Thermal Physics
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Lecture –4
Principle of Equipartition of energy

Hello and welcome back. So, for today's lecture we will be discussing degrees of freedom of a gas molecule. Now what is degree of freedom? We know that there is I mean if you have already studied classical mechanics you have already learned one definition of degree of freedom that is number of independent coordinate that describes the movement or motion of a body motion of an object. So, for example if this is a rigid body something like this we have a rigid body in hand we know that from classical mechanics that this rigid body has six degrees of freedom 3 of them are translational 3 of them are rotational and that is it, if it is a rigid body.

Now there are several other examples will take some other examples of that and if there are six degree of freedom degree of freedom associated with this rigid body we need to have six coordinates that will be describing this motion completely or if for example if we fix one point in this body so in space. So, that is the body is not moving. So, that that particular point is not moving that essentially means we are freezing the translational motion of this body.

So, that means we take away 3 translational degrees of freedom from this party and what is left are only the rotational degrees of freedom. So, in that case we need 3 coordinates in order to you know describe the motion of this body and we know that from our classical mechanics lectures that this tree could be for example 3 Euler's angels but the member that is not the question here. Question here is there any other alternative definition available for degrees of freedom.

And it turns out that there is a thermodynamic degrees of freedom and thermodynamic definition of degrees of freedom that talks about the total number of quadratic terms in the energy expression of system. it is a bit confusing I know but and you will see I will show you very soon I will show you some examples in which you will know that these 2 definitions are to some extent they go hand in hand one can respond to other okay. So, let us take the example yeah.

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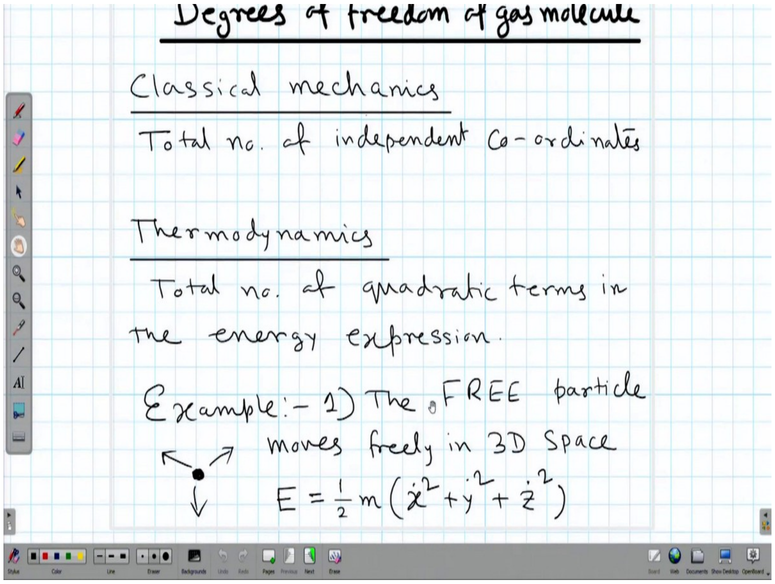

Degrees of freedom of gas molecule

Classical mechanics

Total no. of independent co-ordinates

Thermodynamics

Total no. of quadratic terms in the energy expression.

Example:- 1) The FREE particle moves freely in 3D Space

$$E = \frac{1}{2}m\left(\dot{x}^2+\dot{y}^2+\dot{z}^2\right)$$

So, let us look at it. So, what is there? First of all there is a total classical mechanics the definition is the total number of independent coordinates and is the total number of coordinative terms in the energy expressions. And first let us take the simplest possible example of a free particle. Now a free particle is only a point mass. So, that means there is no rotation associated with it and it can travel anywhere in the 3D space we know that.

Now in 3D and in order to describe the motion of a free particle how many degrees of freedom do we need? We need 3 degrees of freedom. So, that means 3 independent coordinates that will describe the motion of rigid body completely. So, basically what I mean to say is any motion can be decoupled into 3 directions 3 independent along 3 coordinate axis which are typically taken as x y and z coordinate mutually particular to each other and that is it this is very familiar to us.

So, that is a classical mechanics definition. So, according to classical mechanics degree of freedom of a free particle is 3. Now the dynamic definition what is the quadratic term in energy expression? If we write out the energy expression for free particle this will be I will look at this it will be E is equal to half m x dot squared plus y dot squared plus z dot squared right. Actually I should write E T here because this is purely the translational degree and translational energy.

And now let us examine this expression how many quadratic terms are there? Quadratic means a square term how many quadratic terms 1, 2 and 3. So, basically it is half m extra square plus half m y dot squared plus half m z dot square and we cannot reduce it further we cannot reduce it to 2 quadratic terms or one quadratic term 3 has to be there. So, that is why the thermodynamic definition also matches gives you the total number of degrees of freedom as 3.

So, there is absolutely no conflict between the classical mechanics degree of definition and the thermometric definition of degree of it.

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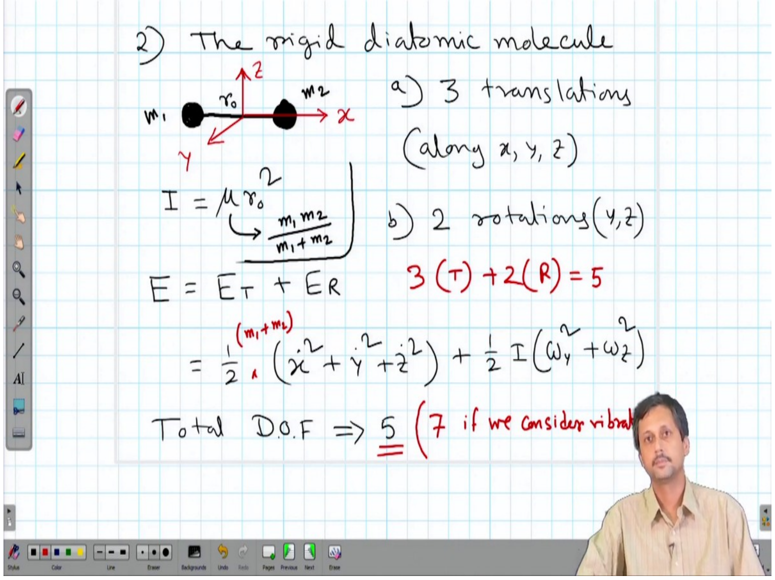

2) The rigid diatomic molecule

a) 3 translations (along x, y, z)

$I = \mu r_0^2$, $\mu \hookrightarrow \frac{m_1 m_2}{m_1+m_2}$

b) 2 rotations (y, z)

$3(T) + 2(R) = 5$

$E = E_T + E_R$

$= \frac{1}{2}(m_1+m_2)(\dot{x}^2+\dot{y}^2+\dot{z}^2) + \frac{1}{2}I(\omega_y^2+\omega_z^2)$

Total D.O.F $\Rightarrow \underline{\underline{5}}$ (7 if we consider vibrat

Second example so for a free particle total D O F is 3. Second of example is when we have a rigid diatomic molecule in hands. So, this is our molecule we have let us say 2 masses m 1 and m 2 connected by some bonding and when we say rigid that means the bond length is not changing it is not vibrating. So, we take the bond length and as I 0 and we write I the moment of inertia I capital I is equal to mu r 0 squared why it is important will know mu is the reduced mass by the way mu is nothing but m 1 m 2 m 1 plus m.

I think you are all familiar with this right. Now how many motions are possible in this body? We can have 3 translation okay we just define an access system where the x axis goes along the molecular axis we have the y axis here and we have the z axis here. So, we can have 3 translation one is along x one is along y one is along that independent of each other of course and so that means what I mean to say is any translation can be decomposed into 3 components in a Cartesian system and there could be rotation.

Now how many rotations there could be rotation about z axis for example it can rotate like this in this I mean in particular to z axis or it can rotate particular to y axis let us say y axis is coming out of the of the surface of this I mean out of this surface and the rotation will be in plan of this paper okay but what about the exportation because it is a molecule we considered that the masses are point masses and the bond is I mean so because these are point masses the rotation about its own axis is not considered.

Because the degree of the moment of inertia will be negligibly small about its own axis the expression for moment to finish your whatever I have written here is for the rotation around the axis perpendicular to the molecular axis. So, that means why no once again. So, according to the classical definition there are 3 translational degrees of freedom and 2 rotational degree of freedom total number of degree of freedom is 3 plus 2 total number of degrees of freedoms are 3 translation plus 2 rotation is equal to 5 good.

Now let us write the energy once again the energy will have 2 components one is the translational kinetic energy and one is the rotational kinetic energy. Please remember there is no potential energy because we are considering these particles are freeing space. So, there is gravitational attraction is neglected although it is present. So, it is just E T plus E R, E T once again will be half. So, sorry it should be it should be mu right it has to be replaced by mu or something else effective mass is for rotation.

I think it should be simply a 1 plus empty I will check and if it is not then I will let you know in the next class. It will be simply a 1 plus m 2 that is the total mass m for translation but for rotation it will be half i omega y squared plus omega z squared where the rotation speed are about y axis and the z axis is given by omega y and omega said. Now once again how many quadratic terms 1, 2, 3 here and 1, 2 here so all together total number of degrees of freedom once again is 5.

So, at even for this case the classical mechanics definition and the thermodymamic definition they tell you.

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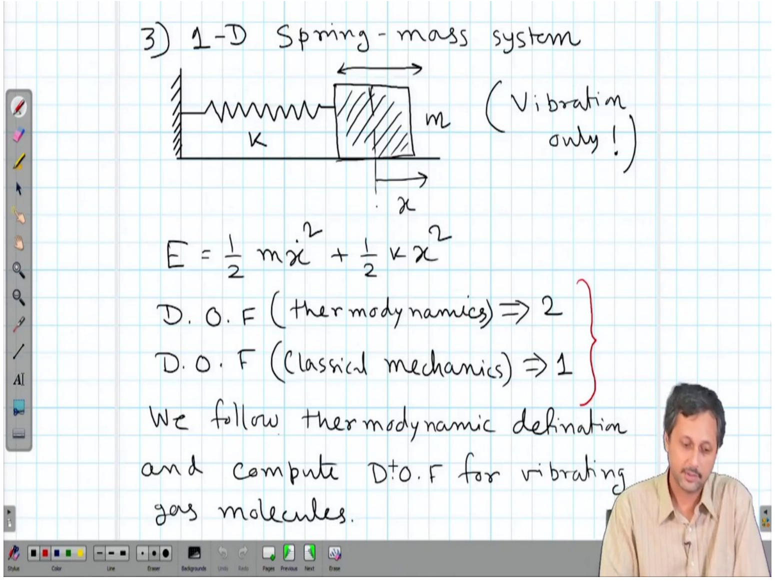

3) 1-D Spring-mass system

(Vibration only!)

$E = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} k x^2$

D.O.F (thermodynamics) ⇒ 2

D.O.F (Classical mechanics) ⇒ 1

We follow thermodynamic defination and compute D.O.F for vibrating gas molecules.

Now let us take another very simple example of a one dimensional spring system. We all know this right we have all studied this is in our school days starting from our school days the simple harmonic oscillator k is the spring constant m is the mass and there is only one motion possible there is no translation no rotation one d that is constrained to move on one plane only and the only motion possible is a vibration.

Now according to the classical mechanics definition of if we just considered the number of independent coordinates x is sufficient where x is the displacement from this equilibrium position. Let us say this is my equilibrium position it can go like this or like this actually x could be from in this side or in this side both ways x can go we need only one degree of freedom or one independent coordinate in order to determine the motion right. Once we write the energy expression things changes look at the energy expression.

So, energy here is the vibrational energy only. So, we call it the E v this is half m extraordinary squared plus half k x x squared okay. So, there are 2 degrees of freedom whereas according to classical mechanics there is only one degree of freedom. Now there is a conflict. So, we follow the thermodynamic definition and compute the degree of freedom of vibrating gas molecule. Now let us go back here go back to before this system once again if we consider vibrational degree of freedom present that means a molecule that can vibrate along this axis please remember it is a 2 dimensional molecule.

So, vibrational vibration is possible only along the bond axis. Once again this although it is a 2 body problem it can be effectively reduced to a simple one, one body problem and we can write an effect I mean we can define a you know system which is which has an equivalent spin constant and a single mass is moving. So, we have to have one vibrational independent coordinate for vibration okay.

So, because in you know we do not have that much time we are not going into the details of this independent coordinates and all but I think you all understand that you know if this dynamic molecule vibrates we need to have one coordinate one coordinate I am not talking about degree of freedom 1 coordinate in order to describe the motion okay. So, now if I go back here at present we have 3 translation and sorry 3 translation and 2 rotations as we have already described it.

Moment to introduce vibration in a diatomic molecule system how many more degrees of freedom do we need? We need 2 more degrees of freedom because each vibrational normal mode as we call it contributes to 2 degrees of freedom. So, we have 5 and it will be 7 if we consider vibration, okay. So, please keep this in mind moment you have one vibration you need to have 2 degrees of freedom added to the total numbers because if you add one it will be a mistake right.

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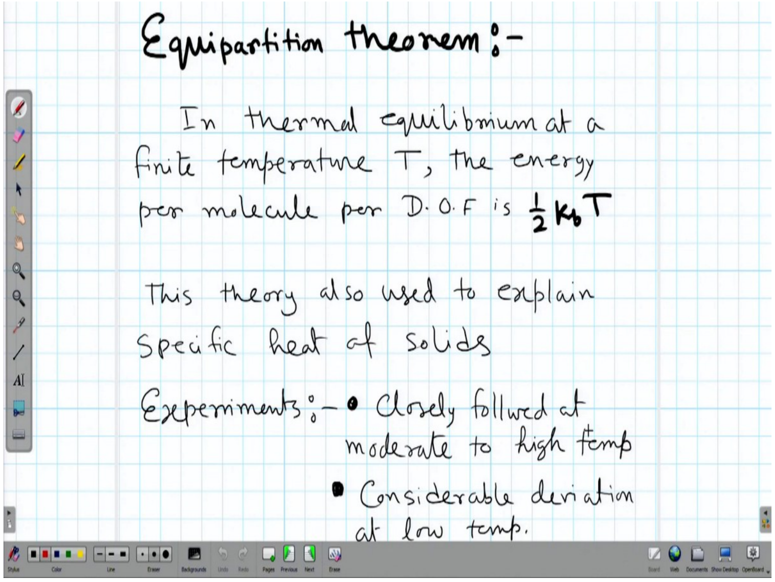

Equipartition theorem:-

In thermal equilibrium at a finite temperature T, the energy per molecule per D.O.F is $\frac{1}{2}K_bT$

This theory also used to explain specific heat of solids

Experiments:-
- Closely follwed at moderate to high temp
- Considerable deviation at low temp.

So,. Now let us first of all why are you discussing this? I mean in our case the gas molecules they just translate I mean we do not consider the vibration at all in the kinetic theory. But it turns out that vibration is also important because there is something called the equipartition theorem that says internal equilibrium at a at a finite temperature T the energy per molecule part degree of freedom is half k B T.

This theory also used to explain specific heat of solids which will be discussed later on. So, this is the you know what you call the theory that gives us I am very you know very elegant not very elegant but very straightforward and simple tool to calculate or estimate the total energy of a gas assembly by using simply by using equipartition theorem and from there we can compute the heat capacity of a gas assembly.

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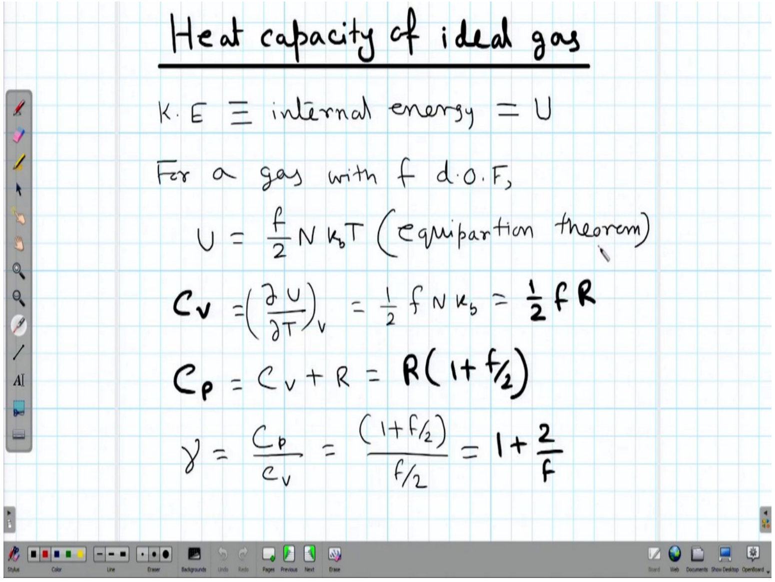

Heat capacity of ideal gas

K.E $\equiv$ internal energy $= U$

For a gas with f d.o.F,

$$U = \frac{f}{2} N k_b T \text{ (equipartition theorem)}$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{1}{2} f N k_b = \frac{1}{2} f R$$

$$C_p = C_v + R = R(1 + f/2)$$

$$\gamma = \frac{C_p}{C_v} = \frac{(1+f/2)}{f/2} = 1 + \frac{2}{f}$$

So, how do we calculate that? The total energy is all kinetic energy which is equivalent to the internal energy of the system because that is the only source of energy we have. So, internal energy of an ideal gas assembly is the kinetic energy or rather I should say internal energy that is usable in a thermal dynamic force process. Of course you all know that formula of E equal to m 0 six square by that is that is the most famous formula by Einstein but that is the rest mass energy that is only present everywhere but in thermodynamic processes the only energy we are worried about is the kinetic energy for a guess or the internal energy.

Now for a gas assembly ideal gas assembly internal energy if you want to kinetic energy right. So, if we have a gas assemblies with F degrees of freedom okay. I just write this in bold. So, that you understand sorry if degrees of freedom then U is equal to F by 2 N k B T where N is the total number of molecules because each degree of freedom will contribute half k B T total number of molecule total number of degree of freedom is f.

So, we multiplied by f and we multiply the total number with n which is the total number in gas and. So, whether I would just break it just for your convenience it will be half k b T times if times. So, 3 terms 4 3 this one three contributions. So, C v is equal to del U del T V which will be equal to half f N k b T which is half f R because we all know that N k B T is equal to R that was discussed in the very first lecture similarly C p which is C V plus R once again for ideal gas only because this relation is valid only for ideal gas and later we will see that C p minus C V is not equal to R for a non ideal gas but for ideal gas we can we just add r to this expression and we can write cp is equal to r times 1 plus set by 2 then what is the value of gamma which is C p by C V which is also very important constant for gases and we will see more and more why this come is useful to us and the ratio is 1 plus 2 by f okay.

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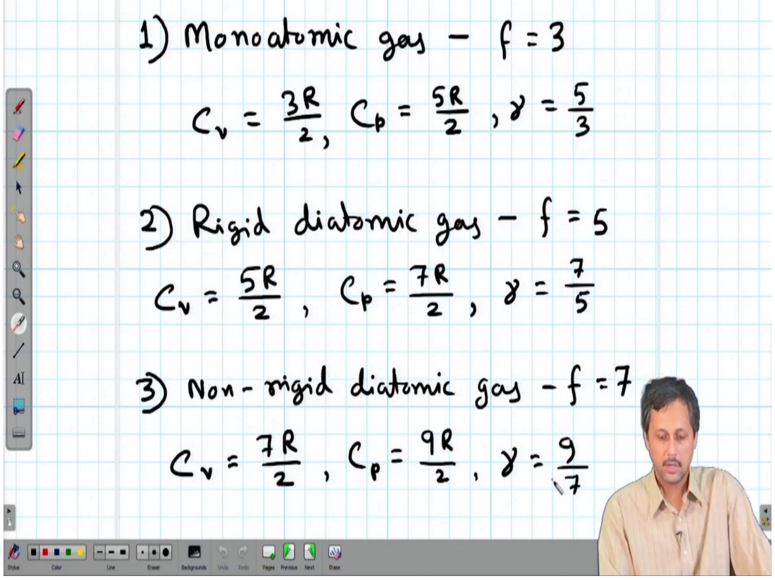

1) Monoatomic gas − $f = 3$

$C_v = \frac{3R}{2}$, $C_p = \frac{5R}{2}$, $\gamma = \frac{5}{3}$

2) Rigid diatomic gas − $f = 5$

$C_v = \frac{5R}{2}$, $C_p = \frac{7R}{2}$, $\gamma = \frac{7}{5}$

3) Non-rigid diatomic gas − $f = 7$

$C_v = \frac{7R}{2}$, $C_p = \frac{9R}{2}$, $\gamma = \frac{9}{7}$

So, we take 3 examples quick examples one is the monotonic gas where we have f equal to 3 we have C V is equal to 3R by 2 C p is equal to 5R by 2 and gamma equal to 5 by 3. Rigid diatomic gas when we do not consider vibration then f is equal to 5 only we have c v is equal to 5 R by 2 C p is equal to 7R by 2 gamma is equal to 7 by 5 and non rigid diatomic gas f is equal 7 we have discussed that because once we have vibration we add 2 degrees of freedom with the existing ones for each vibrational mode we had 2 degrees of freedom with the existing one.

So, for diatomic gas if it is 5 then diatomic vibrating guess it will be 7. So, we have C v equal to 7R by 2 C p equal to 9R by 2 gamma equal to 9 by 7 okay. So, quickly look at but then all this looks very nice but does tally experiment with the experimental results that is very important because as I have already said probably in the first class itself if not then let me tell it say this now if and only if the observed experimental results are at par with the theory only then the theory is correct otherwise the theory has some problems okay.

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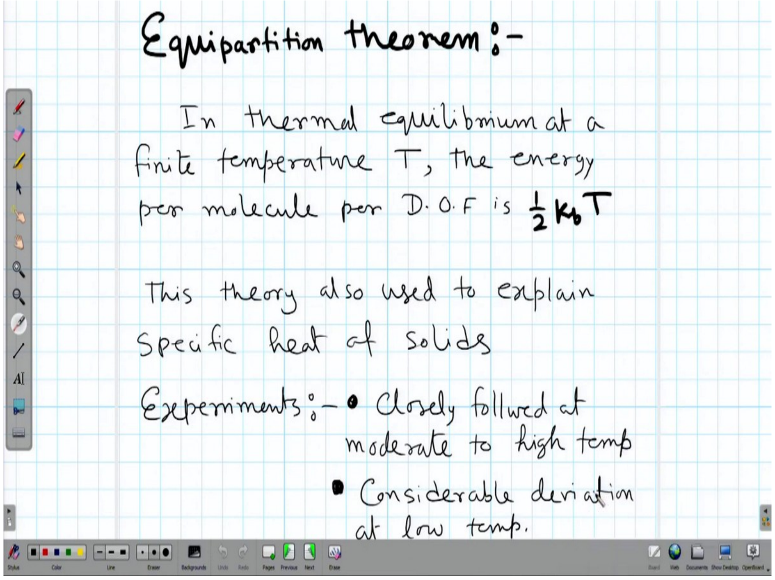

Equipartition theorem:-

In thermal equilibrium at a finite temperature T, the energy per molecule per D.O.F is $\frac{1}{2}k_bT$

This theory also used to explain specific heat of solids

Experiments:-
- Closely follwed at moderate to high temp
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So, what happens is experimentally we can we see that for gas molecules at a moderate to high temperature the equipartition theorem is more or less closely followed. But sometimes there are considerable deviations at low temperature especially when we try to explain the specific heat of solids using the same theory. We will not discuss that at present but we will keep it for future when we will be before going into the classical thermodynamics we will have a quick discussion on the specific capacities of solid.

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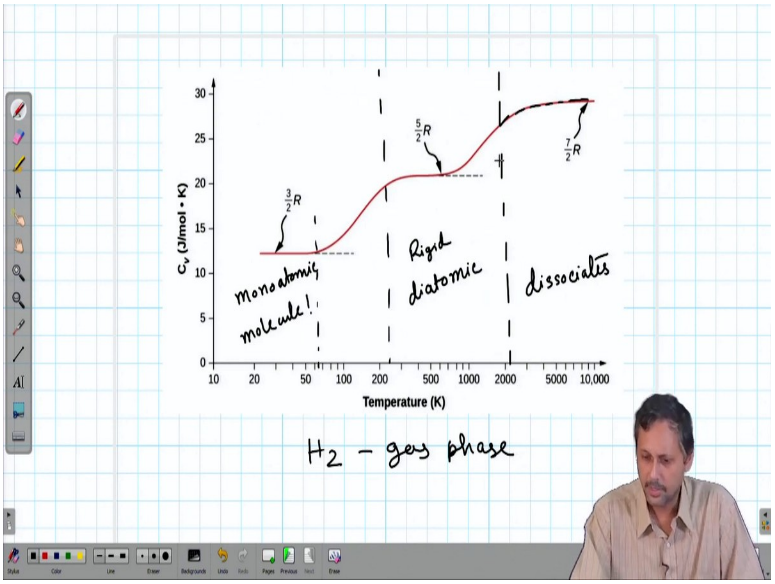

H_2 - gas phase

But and we will just end this lecture by showing you. Now we I will show you data on hydrogen molecule. Now this is the data for hydrogen molecule. So, this is H 2 gas phase. Now the plot shows temperature versus C V for h 2 in gas phase. Now first of all let me tell you that the last part of the plot is kind of hypothetical in nature because what happens is around this temperature the molecule dissociates.

Look at the temperature scale it is around 2000 Kelvin. Now 2000 Kelvin is high enough temperatures. So, that the molecule does not stay in this H 2 form anymore it becomes it separates into 2 H atoms. But anyway the actual experimentally measured trend is found up till this point and after that this is more of a extension hypothetical. But what is important here is hydrogen is a diatomic molecule.

Now for a diatomic molecule we have we should have for the rigid dynamic molecule we should have a C V value of 5 by 2R just now we have seen that from here. So, it should be 5 by 2R and we are getting 5 by 2R somewhere between let us say 300 Kelvin to all the way to 500 or 600 Kelvin in this range which is absolutely fine. So, in this case in this in this temperature region it is like a rigid diatomic.

Now what happens is below 200 degree centigrade's 200 degree Kelvin 200 Kelvin the C V value starts changing downwards and at very low temperatures roughly around 50 Kelvin or below it levels off to 3 half R. Now what is 3 half R? Let us go back. So, 3 half R is that is for the monotonic gas. Now hydrogen we know that it is a diatomic gas but why then we are getting 3 half R in this region.

The reason being at very low temperature even in gas phase please remember that in order to maintain this gas phase at a very low temperature we have to have very low pressure inside this time chamber. But whatever maybe the experimental set up we are not going into the details of that but at very low temperature let us say below 50 Kelvin or so the molecule does not have enough energy to execute the rotation.

So, only movement that is possible is the translation. Now why it is not possible to execute the rotation in order to do that we are understand that we have to go into the details of quantum mechanics details of vibrational and rotational spectrum we are not a details of rotational spectrum we are not going into that. But let me tell you that the rotational levels are frozen because even the thermal energy is not sufficient for the second rotational energy level to attend.

So, we will come back to that in the next lecture in some more details what is thermal energy and why it is important of course we have some idea by now but we will go into the details of that. So, here in this region this behaves like a mono atomic gas mono atomic molecule. Although we know that the molecule is diatomic in nature but because of the very low available thermal energy we have a monoatomic behavior in this region. As the temperature increases the motion starts unfreezing.

So, that means the rotational motion is slowly and slowly possible and around 200 degrees or slightly above 200 degrees it starts behaving like a proper rigid diatomic molecule but again even at this temperature the vibrational modes are not active. So, the thermal energy available thermal energy is not sufficient for the vibrational modes to be activated once again we will go into the details of that in the next lecture.

And for the last part and then what happens is around this temperature around 600, 700 degrees centigrade's it starts getting enough thermal energy 700 typical 700 kelvin it starts getting enough thermal energy. So, that the vibrational modes are getting activated and eventually around before up I mean up to the dissociation temperature of approximately 2000 Kelvin we start seeing an upward trend.

Now hypothetically if we extend the experimental data we finally get the 7 by 2R value which is the specific heat or C v for a vibrating diatomic molecule ok. So, this is what the molecular hydrogen looks like.

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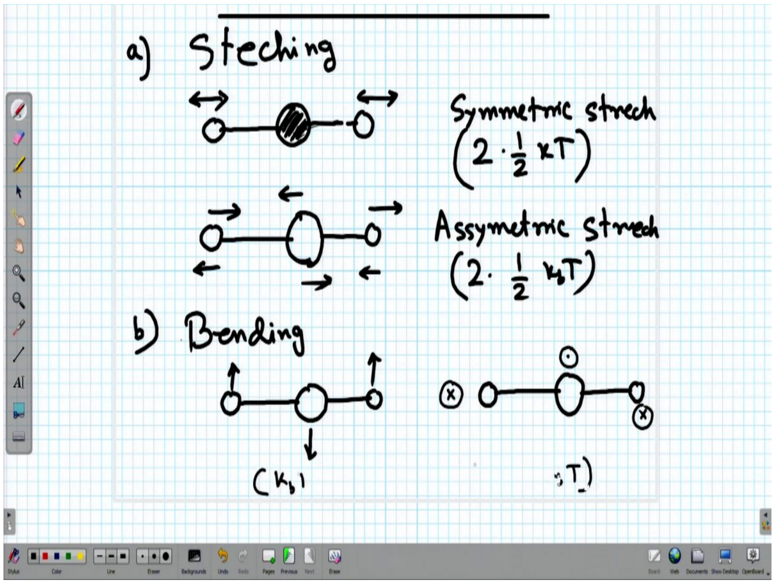

Last we will talk about triatomic molecule which is slightly complicated in nature, just a minute. Now what is triatomic molecule? Triatomic molecule could be a linear molecule could be a linear molecule. So, we have 2 broad classes of that one is the linearly where we have a molecule of this form okay it can have 2 types of vibration if the molecule stays linear all throughout it can have 2 types of vibration.

One is called the symmetry stretch and the other one is called the asymmetry stretch. In symmetric stretch the central molecule stationery and we can have these 2 molecules going in or out in asymmetric stretch we can have this molecule and this atom and this atom going in this direction whereas the central atom is going in that direction. And in the next cycle this one will go into that direction whereas this one's will be coming into that direction.

And overall the C V that is the c m that is the center of mass of the molecule stays stationary. So, this is called the symmetric stretch and the antisymmetric stretch of a linear molecule triatomic molecule. Now there are 2 normal modes and this will contribute to 2 into half kT of energy and this will contribute to 2 into half kT of energy. So, altogether there will be kT plus kT 2 kT of energy. And in case of not only near molecule for example water, water is non linear molecule we have H we have O and we have H.

Let us take the example of water we have oxygen hydrogen and hydrogen motion can be really

really complicated. If it is a linear triatomic molecule which is actually I should say that we can have let us consider the triatomic linear tragic molecule also let us call it stretching and in case we have bending okay. So, for the linear atomic molecule also we can have bending for example carbon dioxide we will take up an example where we can have 2 bending modes in which in one this one goes up this one goes up this one comes down okay.

And in the other one this one goes into the plane. So, we just marked with negative sign or rather cross sign and this one comes out we market with a dot sign. So basically these 2 more search degenerate. So, they basically they basically mean the same thing but they are degenerate in nature. So, that is why in one case the bending is taking place in the plane of the paper and in other case the bending is taking place in the plane part particular to the in a plane part of the plane of this paper.

So, these 2 are the 2 bending modes which are degenerate exactly the similar exactly similar but takes place can take place simultaneously. So, each of these will contribute to 2 into half kT that is kT of energy all together we can have once again 2kT or I should say this one contributes k b T of energy this one contributes k b T of energy. So, altogether we have 2 k b T of energy for the bending for the linear triatomic molecule.

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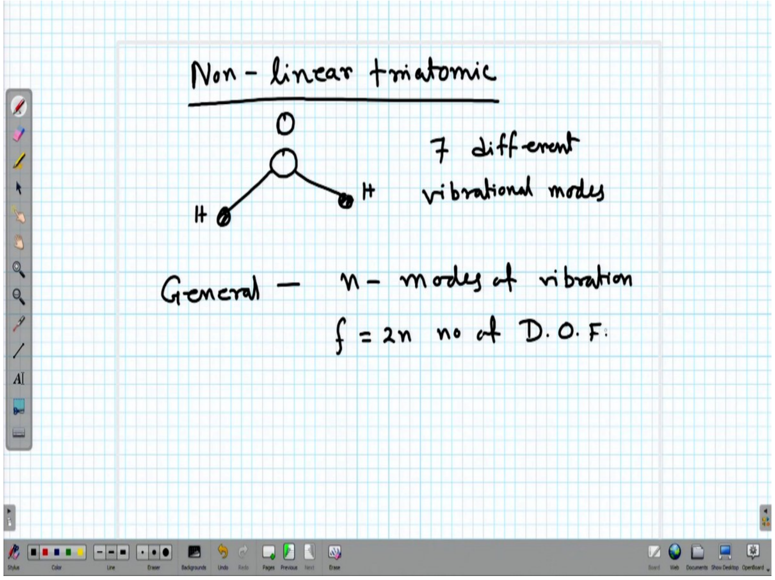

Non - linear triatomic

7 different vibrational modes

General — n - modes of vibration

$f = 2n$ no of D.O.F.

Now, for the nonlinear triatomic molecule it is even more complicated, non linear triatomic okay. For nonlinear triatomic molecule we can have many different types of stretching and bending possible we are not going into this at this point for water example for example as far as I remember I can be wrong there are at least 7 different vibrational modes. So, it becomes very complicated up to diatomic molecule it is straightforward diatomic molecule we have either only one type of vibration that will give rise to 2 k T.

Of course rather half in half into 2 kT that means kT of total of k T times the number of molecule amount of energy but in case of linear triatomic molecule we have once again if we have only stretching vibration there are 2 if we have bending vibration there 2 up to this it is still manageable but when it comes to non-linear triatomic molecules it depends on what type of molecule we have and how many bending modes are vibrational modes are possible it could be stretching bending and many other movements. So, it becomes very complicated.

So, in general, the general treatment is if we know that there are F degrees of freedom associated with vibration of a molecule or rather if I should say n modes of vibration then we have f is equal to 2n number of degrees of freedom please remember one vibration, one vibrational mode will contribute to 2 degrees of freedom. So, it becomes very complicated unless and until we know exact number of normal modes associated with this vibration we cannot deal with a complicated molecule okay.

So, that is where we stop today and in the next class we will be starting with the concept of temperature and energy scale okay, thank you.