Introduction to Molecular Thermodynamics
Prof. Srabani Taraphder
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 30
Statistical Thermodynamics of Diatomic Ideal Gases

Welcome. So, today we are going to discuss the application of the principles of statistical thermodynamics or molecular thermodynamics to a diatomic ideal gas, starting from the canonical partition function..

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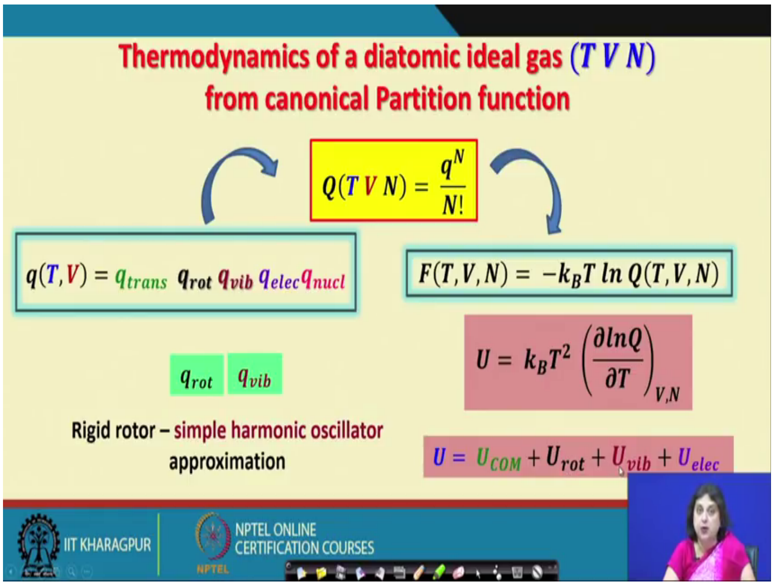

Thermodynamics of a diatomic ideal gas ($T\ V\ N$)
from canonical Partition function

$$Q(T\ V\ N) = \frac{q^N}{N!}$$

$$q(T,V) = q_{trans}\ q_{rot}\ q_{vib}\ q_{elec} q_{nucl}$$

$$F(T,V,N) = -k_BT \ln Q(T,V,N)$$

$$U = k_BT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$$

q_{rot} q_{vib}

Rigid rotor – simple harmonic oscillator approximation

$$U = U_{COM} + U_{rot} + U_{vib} + U_{elec}$$

We have already seen that if I have a diatomic ideal gas maintained at a given temperature, volume and there are capital n molecules present in the system. Then the canonical partition function can be expressed in terms of the single particle partition function like this and then in order to calculate capital Q we need to model a small q and we have discussed at length, how to use the rigid rotor simple a harmonic oscillator approximation to estimate this small q; and once you know how to estimate small q for a given value of temperature volume and number of particles one can go ahead and calculate capital Q, and from there using the bridging relationship in the canonical ensemble we can directly obtain the Helmholtz free energy and of course, when you know one thermodynamic property then you can derive all other thermodynamic properties such as by knowing lnQ, I can find out what capital Q is and then analyze the different contributions coming to this overall value of this internal energy from the motion of the center of mass of the molecule or the rotational motion of the molecule or the vibrations of the chemical bond connecting the 2 nuclei in the nucleus; and also the electronic energy of the molecule constituting the diatomic ideal gas.

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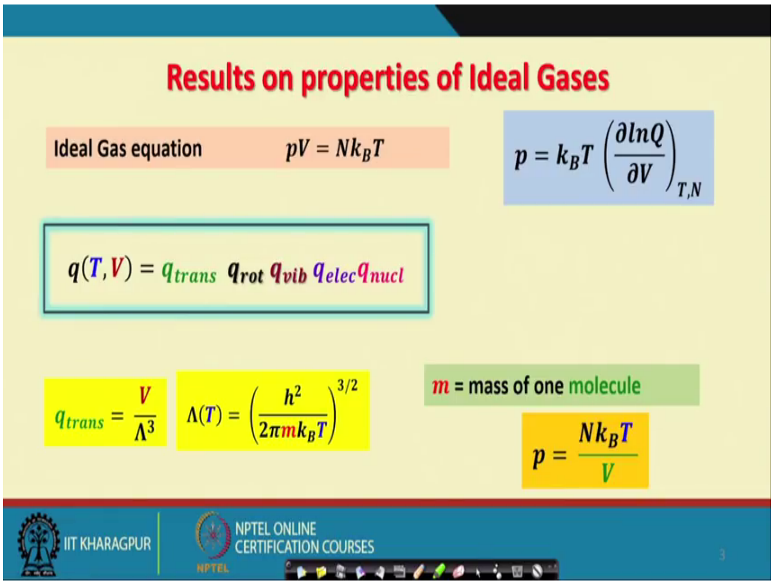

Results on properties of Ideal Gases

Ideal Gas equation $pV = Nk_BT$

$$p = k_BT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

$$q(T,V) = q_{trans}\, q_{rot}\, q_{vib}\, q_{elec} q_{nucl}$$

$$q_{trans} = \frac{V}{\Lambda^3}$$

$$\Lambda(T) = \left(\frac{h^2}{2\pi m k_BT}\right)^{3/2}$$

m = mass of one molecule

$$p = \frac{Nk_BT}{V}$$

Now, we have already seen how to obtain the ideal gas equation for any such system, where basically by knowing small q and knowing capital Q hence we can find out the pressure as the volume derivative with respect to constant temperature and the number of particles of the quantity lnQ and therefore, it is very easy to see that that explicitly volume dependent term in capital Q arises through q trans and in the diatomic case this small m that appears in q trans that is a mass of one molecule and explicit dependence on V comes through this factor and therefore, if you estimate p using the well-known relation between p and the derivative of lnQ you get back the ideal gas equation .

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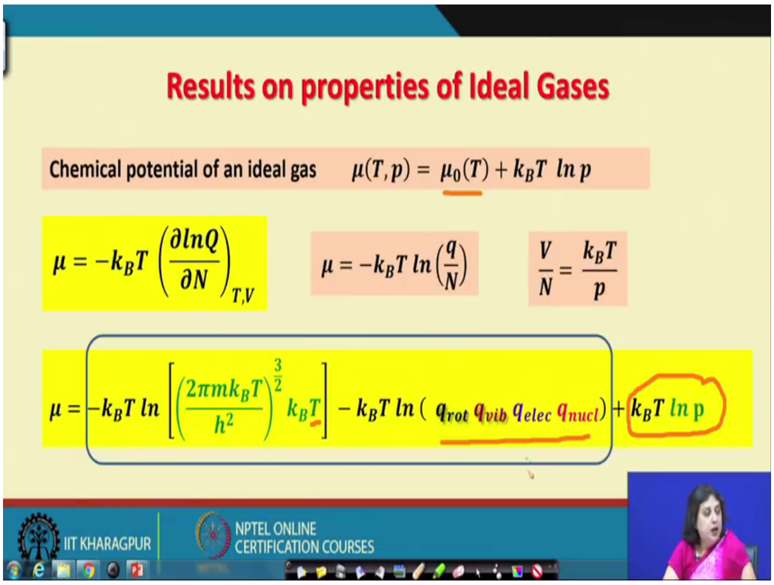

Results on properties of Ideal Gases

Chemical potential of an ideal gas $\mu(T,p) = \underline{\mu_0(T)} + k_BT\ \ln p$

$$\mu = -k_BT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}$$

$$\mu = -k_BT\ \ln\left(\frac{q}{N}\right)$$

$$\frac{V}{N} = \frac{k_BT}{p}$$

$$\mu = \boxed{-k_BT\ \ln\left[\left(\frac{2\pi m k_BT}{h^2}\right)^{\frac{3}{2}} k_BT\right] - k_BT\ \ln(\underline{q_{rot}\, q_{vib}\, q_{elec}\, q_{nucl}})} + k_BT\ \ln p$$

We have also discussed in the last lecture how to establish the variation of chemical potential as a function of temperature and pressure for an ideal gas so; obviously, we do expect that irrespective of whether I have a monatomic ideal gas or a diatomic ideal gas, this kind of form should hold . Now if I look at what mu is by definition mu can be obtained from lnQ by taking a derivative with respect to the number of particles under the condition of constant temperature and constant volume..

Now following the steps that we have used in the previous lecture, it is possible to show now; that we are capable of writing down the explicit expression for mu , which involves contribution from the translational term ; which also involves the other degrees of freedom which contribute in terms of q rot q vib q electronic and q nuclear and therefore, we can say that well we now identify here at pressure p naught equal to 1 bar, one term that appears that is dependent on the nature of the gas; that you have and the only thermodynamic parameter that appears is temperature ok. And therefore, the dependence on pressure comes through this particular term just as in the case of the monoatomic ideal gas and therefore, the source is once again yes, the translational motion of the molecule on the whole in the overall volume capital V.

Now, once we understand this therefore, even for the chemical potential we understand that if these terms are important , if they have some significant values then the value of mu naught T which is represented here in this box is going to have signature of the underlying microscopic structure of the diatomic molecule ok. So, in the next part what we do is we will now go ahead and try to look at the calculation of q vibration, because in the case of diatomic molecules; this is the first factor where the diatomic molecules is are going to be different from the monatomic cases. Now we have already discussed what happens if there is a harmonic potential describing the stretching and compression of the chemical bond connecting the 2 atoms in our diatomic molecule..

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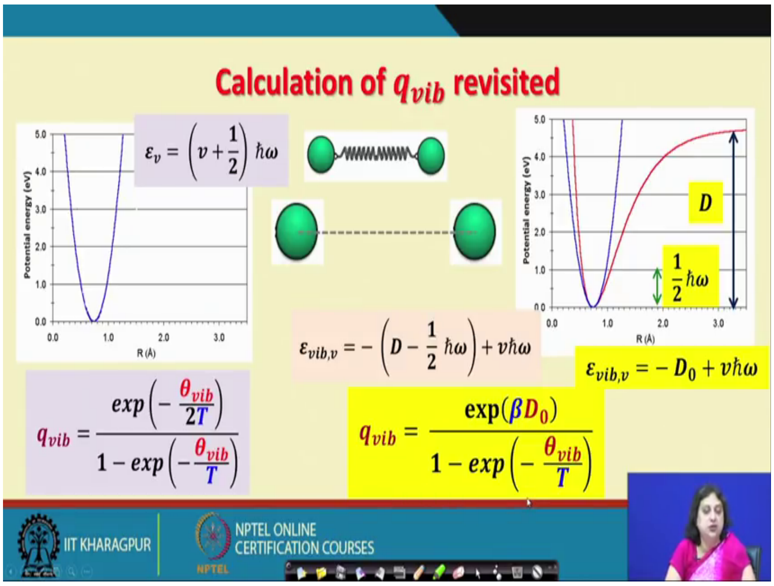

Calculation of q_{vib} revisited

$$\varepsilon_v = \left(v + \frac{1}{2}\right)\hbar\omega$$

$$\varepsilon_{vib,v} = -\left(D - \frac{1}{2}\hbar\omega\right) + v\hbar\omega$$

$$\varepsilon_{vib,v} = -D_0 + v\hbar\omega$$

$$q_{vib} = \frac{exp\left(-\frac{\theta_{vib}}{2T}\right)}{1 - exp\left(-\frac{\theta_{vib}}{T}\right)}$$

$$q_{vib} = \frac{\exp(\beta D_0)}{1 - exp\left(-\frac{\theta_{vib}}{T}\right)}$$

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So, here is a representation of a typical diatomic molecule where for the sake of simplicity we have used a spring as shown here to represent the vibrational behavior of the chemical bond connecting the 2 atoms.

So, this is a simple ball and spring model; for which the potential energy is known and as a result we can very easily say that this is how the potential energy on which the 2 atomic nuclei move with respect to each other would vary as a function of R where R is the inter nuclear distance between the 2 atoms..

Now when you see this you also know that we know that the different vibrational energy states are the ones corresponding to v equal to 1 or 2 or 3 etcetera . And there are a discrete number of a discrete energy states possible depending on which value of small v is accessible to the system ok.

So, then we could calculate q vib, in terms of this theta y which is a vibrational temperature which depends on the annular frequency with which this spring moves and then one can find out q vib, but when we talk about the diatomic molecule as you understand; that the use of the harmonic potential for the movement of the 2 nuclei with respect to each other is not only approximate, it does not work at long internuclear separations; simply because if you have 2 atoms held by a chemical bond and if you are cooling them apart at very large distances what will happen to the chemical bond, the chemical bond will disrupted will get disrupted this chemical bond will get broken.

Now, this scenario is not present when I look at the harmonic potential, see in the harmonic potential it says that the energy goes on increasing, but it does not correspond to the fact that there will be at some point beyond certain distance the chemical bond between the 2 atoms will be broken. So, at the level of quantum mechanics this can be rectified by noting that if you actually solve the Schrodinger equation for the diatomic case like the hydrogen molecule, you find that this is a red curve in this picture that gives you the actual potential energy over which the 2 nuclei move with respect to each other..

And this can be modeled using for example, the morse potential, but we are not going to do work with that, but rather what I would like to mention here is although the 2 potentials are more or less similar very close to the equilibrium bond length ; which is here I understand that when the bond length becomes much larger there is a disruption of bonds and the energy limit here is the energy of 2 non interacting isolated atoms which are no longer bonded to each other.

So, what happens here is, we note that in this case from the bottom of the potential energy well up to this limit this is the estimated dissociation constant. So, this is the amount of energy that you will require if there is no vibrational structure, and this is your 0 of energy. So, the difference between the 2 energy levels will give you the bond dissociation energy, but in practice. What happens? We have to worry about let us say that the 0-point energy or the vibrational structure of the system when I am considering this red curve representing the presence of the 2 nuclei still in there ground electronic state. So, in that case the actual energy that I should be taking into account is from here to here ok.

Now, if I use this then the vibrational energy states allowed for this kind of a system where we have taken into account the disruption of the bond at long a large separations, that is given by an expression like this . And this is actually rewritten by indicating this term, that is D minus half h cross omega by D naught. And D naught is known as the bond dissociation energy corrected for the 0.5 rational energy ok..

Now once we know this, as you see that instead of half h cross omega, now I have this minus D naught term. But still one can very easily find out what the single particle vibrational partition function would be, and that you can work it out yourself I will not be doing the algebra here, but following the same logic and the same steps, that we have discussed previously. You will be able to show that the single particle vibrational partition function now will depend on b naught as expected. And as before there will be this term in the denominator 1 minus a to the power of minus theta vib by T, where this is the vibrational temperature.

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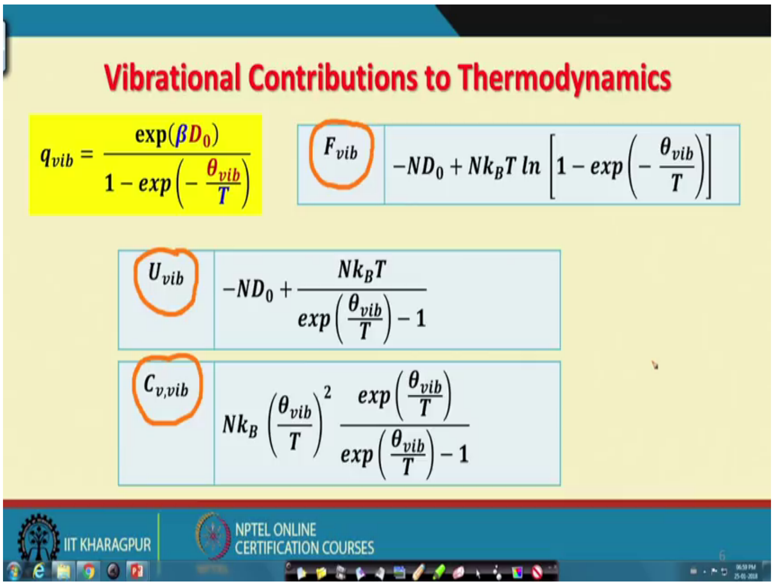

Vibrational Contributions to Thermodynamics

$$q_{vib} = \frac{\exp(\beta D_0)}{1 - exp\left(-\frac{\theta_{vib}}{T}\right)}$$

F_{vib}	$-ND_0 + Nk_BT\, ln\left[1 - exp\left(-\frac{\theta_{vib}}{T}\right)\right]$
U_{vib}	$-ND_0 + \frac{Nk_BT}{exp\left(\frac{\theta_{vib}}{T}\right) - 1}$
$C_{v,vib}$	$Nk_B\left(\frac{\theta_{vib}}{T}\right)^2 \frac{exp\left(\frac{\theta_{vib}}{T}\right)}{exp\left(\frac{\theta_{vib}}{T}\right) - 1}$

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And now once we know this then we understand that if I know the vibrational contribution to the single particle canonical single particle canonical partition function, then I can go ahead and try to understand what is going to be the vibrational contribution to the overall thermodynamic properties of the system. So, that can be very easily found out, and these are the some of the results that you can check as an exercise; using everything that we have learnt so far in this course. So, what is F vib? F vib is the vibrational contribution to the overall Helmholtz free energy of the system .

This is the vibrational contribution to the overall internal energy, and if you take a temperature derivative with respect to this what we you arrive at is the vibrational contribution to the overall Cv, or the specific heat at constant volume . Furthermore, you can go ahead and find out for example, the vibrational contribution to the entropy, and the vibrational contribution to chemical potential, when there is one mole of the substance present..

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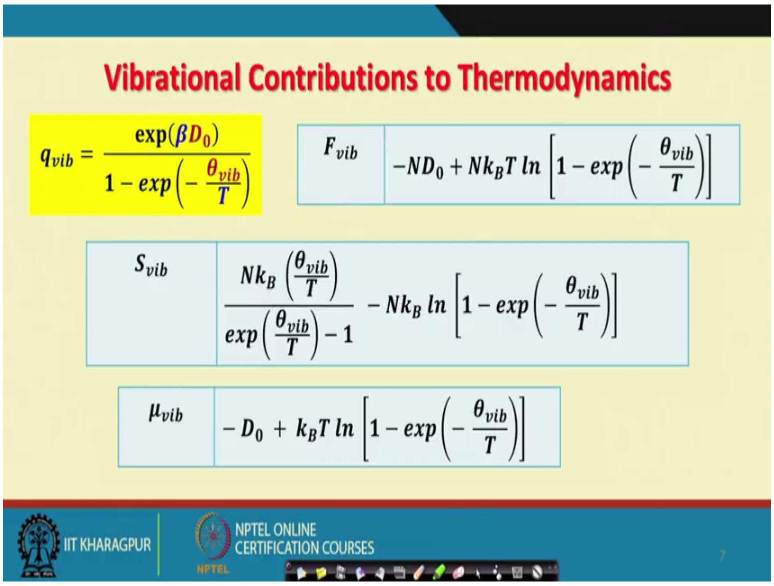

Vibrational Contributions to Thermodynamics

$$q_{vib} = \frac{\exp(\beta D_0)}{1 - exp\left(-\frac{\theta_{vib}}{T}\right)}$$

F_{vib}	$-ND_0 + Nk_BT\ ln\left[1 - exp\left(-\frac{\theta_{vib}}{T}\right)\right]$
S_{vib}	$\frac{Nk_B\left(\frac{\theta_{vib}}{T}\right)}{exp\left(\frac{\theta_{vib}}{T}\right) - 1} - Nk_B\ ln\left[1 - exp\left(-\frac{\theta_{vib}}{T}\right)\right]$
μ_{vib}	$-D_0 + k_BT\ ln\left[1 - exp\left(-\frac{\theta_{vib}}{T}\right)\right]$

Now with all this formula, it is very difficult to understand, what is the use of all these formula. So, what we are going to do is, let us once again check for the additional part as well, and then try to see what these equations and their values eventually in imply and how we can use them.

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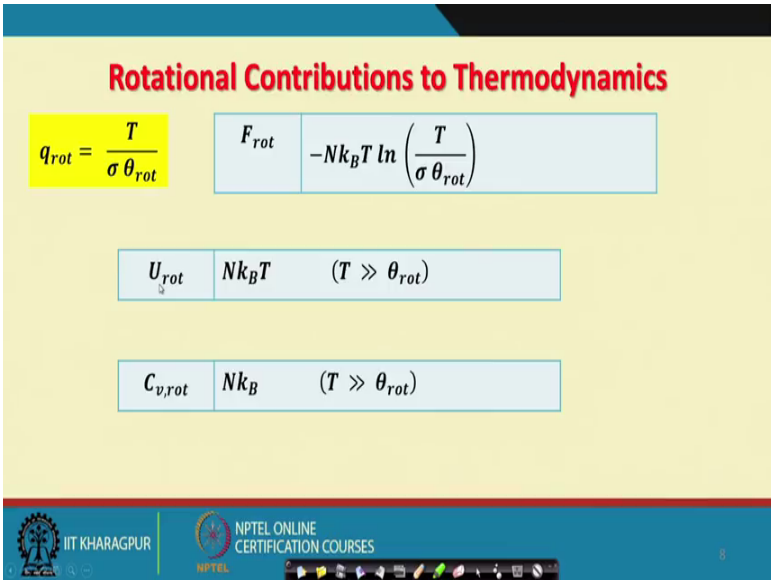

Rotational Contributions to Thermodynamics

$$q_{rot} = \frac{T}{\sigma\,\theta_{rot}}$$

F_{rot}	$-Nk_BT\ln\left(\frac{T}{\sigma\,\theta_{rot}}\right)$

U_{rot}	$Nk_BT \quad (T \gg \theta_{rot})$

$C_{v,rot}$	$Nk_B \quad (T \gg \theta_{rot})$

Now, if I look at the rotational contribution to thermodynamics in the case of a diatomic ideal gas, we know that this contribution will come through q rot, and here sigma is the symmetry number which depends and it is value depends on whether we have a homonuclear, or a heteronuclear diatomic system. Now if I go back then once again I can find out very easily what is going to be the rotational contribution to the Helmholtz free energy or to the internal energy or to the specific heat at constant volume .

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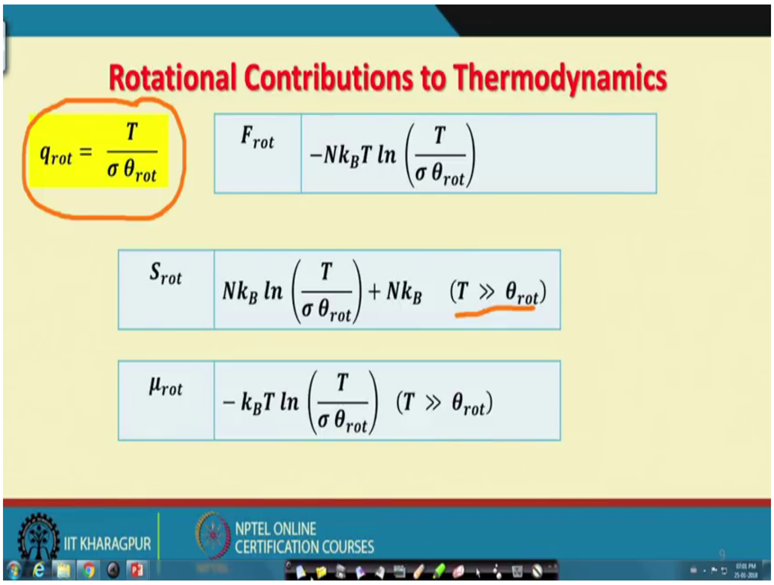

Rotational Contributions to Thermodynamics

$$q_{rot} = \frac{T}{\sigma\,\theta_{rot}}$$

F_{rot}	$-Nk_BT\ln\left(\frac{T}{\sigma\,\theta_{rot}}\right)$

S_{rot}	$Nk_B\ln\left(\frac{T}{\sigma\,\theta_{rot}}\right) + Nk_B \quad (T \gg \theta_{rot})$

μ_{rot}	$-k_BT\ln\left(\frac{T}{\sigma\,\theta_{rot}}\right) \quad (T \gg \theta_{rot})$

Similarly, you can extend these calculations and find out what s rot is going to be, and what mu rot is going to be. But please remember, because we are using this very simple expression for q rot we are getting away by not evaluating the infinite series summation involving the rotational quantum number j. And therefore, this limit is valid only at temperatures where the temperature is much higher than the rotational temperature of the system that we are interested in .

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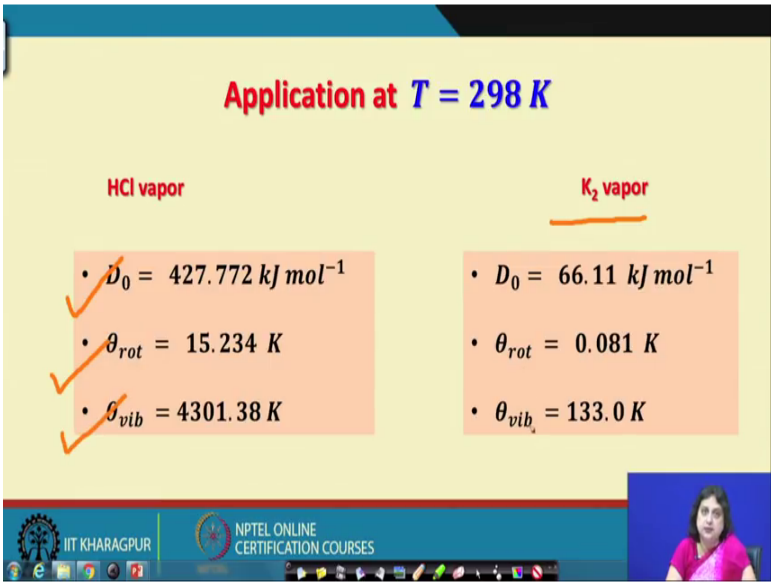

Application at $T = 298\ K$

HCl vapor

- $D_0 = 427.772\ kJ\ mol^{-1}$
- $\theta_{rot} = 15.234\ K$
- $\theta_{vib} = 4301.38\ K$

K_2 vapor

- $D_0 = 66.11\ kJ\ mol^{-1}$
- $\theta_{rot} = 0.081\ K$
- $\theta_{vib} = 133.0\ K$

Now when I go ahead and then look at the experimental data as you understand like if you have a heteronuclear diatomic system, or if you have a homonuclear diatomic system, these data the characteristic data of these gases are available in the literature. People have used many different methods to estimate for example, the D naught value and also, the vibrational and rotational temperatures for different systems..

Now once this information is available to you, then what you can do is you can go ahead and estimate the contributions like, a F rot or F vib or u vib or u rot, and you can try and start understanding that whether a particular degree of freedom is going to contribute to the overall value of a given thermodynamic property at a given temperature .

So, at this stage I am not going to do the calculations, rather I would like to take up this very simple case, where one is wondering about the specific heat of a diatomic ideal gas. Now in the experimental measurements if you employ something like a hydrogen gas or some HCL gas, this is a typical observation that one makes..

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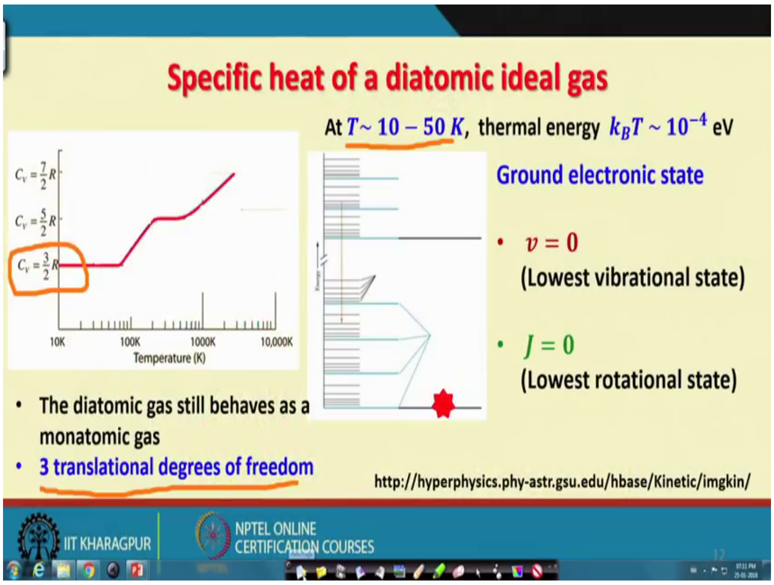

Specific heat of a diatomic ideal gas

At $T \sim 10-50\ K$, thermal energy $k_BT \sim 10^{-4}$ eV

Ground electronic state

- $v = 0$ (Lowest vibrational state)
- $J = 0$ (Lowest rotational state)

- The diatomic gas still behaves as a monatomic gas
- 3 translational degrees of freedom

http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/imgkin/

So, we find that Cv is a quantity that is being measured as a function of temperature ok. So, initially at T going to 0 Cv is nearly 0. If you are at a very low temperature, say like 10 to 50 kelvin. Then Cv remains constant over this range of temperature, and we find that this value is 3 by 2 R. And then on further increase in temperature as you must realize that we have logarithmic scale on the x axis . So, if I look at another range of temperature say betweens around the room temperature 300 kelvin, once again the specific heat or constant volume of the diatomic gas, that turn outs it turns out to be one unit more.

So, here it is 3 by 2 R, and here it is 5 by 2 R. So, that is the Cv has increased by an amount R as I went from this low temperature region to this high temperature region. It remains constant for over certain temperatures and then finally, when I am above a few thousands of kelvin then I can see that it starts rising again. And if you can go to even higher temperatures, then you will see that another flat region is coming into the picture. Now this kind of observation is actually rather baffling. I mean, can you explain this qualitatively the answer is no. So, let us try and see how we can use our understanding of the statistical thermodynamics or the molecular thermodynamics of a diatomic ideal gas that can help us in explaining the experimental data as shown .

So, as I understand that at temperature T going to 0 the at very low temperature near 0 temperature the thermal energy for all practical purposes, which is given in terms of the kb that is a Boltzmann constant into the temperature in absolute unit, that is practically 0. So, what is the underlying microscopic state of the gas under such condition..

So, this is what we have seen as the underlying microscopic structure of the molecule at 0 Kelvin. So, what we understand that here all the molecules constituting the ideal atomic gas will be populating a state like this. So, what is this state this is a state that corresponds to the ground electronic state of the molecule and it is the lowest energy possible state of the system. Therefore, it goes so; it is residing at v equal to 0. That is the lowest vibrational energy state, and j equal to 0 that is the lowest rotational state.

Now, if I think of a little higher temperature like 10 to 50 Kelvin; that is, where I am here, this means that now the accessible thermal energy to the system is KBT. So, T has increased. So, this thermal energy is small, but and of the order of 10 to the power minus 4 electron volt. And with this thermal energy, I ask this question now will it with availability of this very small amount of thermal energy, is it possible that I will have some different microscopic states now accessible to the system? I would see that still the most probable microscopic states would correspond to the molecules being in the ground electronic state with v equal to 0 and j equal to 0.

Now, why is that so? That is because here I find that it is essentially behaving as a monatomic ideal gas, in a monatomic ideal gas, if you see that there are 3 parts in the contributions, here that is the underlying structure and the translational motion. So, in order to understand this the first thing that you realize is if I look at look back at what typically are the differences in the energy levels..

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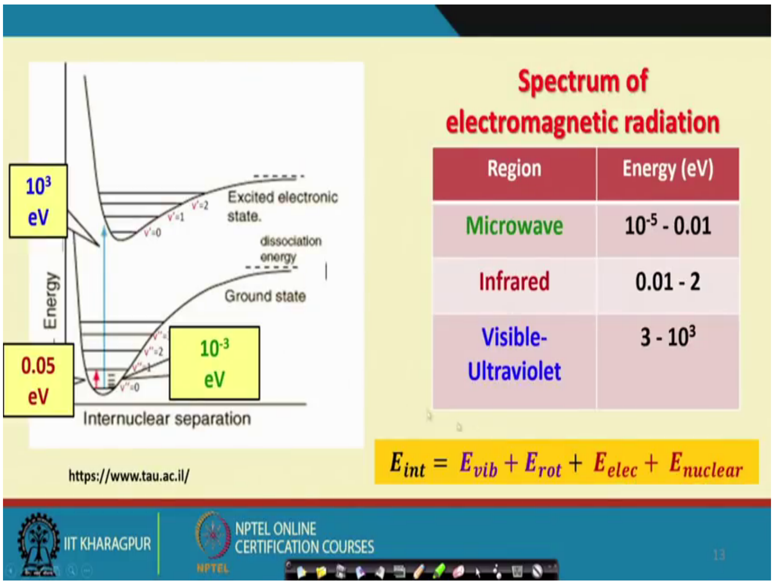

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Spectrum of electromagnetic radiation

Region	Energy (eV)
Microwave	10^{-5} - 0.01
Infrared	0.01 - 2
Visible-Ultraviolet	3 - 10^3

$$E_{int} = E_{vib} + E_{rot} + E_{elec} + E_{nuclear}$$

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We find that the rotational energy levels are of the order of about 10 to the power of minus 3 electron volt whereas, the vibrational energy levels are of the order of 0.05 electron volt, and this is about thousand electron volt between the ground and the first excited electronic state. And the basic idea is, you can transfer population from one energy state to the other if the difference in the 2 energy levels . The difference in values of the 2 energy levels is roughly approximately equal to KT.

Therefore if you are supplying thermal energy at a temperature T, the amount of energy being transferred is KT. Therefore, I understand that the rotational states will be excited if you supply the system with an amount of energy to the tune of one thousands of electron volt. Now if I go back, I see that I have now a thermal energy in this temperature range a thermal energy which is less than that. And therefore, even if I am heating up the system and supplying thermal energy to the system the supplied energy is not sufficient to excite the molecule from it is neither does it excite it from the ground electronic state to the first excited electronic state.

This is ins sufficient to excite it from the vibrational ground state to say v equal to 1 for the ground electronic state . It is not even possible to excite the population j from j equal to 0 to j equal to 1 corresponding to the ground electronic state. And therefore, as I understand the underlying structure of the molecule is not important in this temperature range. So, all I have is structureless molecule having a mass capital. That is moving about in the 3-dimensional box. So, how many degrees of freedom do I have here. I have 3 degrees of freedom corresponding to translation in the x y and z axis.

Now, equipartition theorem tells me that each degree of freedom contributes an amount of half R ok, per mole . So, in this case what happens is I see that I have 3 translational degrees of freedom, each contributing half R and therefore, in this region I have the Cv constant at 3 by 2 R . Therefore, when I am in this temperature range, whatever thermal energy I supplied to the system, it is being used up by the molecules to execute translational motion in the x y z direction. And no and the and the system in this temperature range is frozen in it is ground electronic state, ground vibrational state, and ground rotational state corresponding to the ground electronic state. So, it essentially behaves as if it is like whatever would happen to a monatomic ideal gas .

In the next stage now consider what happens to the next level of temperature.

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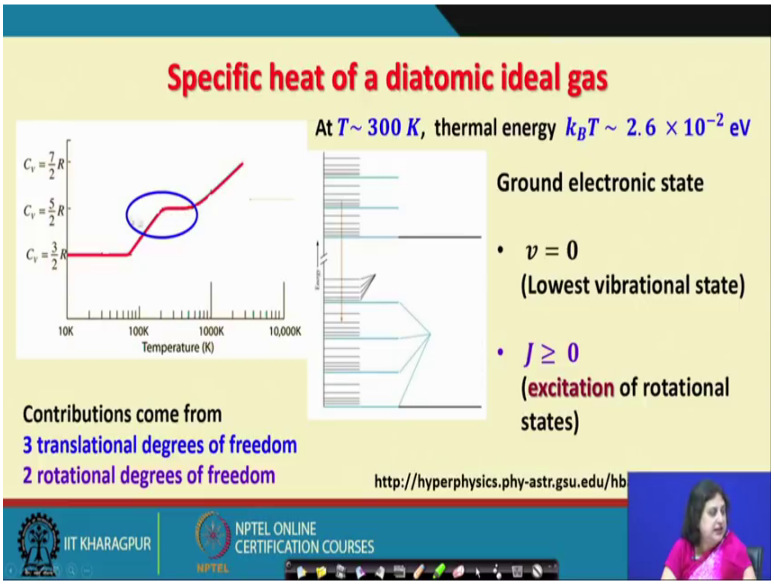

Specific heat of a diatomic ideal gas

At $T \sim 300\ K$, thermal energy $k_B T \sim 2.6 \times 10^{-2}$ eV

Ground electronic state

- $v = 0$
  (Lowest vibrational state)
- $J \geq 0$
  (excitation of rotational states)

Contributions come from
3 translational degrees of freedom
2 rotational degrees of freedom

http://hyperphysics.phy-astr.gsu.edu/hb

So, in the next level of temperature, let us consider this range where the Cv changes gradually from this value of 3 by 2 R to 5 by 2 R ok. Now in this case, what I find is at around 300 kelvin, the thermal energy is to the tune of about 3 into 10 to the power minus 2 electron volt. And now I can very easily say that the available amount of energy is sufficient, to excite the population from say j equal to 0 to j equal to 1 or j equal to 1 to j equal to 2 and so on and so forth.

Therefore, I would say that in this temperature range, the available thermal energy is sufficient for the excitation of the rotational states so that now I will have microscopic states of the molecules present whereby all of them are present in the ground electronic state. All of these molecules will have v equal to 0, but they are going to have a range of j values other than 0 in addition to 0 ok. Now if you think about the molecule populating higher energy rotational energy levels. It is basically saying that in addition to this molecule executing translational motion in the 3-dimensional system, if you look at what is happening internally this molecule has started rotating.

Now, this would add not only 3 translational degrees of freedom to the system, but it would the system will now have 2 additional degrees of freedom, coming from rotation around 2 axis of rotation. And therefore, there are now a total of 5 degrees of freedom. Each contributing an amount of half R to per mole of system, and therefore, I understand that with the excitation of the rotational energy states Cv would go and stabilize here at 5 by 2 R. So obviously, what happens when I have g1 over, and looked at from beyond this region at higher temperature?

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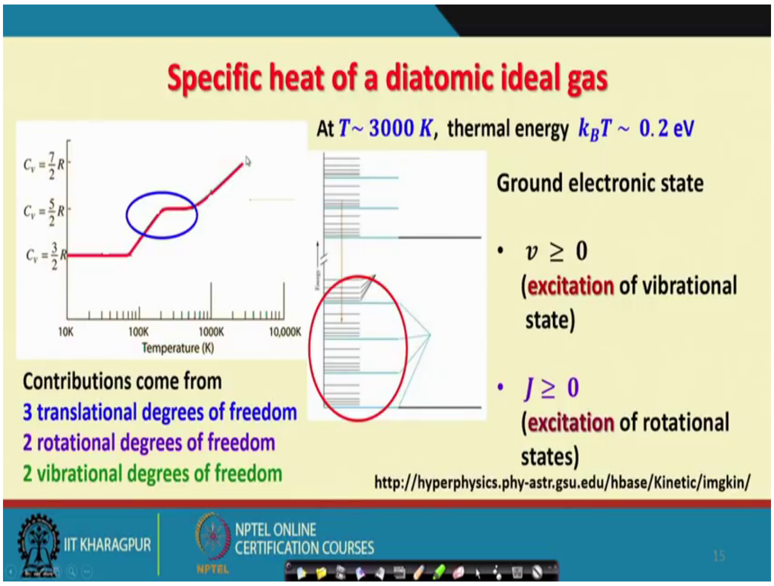

Specific heat of a diatomic ideal gas

At $T \sim 3000\ K$, thermal energy $k_B T \sim 0.2$ eV

Ground electronic state

- $v \geq 0$ (excitation of vibrational state)
- $J \geq 0$ (excitation of rotational states)

Contributions come from
3 translational degrees of freedom
2 rotational degrees of freedom
2 vibrational degrees of freedom

http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/imgkin/

Say at around 3,000 kelvin the thermal energy is about 0.2 electron volt and this is that now the molecules will be present in a range of microscopic states the most probable micro scopic states will be associated with the ground electronic state no doubt, but now you will have excitation of both the vibrational energy states and excitation of the rotational energy states..

And therefore, you see that at present , the most probable microscopic states will correspond to the ground electronic state as shown here. But all these levels here v equal to 0 v equal to 1 v equal to 2 they will gradually get populated as temperature increases. And similarly, each of their rotational sub states they are also going to get populated . Therefore, now I have 3 translational degrees of freedom 2 rotational degrees of freedom and 2 vibrational degrees of freedom adding up to 7 degrees of freedom so that as the overall heat capacity increases , it tends to the value of 7 by 2 R.

So, in this lecture what we have learnt is, it is not impossible to summarize the observed experimental behavior in terms of the a single particle partition functions, and the population of the underlying microscopic energy states of the molecules..

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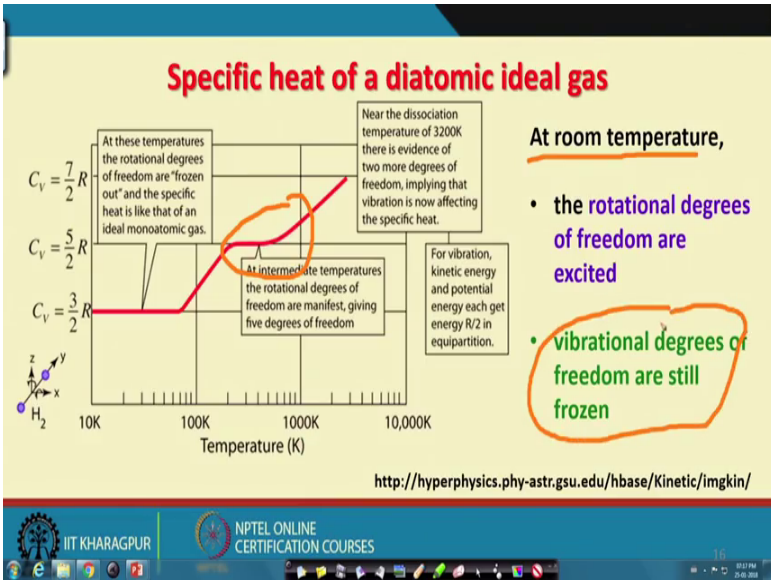

Specific heat of a diatomic ideal gas

At these temperatures the rotational degrees of freedom are "frozen out" and the specific heat is like that of an ideal monoatomic gas.

At intermediate temperatures the rotational degrees of freedom are manifest, giving five degrees of freedom

Near the dissociation temperature of 3200K there is evidence of two more degrees of freedom, implying that vibration is now affecting the specific heat.

For vibration, kinetic energy and potential energy each get energy R/2 in equipartition.

At room temperature,

- the rotational degrees of freedom are excited
- vibrational degrees of freedom are still frozen

http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/imgkin/

And the crucial point to note here is as follows. So, what we have here is it is indeed possible by using the concepts developed through molecular thermodynamics to understand the observed experimental behavior, and not only that we realize that what happens at room temperature..

At room temperature that is, in this range the rotational degrees of freedom are excited, because the thermal energy is comparable to the energy difference between subsequent energy levels of the rotational energy states. But the available energy is still not enough to start transferring population from v equal to 0 to v equal to 1 or v equal to 1 to v equal to 2. And this basically means that the vibrational degrees of freedom are still frozen.

So, this has given us some idea as to why people spend so much effort in understanding and developing the microscopic nature of a system with respect to the underlying microscopic structure. In the next lecture, we will have a closer look at a homonuclear diatomic atom and trying to explain seemingly disturbing mismatch between theoretical predictions and experimental data.

Thank you.