kinetic energy of the gas the kinetic energy when the center of mass of the molecule is under is moved that is what is going to be contributed to the translation form. Then you have the potential energy associated with the intermolecular forces and our potential energy associated with the intramolecular forces.

Intramolecular within the molecule of forces which is existing intra is between the molecules molecule molecules the forces which is which are existing. So, what we are looking into? We are a looking into one kinetic energy component and two potential energy component and what are these component what are the components which is what is the energy which is contributed to the kinetic energy? What is contributing to the kinetic energy of the molecule and what we are talking about we are talking about the center of mass of the molecule being moved when we are talking about a translational movement.

So, what happens when you are talking about the in the potential energy? Potential energy if I talk about inter is nothing, but the repulsive forces which is which is going to be equal to the repulsive forces which is going to exist between the molecule when the separation of the two molecules are smaller. This separation when it increases then, the you have the intermolecular forces acting as attractive and this is how you represent in the repulsion and the attractive forces.

At low temperature what happens? Low temperature the average kinetic energy is small. Low temperature means the speed of the molecules are going to be less and if the speed is less that the temperature of the total temperature of the system will be lower. So, at low temperature the average kinetic energy is small. The molecules can form bonds or in bonded states and hence what happens; that means, these the attractive forces are going to be take in place, the intermolecular forces which are at in attractive in nature will be in force so, in play. So, what will have you will have a negative value of the internal energy and this will give rise to say condensation performing a gas forming into a liquid or a solid.

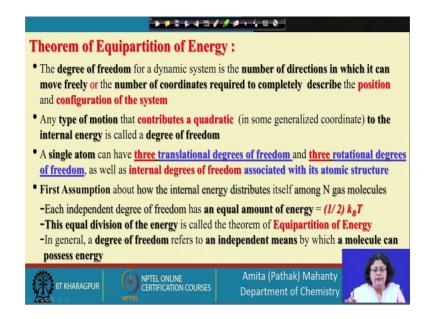
So, what is contributing? So, the attractive forces are contributing giving rise to a potential energy contribution, where you have the kinetic energy very small at low temperature. So, potential energy dominates and the potential energy is negative because of attractive forces between the two molecules and this is going to give rise to condensation or bond formation or bonded states. At high temperature what happens? At high temperature; obviously, the temperature is increased. So, the kinetic energy of the molecules will is going to increase.

So, the large kinetic energy what happens the internal energy increases becomes positive and in this case it has sufficient energy to bring a break up the bonds or the attractive forces between the molecules and they behave like a gas. So, this is what we are looking into when we have high temperature we have the kinetic energy contribution at the large.

So, you understand when we are talking about the translational kinetic energy we are talking about a molecule where only translational mode of mode is contributing to the total energy of the system, we are not talking about the intra or any intermolecular forces. What happens, when the potential energy of these two whatever you are having is attractive and the repulsive forces, the energies a potential energy becomes minimum. At

this point if you remember the potential energy curve it is a potential energy curve is like this something, you will have a minima here and this is the at the minima of the potential energy what you have the atom starts vibrating like a spring.

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So, this is what we are having in the background. Now, let us see what the degree of freedom means and what is actually the concept of equipartition of energy? The degree of freedom for a dynamic system is the number of directions in which it can move freely. The number of directions it can it is it is actually a spatial coordinate by which we can describe this configuration as well as the position of the system exactly, ok.

So, it is a number of coordinates we require to describe the position is what is important when we are talking about the degree of freedom. Am I clear? It is actually in that when we say the degree of freedom in this concept of when you have energy distributed in the degrees of in various forms we say in which form the energy is stored is another form of describing the degree of freedom.

Any type of motion that contributes to a quadratic in a general coordinate to the internal energy is called the degree of freedom, any type of motion. Any type of motion that contributes a quadratic you may understand it is a square it contributes a quadratic to a to the internal energy is called the degree of freedom. If I talk about a single molecule what I when I have a single molecule what are the forms of motions we can look into.

See we are looking into the degree of freedom is the number of directions in which it can move freely or it is the number of coordinates required to describe the position and the configuration of the system. So, I need to know the number of coordinates which is required to pinpoint the system which we are talking about its position and its configuration.

So, the single molecule; what are what are the motions it can undergo? It can undergo three translational degree means translation degrees of freedom. What does three translational degree of freedom mean? Translation means along x, y or z direction. So, it can the center of mass can move along the x, y or z. When the center of mass moves along with these three axis, we say that they are along the three vibrational modes.

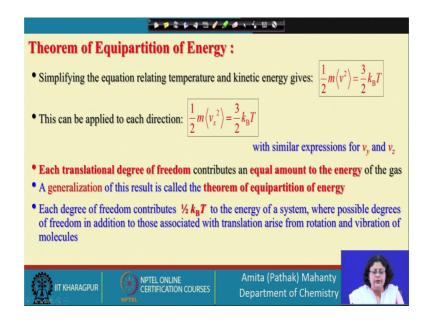
Similarly, it can rotate along axis that. So, along three axis we can have three rotational degrees of freedom and then we can have internal degrees of freedom associated with the atomic structure; that means, we can talk about the vibrational mode of energy. These for understanding this rotational and vibrational mode you need to understand the quantization of energy, that probably will not be part of the course, but understanding that energies are quantized and you have to have sufficient energy to go from one vibrational state to another is what is supposed to require higher energy, is what you need to understand.

So, first assumption; what we are going to look, how the internal energy distributes itself along the N molecules. Each independent degree of freedom has an equal amount of energy. So, each degree of freedom will have equal contribution and that contribution is half kT. This equal division of energy is called the theorem of equipartition of energy. So, for each independent each independent degree of freedom, we have talked about translation, we have talked about rotational, we have talked about other vibrational modes, but what we are talking about each independent degree of freedom has what is what is the contribution of energy has 1 by half kT.

So, in general a degree of freedom refers to an independent means by which a molecule can possess energy. So, it is a degree of freedom can also be referred to the independent means by which a molecule can possess energy. So, if why I say this independent mode independent means? Independent means of by which a molecule can possess energy

because I see that each of the modes I am associating with has 1 kT half half kT associated.

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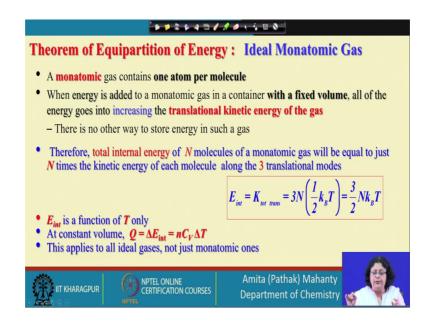


So, if I look into a simplified version of it then according to the kinetic theory of gases we had this is the expression of half mv square or we say this is the root mean square velocity. It can be represented by c or v square equal to 3 by 2 kT. So, this can be applied to each direction.

So, if I have x and y, z direction then that each translational degree of freedom contributes equal to the energy of the gas the generalized a statement of the equipartition of energy. What I have? I have three degrees of freedom three translational mode of mode. So, that is 3 and into what I have per degree of freedom I have half kT associated. So, the total energy which associated will be 3 by 2 kT.

So, each degree of freedom contributes half kT to the energy of the system which possible degrees of freedom in addition to the associated with translation arising from rotate. This is associated with only the translation additional may arise from rotational and vibrational modes of the molecule.

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So, if I take example of a mono atomic gas. Mono atomic gas means it has it has one molecule, right. When I add energy, how is it is going to rise we have said that how it is going to store the energy is the degree of freedom we need to know. How if I put some energy how it is going to store the energy. When energy is added to a mono atomic gas, suppose it is contained in a fixed volume, so, volume is fixed all the gas energy is goes to increase the translational kinetic energy of the system.

When you are having mono atomic gas; gas means we have talking about one molecule or one atom per molecule. So, what whatever energy you put it is going to go and increase this translational kinetic energy of the gas, right. So, now, you understand why we were always talking about the translation average translational kinetic energy when we were talking about the kinetic theory? There is no other way it can store the gas.

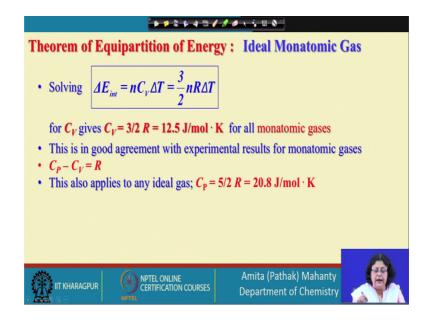
So, therefore, the total internal energy for N molecules of a mono atomic gas will be equal to just N times the kinetic energy associated with each of the molecule along the 3 translational modes and that will be 3 into half kT that is 3 by N k B T. This is the total number of molecules which we are associated.

So, what we can see the internal energy is equal to the total translation energy for a monoatomic gas and that is equal to proportional only to the temperature. And since it is a constant volume system, I can say the amount of heat which is absorbed is equal to the

change in the internal energy which is will be nothing, but nC v dT from the expression which we have. What is C v? C v is the specific mole molar specific heat.

So, molar specific heat, if we can justify for a constant volume the molar specific heat into the change in temperature to the into the total number of moles is the amount of energy or heat which is absorbed. This applies to all with ideal gases not just mono atomic gases.

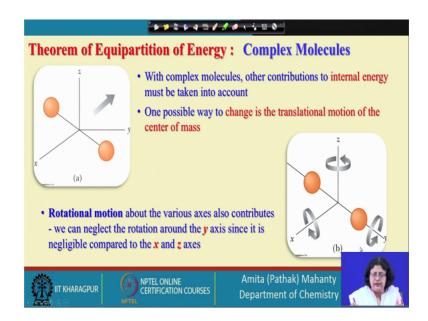
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Now, so, solving that C v equal to if we can write that in the what will the in a internal energy look like the expression of internal energy? You see, you put the expression of C v. C v gives you 3 by R, 3 by 2R. So, you can get what for this what you have is the internal energy change in terms of the per mole of the gas.

So, this is something which is which you can solve for if you know the degrees of freedom. This applies to all ideal gases. This is in this is what we have done through experimental observation whether the internal energy is actually see the C v is a response function. We can measure C v. So, if we can measure C v, and we know the value of the C v which is measured and then we can see what is the internal energy change experimentation has found out that we have a good agreement if we follow the kinetic theory of gases and the equipartition theorem.

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So, next we go into a complex molecule where a complex molecule means you have more than one atom associated with it. So, complex molecules with complex molecules, what happens there are internal energy will be contributed not only by translational energy, but also because of vibrational and rotational modes; The complex molecules the, sorry.

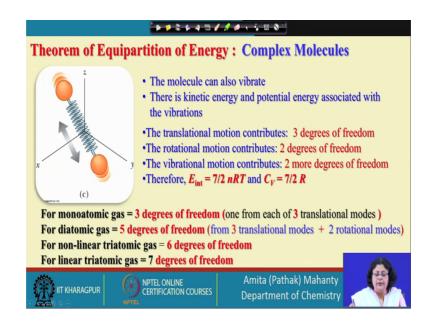
So, the complex molecule we have the contribution to internal energy by number of number of things. What are the contribution we can have? We can suppose, this is the complex molecule just we are talking about only to having two molecule atoms associated. What I can do, I can move this entire the center of mass from one point to the other. So, this is by changing the translation contribution through change in the translation motion of the center of mass. I remove this entirely and what else I can have? I can have the molecules rotating along the axis.

Suppose, I have this molecule along the y axis; Now, I rotate along x or along z, then you have some if the modes which is going to contribute to each of the movement along this x and z. Let us consider since the molecule is along the y axis the contribution in the rotation around this is minimum we say only two modes are contributing. See here when we are talking about translational mode, we can have the molecule moved if the center of mass moves through toward the x direction, towards the y direction, towards the z

directions. So, I get three modes from the movement of the center of mass along the translation mode.

Now, when I talk about the rotational mode if I have taken this molecule as a two molecule system and I am rotating along the if the molecule is along the z y axis then I can rotate it along x axis or according to z axis. These two contributions will be much more then along the y axis along which the molecule exist.

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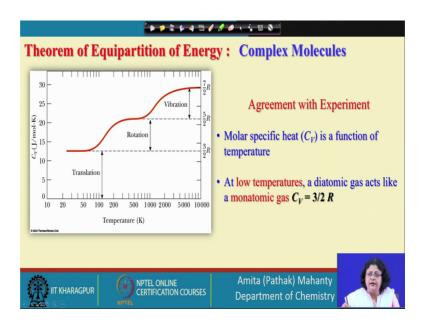
So, next we can think about. Next we can think about a vibration. Vibrational mode, what is this? When you are having the molecules which are vibrating along the axis the this vibration this kinetic energy and thus there is kinetic energy potential energy associated with the vibration. So, that what are the different different modes we have? We have the three transitional motions 3 degrees of freedom, two rotational mode because one we have taken along the molecule the axis y, z y is along the molecule. So, we have not taken the contribution neglected the contribution along that.

So, we have 2 degrees of freedom along for rotation and we have vibrational contribution that is going to be two vibrational degrees of freedom associated with the molecule. So, if I have a mono atomic molecule, then the total number of molecules are degree of freedom I know is 3 only for the when the center of mass is moved along the translational mode x, y, z, 3 modes, when I have a diatomic molecule the degree of freedom is 3, 3 for translation right center of mass of the molecule be moving x, y, z and

z direction plus 2 along the root x axis along which it is rotated, taking the molecule to lie in one particular axis. Suppose, it is y and we have taken x and z as the rotation along which we are looking into.

So, similarly non-linear and tri linear molecules will have different degrees of freedom which we can calculate knowing the contributions of each.

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So, now we need to verify whether a system which we are doing finding out the energy at associated with the internal energy associated with the molecule. Whether which is which we have equated that to the system is proportional to the C v of the system that is the molar specific heat at constant volume. Since this being a response function we can measure that.

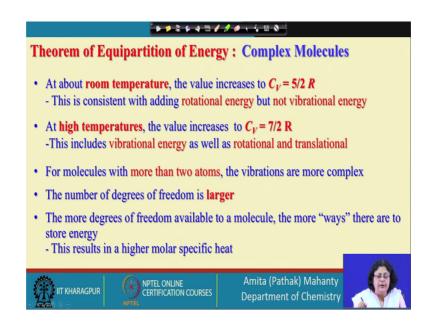
So, if I if we measure that we it is found that whatever we have found for the monatomic or diatomic gases is more or less agreeable to whatever we find using the kinetic theory of gases or equipartition theorem and at low temperature we have you can see that the diatomic molecule acts or behaves like a monatomic gas and it is C v is equal to 3 by 2R.

So, you can see how the C v is varying in terms of the value of R a whether it is 3 by 2R, 5 by 2R, 7 by 2R. 7 by 2 R means obviously the vibrational contribution is there, 5 by 2R means rotational to rotational contributions and translational modes are there and here means only translation three translation motion modes are contribution contributing. So,

you can see when you have a translation only 3 modes are active when you are having rotation we have 5 and when you have vibrational you have 7 by 7 modes which is active.

So, this is what we have which is experimentally seen how C v changes with temperature and with you see if the temperature scale it is around 100 that you see this transition. When a molecule is at 1000 degree centigrade you will see the rotational contribution and when it is more than 10000 the degree Kelvin then you will see the contribution of the vibrational mode.

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So, if I if we can summarize at room temperature the increase the value of when you increases to C v equal to 3 by 2. This is consistent with the addition of adding rotational energy, but not vibrational. At high temperatures the value increases C C v equal to 7 by 2 that is in the contribution is here we include the vibrational energy as well as the rotational and translational.

For molecules with more than two atoms, the vibrations are more complex. Number of degrees of freedom if the number of degrees of freedom is larger the number of degrees of freedom available for a molecule, the ways which they can store the energy this results in higher values of molar specific heat. Did you understand what I said?

The more degrees of freedom available for a molecule the more number of ways we can have the energy stored; that means, that will give a higher value of C v because C v is nothing, but q equal to nC v dt. So, C v is a direct amount a proportional to the amount of heat which is absorbed. So, we can have this increase in energy associated with the increase in the specific heat.

So, summarizing this the equipartition theorem we will talk about the various distribution of energy and distribution of speed of molecules in the next class.

Thank you.