Statistical Thermodynamics for Engineers
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Lecture 53
The zero of energy (rotational and vibrational)

So, welcome to lecture number 42 of the Statistical Thermodynamics course. So, in this particular thing we have already said that the 0 of energy or the 0 of energy is pretty critical and we said the 4 ways the 4 possibilities that we can calculate it.

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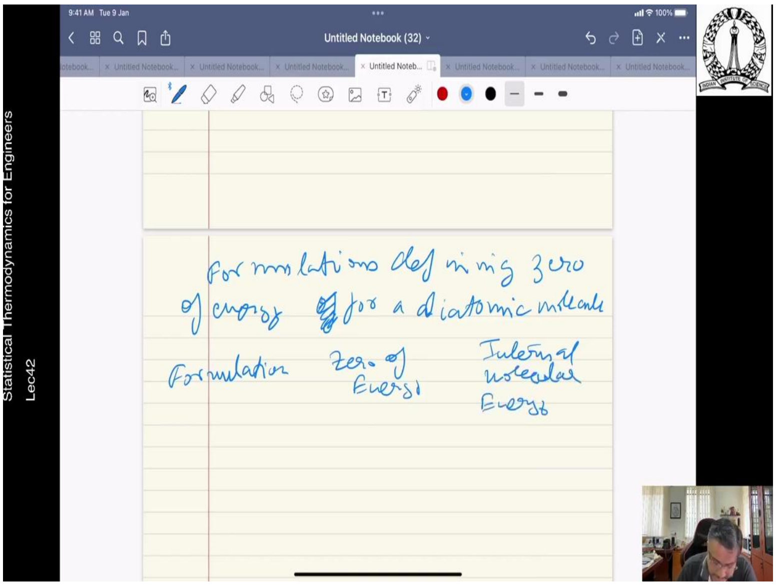

Formulations defining zero of energy for a diatomic molecule

Formulation   Zero of Energy   Internal molecular Energy

That is write. (())(0:24) formulations defining 0 of energy for a diatomic molecule in sort of formulation first we write the formulation then the 0 of energy and then the internal molecular energy.

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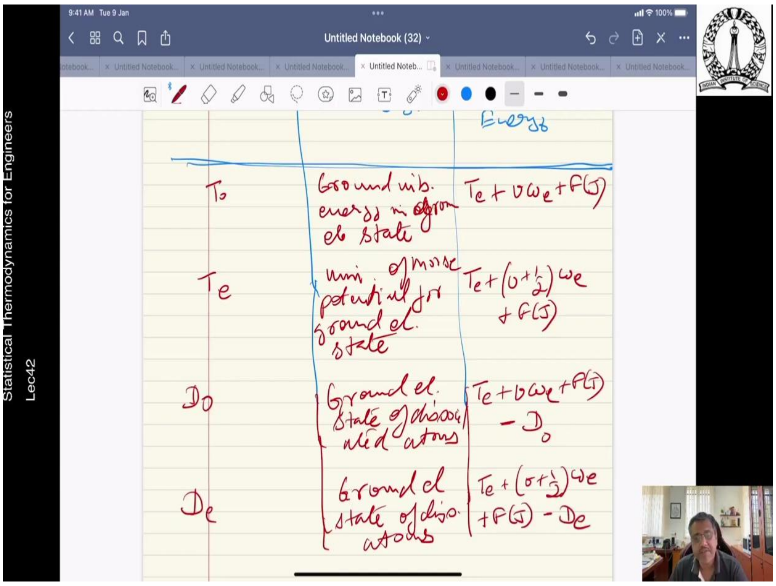

		Energy
T_0	Ground vib. energy in ground el. state	$T_e + v\omega_e + F(J)$
T_e	min. of Morse potential for ground el. state	$T_e + (v + \frac{1}{2})\omega_e + F(J)$
D_0	Ground el. state of dissociated atoms	$T_e + v\omega_e + F(J) - D_0$
D_e	Ground el. state of diss. atoms	$T_e + (v + \frac{1}{2})\omega_e + F(J) - D_e$

So, the formulation T naught which we already know what it is. So, the 0 of energy is the ground vibrational energy in ground electronic state electronic state. Internal molecular energy therefore becomes Te plus v omega plus fJ than if it is Te this is the minimum of the most potential for ground electronic state. So, the total energy will be now it omega v plus half omega e plus fJ it and then there are two more kind of new one is d naught which is a ground electronic state, electronic state of dissociated atoms. So, this is Te plus v omega e plus fJ plus sorry minus D naught and then there is of course De which is ground electronic state of dissociated atoms. So, this is Te plus e plus half plus fJ minus De.

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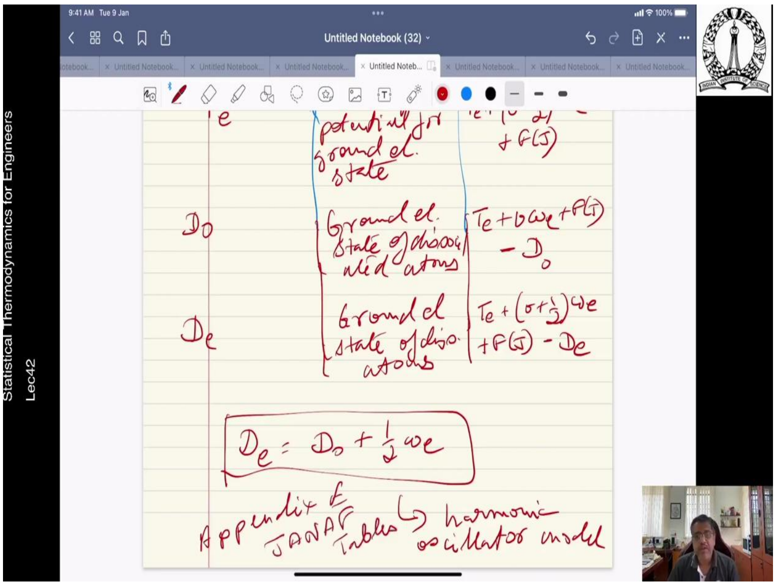

e	potential for ground el. state	$+ F(J)$
D_0	Ground el. state of dissociated atoms	$T_e + v\omega_e + F(J) - D_0$
D_e	Ground el. state of diss. atoms	$T_e + (v + \frac{1}{2})\omega_e + F(J) - D_e$

$$\boxed{D_e = D_0 + \frac{1}{2}\omega_e}$$

Appendix E JANAF Tables → harmonic oscillator model

So, the T naught so, there are varieties of options T naught option is most common in which is available the mention of tables and stuff like that we also for assembly containing reactive mixture do not formulation is mandatory. So, the D naught and De are related. So, De equal to D naught plus half omega e this is the relation. And implying a harmonic oscillator model valid for harmonic oscillator model.

So, this clearly indicates that ground state vibrational energy can be added included or excluded when you choose the 0 of energy when it is permissible we must obviously not try to mix up the two different formulations when making thermodynamic calculations in the most standard cases to use T naught formulate which is there in the JANAF table appendix E, Appendix E JANAF tables. So, that is what we can we can do.

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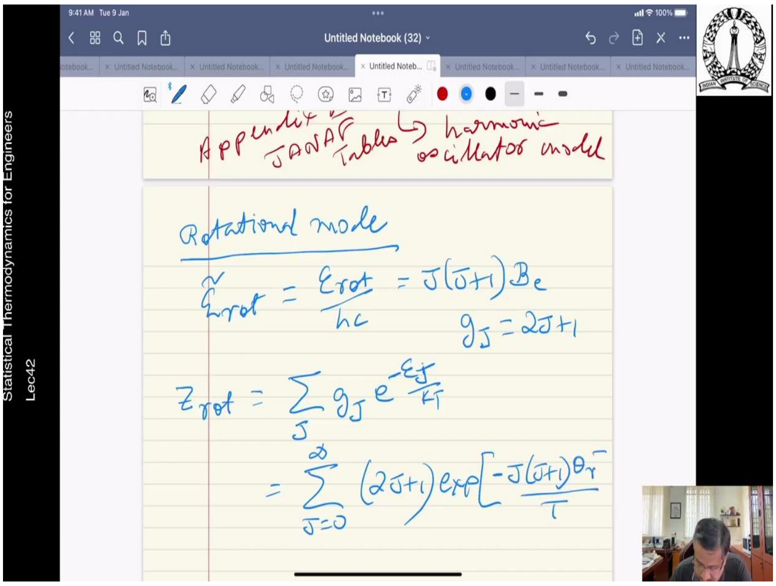

Appendix → JANAF Tables → harmonic oscillator model

Rotational mode

$$\tilde{\varepsilon}_{rot} = \frac{\varepsilon_{rot}}{hc} = J(J+1)B_e \qquad g_J = 2J+1$$

$$Z_{rot} = \sum_J g_J e^{-\frac{\varepsilon_J}{kT}}$$

$$= \sum_{J=0}^{\infty} (2J+1)\exp\left[-\frac{J(J+1)\theta_r}{T}\right]$$

Now let us go to the rotational mole, so the rotational mode, the energy the rotational mode E rotation divided by hc this we have written countless number uptimes now J into J plus 1 into Be where the degeneracy is 2J plus 1 the rotational partition function becomes Z rotation summing over all J gJ exponential EJ that is J by KT which now becomes if you write properly J equal to 0 to infinity 2J plus 1 exponential minus J into J plus 1 into theta r remember this is the rotational temperature now.

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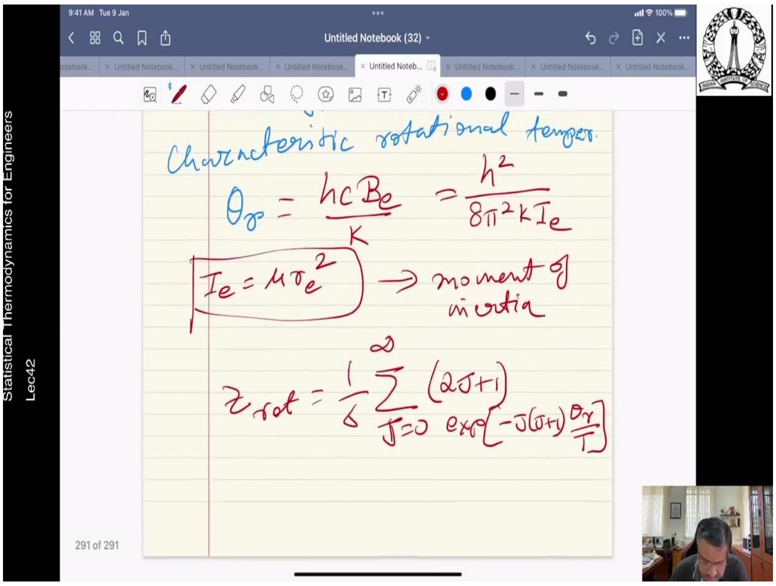

Characteristic rotational temper.

$$\theta_r = \frac{hcB_e}{k} = \frac{h^2}{8\pi^2 k I_e}$$

$$\boxed{I_e = \mu r_e^2} \rightarrow \text{moment of inertia}$$

$$Z_{rot} = \frac{1}{\sigma}\sum_{J=0}^{\infty} (2J+1)\exp\left[-J(J+1)\frac{\theta_r}{T}\right]$$

This is where the characteristic rotational temperature, rotational temperature is theta r and the (())(6:07) is hc into Be by K this is equal to h square divided by 8pi square KIe where Ie is basically mu re square. So, this is the moment of inertia. So, for homo nuclear diatomic fiver we have inadvertently over counted the number of available quantum states by a factor of 2 because of the inherent indistinguishability of the nuclear pair this complication derives from the symmetry requirements of the molecular wave function.

So, as a result partition function is restricted to the only odd or even value is the rotational quantum matters. So, the rotational partition function can be expressed more generally as without going into too much of a detail, it is the same expression similar type of expression but by we have a Sigma J plus 1 exponential and as JJ plus 1 theta r by T where it closes.

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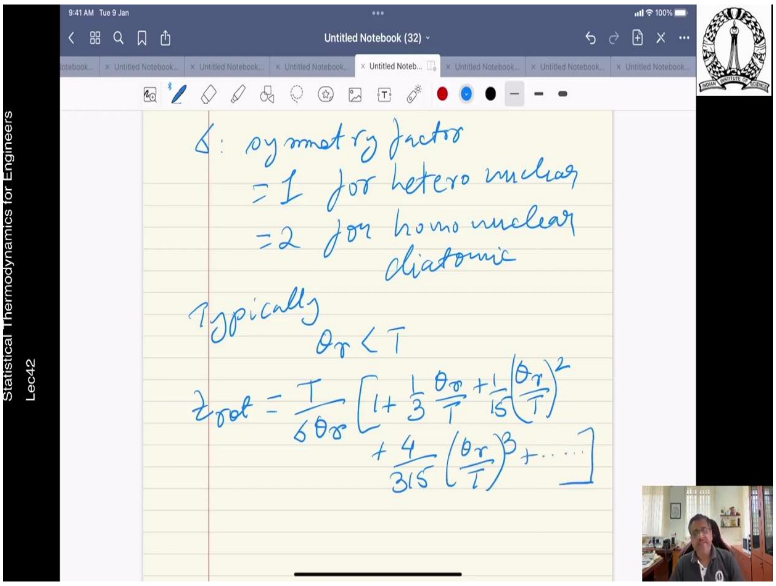

σ : symmetry factor

$= 1$ for hetero nuclear

$= 2$ for homo nuclear diatomic

Typically

$\theta_r < T$

$$Z_{rot} = \frac{T}{\sigma\theta_r}\left[1 + \frac{1}{3}\frac{\theta_r}{T} + \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\theta_r}{T}\right)^3 + \cdots\right]$$

So, sigma is basically a cemetery factor which takes of the value of unity for a hetero nuclear and two for a molecule equal to 1 for hetero nuclear equal to 2 for homo nuclear diatomic. So, typically theta r is less than T. So, if you do a sanction off the rotational partition function, you get Z rotation is equal to T by sigma theta r 1 plus 1/3 theta r by T plus 1/5 theta r by T square plus 4 by 3 by 5 theta r by T cube…

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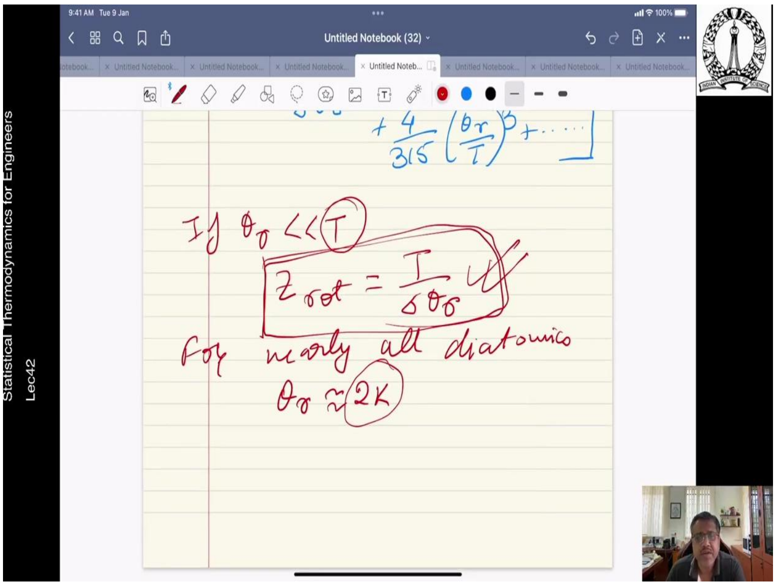

$+ \frac{4}{315}\left(\frac{\theta_r}{T}\right)^3 + \ldots \Big]$

If $\theta_r << T$

$$\boxed{Z_{rot} = \frac{T}{\sigma\theta_r}}$$

For nearly all diatomics

$\theta_r \approx 2K$

Now, if on the other hand now, if theta r is much much less than T now, this therefore, can be converted to an integral and Z rotational therefore, will become T by sigma. So, for all for nearly all nearly all diatomic theta r (())(9:28) 2 kelvin. So, this expression this expression is more or less suitable because this is much much less than the temperature T. So, for certain molecules of course, like hcl or h (())(9:48) is about 15. So, in that case you need to do this series but for like 2 Kelvin This is sufficient to calculate. The rotational partition function.

Now, for hydrogen for example, theta r is 87.55. So, you did not need to do the full inspection, you need to integrate because then you need to go to this damage. So, there are a variety of ways in which you can do this.

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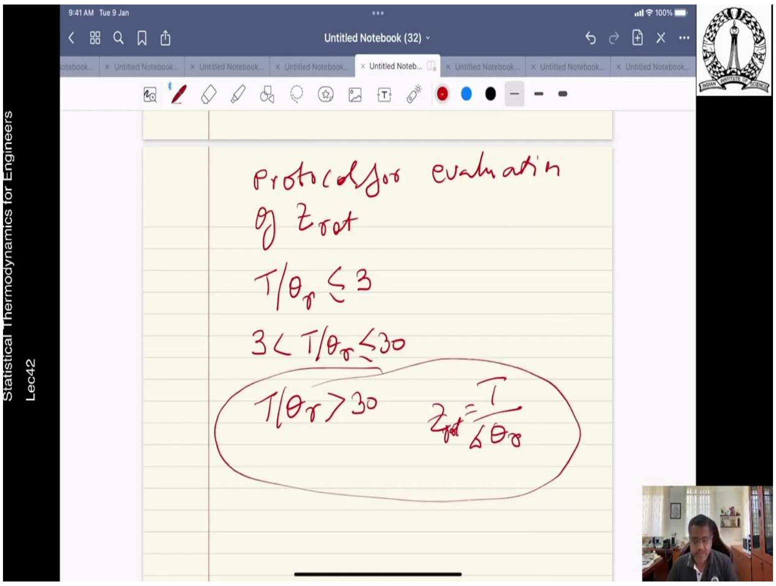
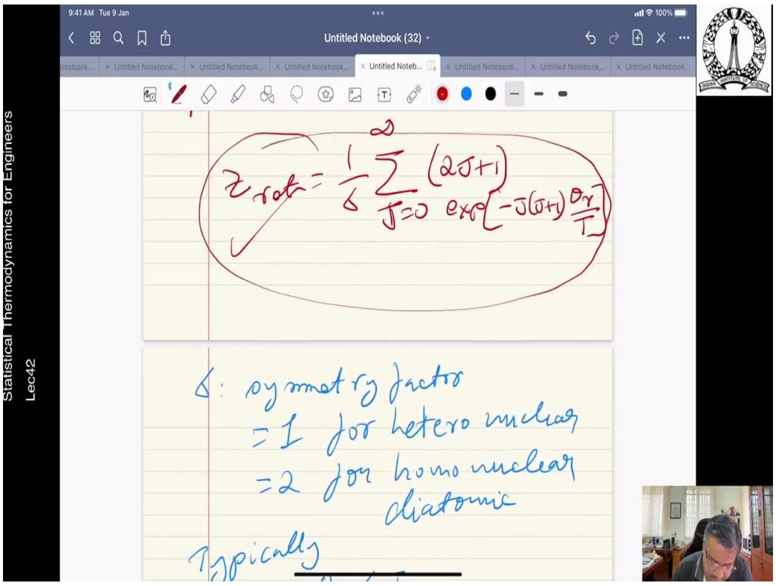


Protocol for evaluation of Z_{rot}

$T/\theta_r \leq 3$

$3 < T/\theta_r \leq 30$

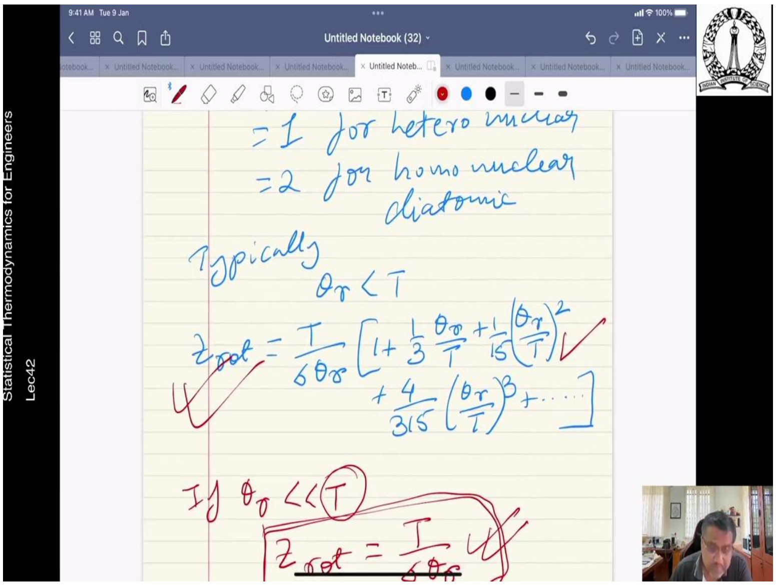
$T/\theta_r > 30$ $\quad Z_{rot} = \frac{T}{\sigma\theta_r}$



$$\boxed{Z_{rot} = \frac{1}{\sigma}\sum_{J=0}^{\infty}\frac{(2J+1)}{\exp\left[-J(J+1)\frac{\theta_r}{T}\right]}}$$

σ: symmetry factor
=1 for hetero nuclear
=2 for homo nuclear diatomic

Typically



=1 for hetero nuclear
=2 for homo nuclear diatomic

Typically
$\theta_r < T$

$$Z_{rot} = \frac{T}{\sigma\theta_r}\left[1+\frac{1}{3}\frac{\theta_r}{T}+\frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\theta_r}{T}\right)^3+\dots\right]$$

If $\theta_r << T$

$$\boxed{Z_{rot} = \frac{T}{\sigma\theta_r}}$$

So, the condition we can write some protocols, this is just to give I give some idea protocols for evaluation, evaluation of Z rotation, so if theta by r is less than equal to 3 then we use then we use the appearing depression which is full exception which is the registered session that we this this particular equation essentially this If on the other hand 3 is less than T by theta r which is less than equal to 30 then we use the this exception.

Now, lastly, if it is greater than 30 then we use the last equation which is T by sigma theta r it would be Z rotation. So, there are varieties of ways in which you can do it. So, the most common scenarios corresponds to this because this is where most of the diatomic such you would like.

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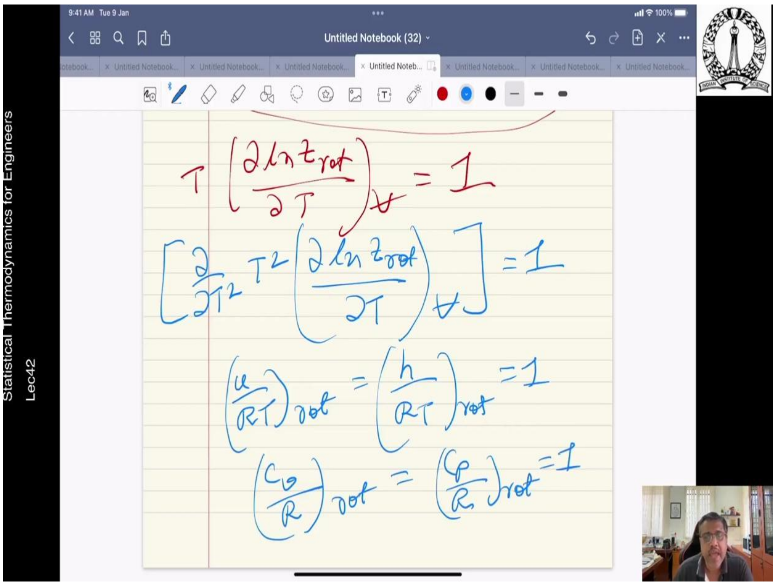

$$T\left(\frac{\partial \ln z_{rot}}{\partial T}\right)_v = 1$$

$$\left[\frac{\partial}{\partial T^2} T^2\left(\frac{\partial \ln z_{rot}}{\partial T}\right)_v\right] = 1$$

$$\left(\frac{u}{RT}\right)_{rot} = \left(\frac{h}{RT}\right)_{rot} = 1$$

$$\left(\frac{C_v}{R}\right)_{rot} = \left(\frac{C_p}{R}\right)_{rot} = 1$$

So, therefore, a not to standard partial derivatives. So, 1 is this Z rotation divided by dT (())(12:05) constant is becomes equal to 1 alright. The other one which is d by dT square T square d ln Z rotation divided by dT del v this becomes equal to 1 also. So, therefore, therefore, as for the translational mode we again replicate the classical results predicted by T (())(12:37) principle. So, u by RT rotation is equal to h by RT rotation is equal to 1 let of course, your Cv by R rotation is equal to Cp by R rotation is equal to 1.

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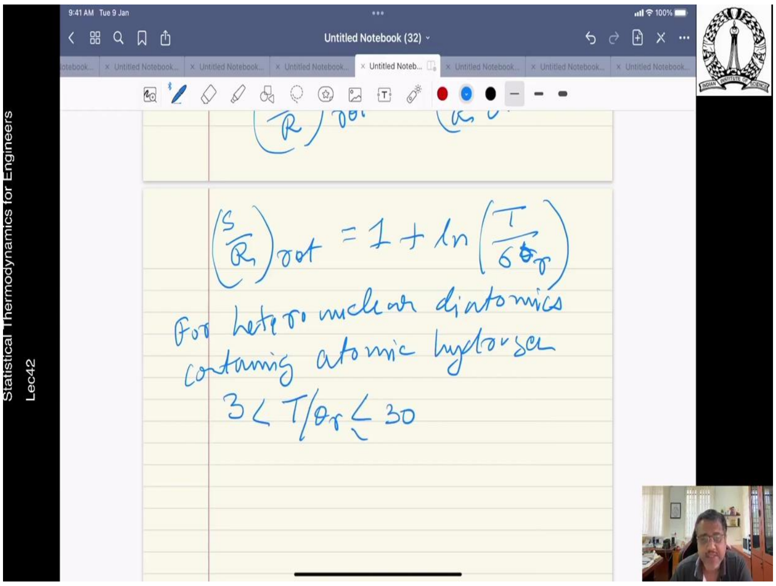

$$\left(\frac{S}{R}\right)_{rot} = 1 + \ln\left(\frac{T}{\sigma\theta_r}\right)$$

For hetero nuclear diatomics containing atomic hydrogen

$3 < T/\theta_r \leq 30$

And the rotational contribution of entropy therefore becomes is S by R rotation is equal to 1 plus ln T by sigma theta r. so, what hetero nuclear diatomic stage atomic hydrogen a partition function can be similarly expressed as form that we already predicted earlier. So, so, this now for hetero nuclear diatomic contemning atomic hydrogen. This is T by theta r is therefore something like this which requires that you use the expansion.

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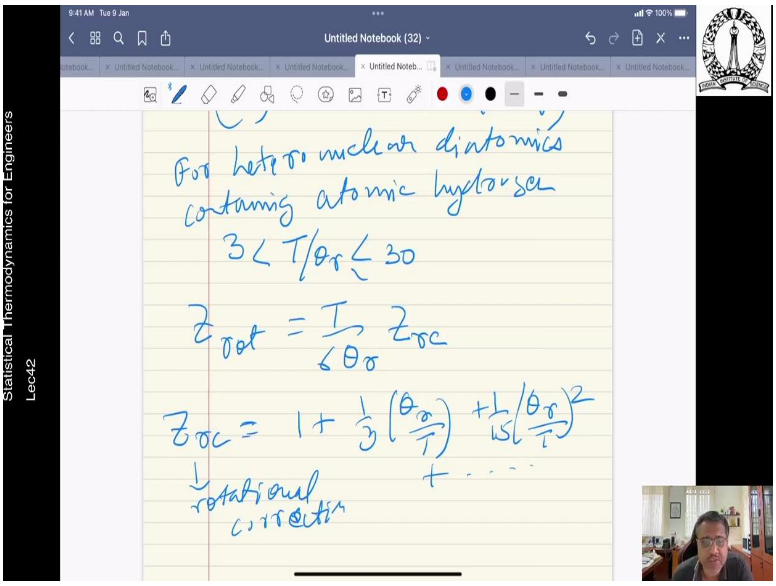

For hetero nuclear diatomics containig atomic hydrogen

$3 < T/\theta_r \leq 30$

$$Z_{rot} = \frac{T}{\sigma\theta_r} Z_{rc}$$

$$Z_{rc} = 1 + \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \dots$$

$\downarrow$ rotational correction

That means Z Rotation T by sigma theta r and some correction term. So, this is a correction term is the rotational correction term is equal it rotational correction this is basically the expansion that we talked about is 1/3 theta r by T plus 1 by 15 theta r by T square so on and so forth. So, we just evaluate the first two partial derivatives this time term by term.

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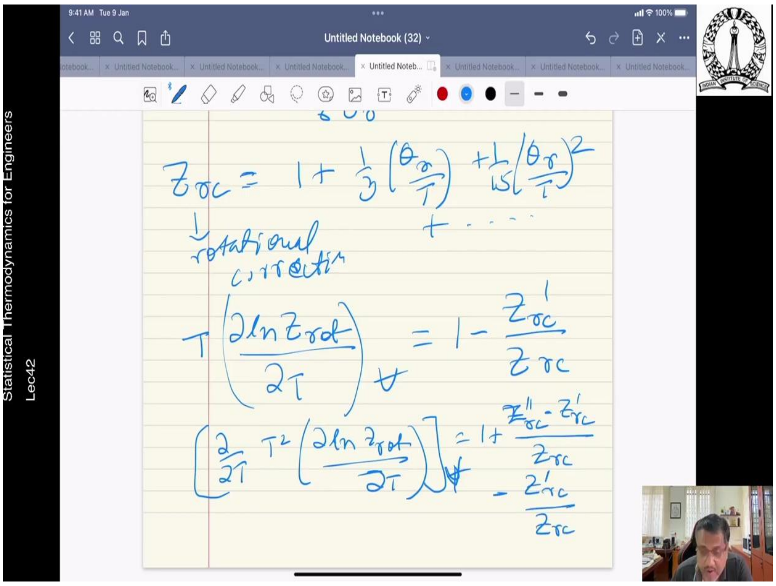

$$Z_{rc} = 1 + \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \dots$$

$\downarrow$ rotational correction

$$T\left(\frac{\partial \ln Z_{rot}}{\partial T}\right)_V = 1 - \frac{Z'_{rc}}{Z_{rc}}$$

$$\left[\frac{\partial}{\partial T} T^2\left(\frac{\partial \ln Z_{rot}}{\partial T}\right)\right]_V = 1 + \frac{Z''_{rc} - Z'_{rc}}{Z_{rc}} - \frac{Z'_{rc}}{Z_{rc}}$$

So, for those cases ln Z rotation divided by dt at constant v volume is 1 minus Zrc by Zrc and the other one is this ln Z rotation divided by dT constant v is seven as l plus Zrc double prime minus Zrc prime by Zrc minus Zrc (())(15:51) square.

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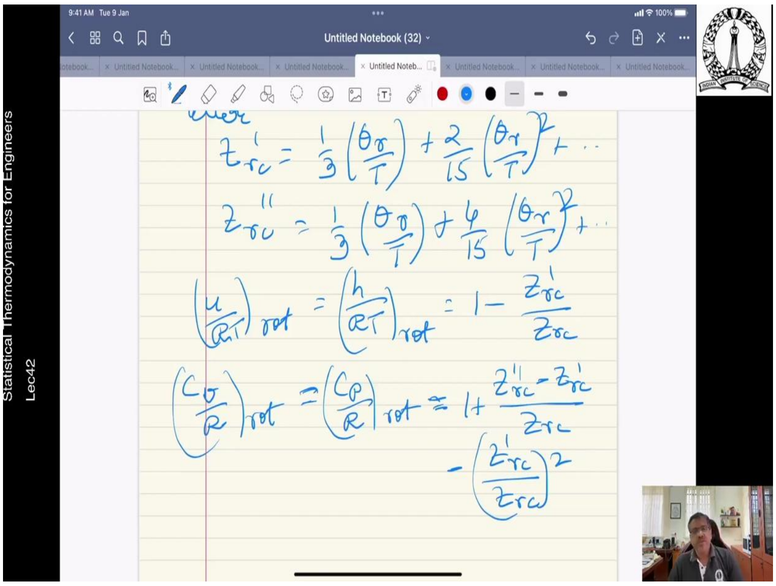

$$Z'_{rc} = \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{2}{15}\left(\frac{\theta_r}{T}\right)^2 + \ldots$$

$$Z''_{rc} = \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{4}{15}\left(\frac{\theta_r}{T}\right)^2 + \ldots$$

$$\left(\frac{u}{RT}\right)_{rot} = \left(\frac{h}{RT}\right)_{rot} = 1 - \frac{Z'_{rc}}{Z_{rc}}$$

$$\left(\frac{C_v}{R}\right)_{rot} = \left(\frac{C_p}{R}\right)_{rot} \approx 1 + \frac{Z''_{rc} - Z'_{rc}}{Z_{rc}} - \left(\frac{Z'_{rc}}{Z_{rc}}\right)^2$$

Where Zrc prime is one third theta r by T plus 2 by 15 theta r by T square, so on and so forth, Zrc double prime is equal to one third theta r by T plus 4 by 15 theta r by T square. so on so forth, this we have the rotational contribution for internal energy and enthalpy and specific heats will be u by RT rotation is equal to h by RT rotation is equal to 1 minus Zrc prime by Zrc.

And similarly, Cv by R Cp by R rotation is equal to 1 plus Zrc double prime minus Zrc prime divided by Zrc minus Zrc prime Zrc square. So, you can develop base for all the remaining thermodynamic properties including entropy and a lot of other things, it is like some tedious calculations, but effectively it is the same way.

So, some of the unique features associated with the partition with a particle distribution over rotational energy levels can also be found you are we can give this study material that you can study the rest of the chapter where you can find out that what would be the what will be the what are some of the unique features of this rotational quantum numbers.

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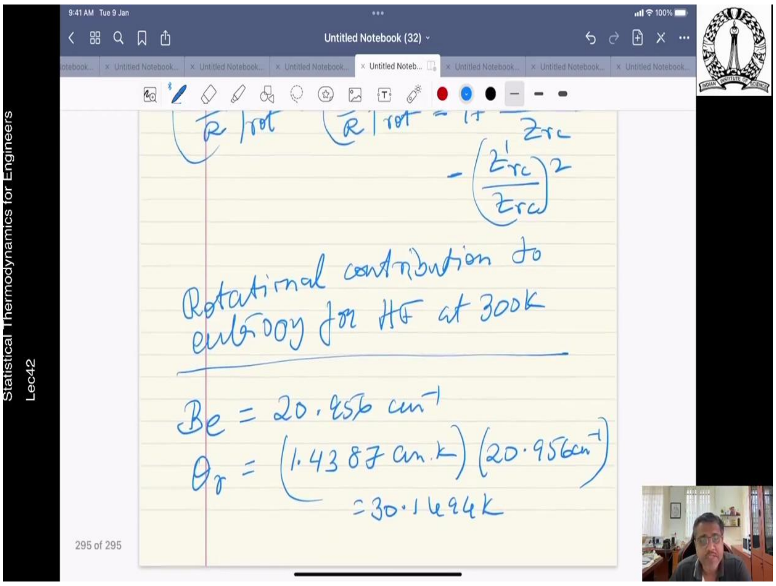

$$- \left(\frac{Z'_{rc}}{Z_{rc}}\right)^2$$

Rotational contribution to entropy for HF at 300K

$B_e = 20.956\ cm^{-1}$

$\theta_r = (1.4387\ cm.K)(20.956\ cm^{-1})$

$= 30.1494K$

So, the rotational contribution we can just do a solve net rotational contribution to entropy for example, entropy or say HF at 300 kelvins. So, HF has got a rotational constant, this you can find it up the tables, this is got a rotational function v 20.956 centimeter inverse. So, the characteristic rotational temperature theta r is 1.4387 centimeter Kelvin multiplied by 20.956 centimeter inverse, which gives rise to a temperature of 30.1494 Kelvins. Which is very reasonable.

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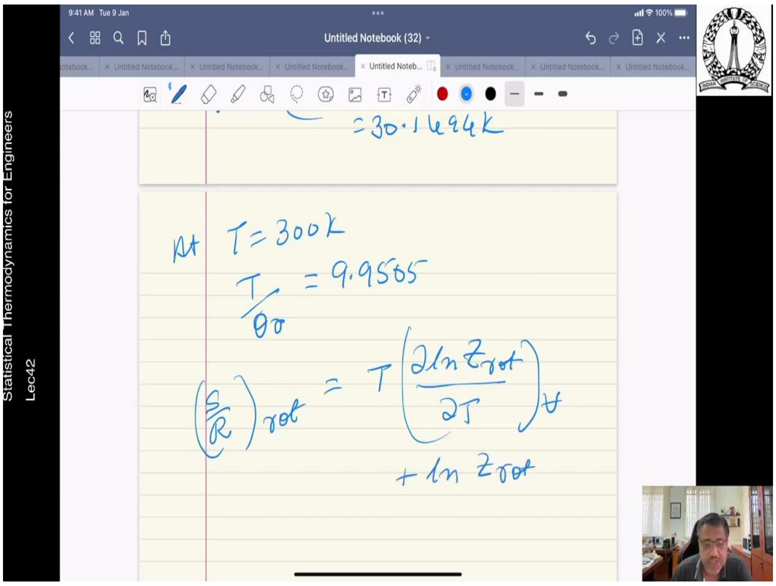
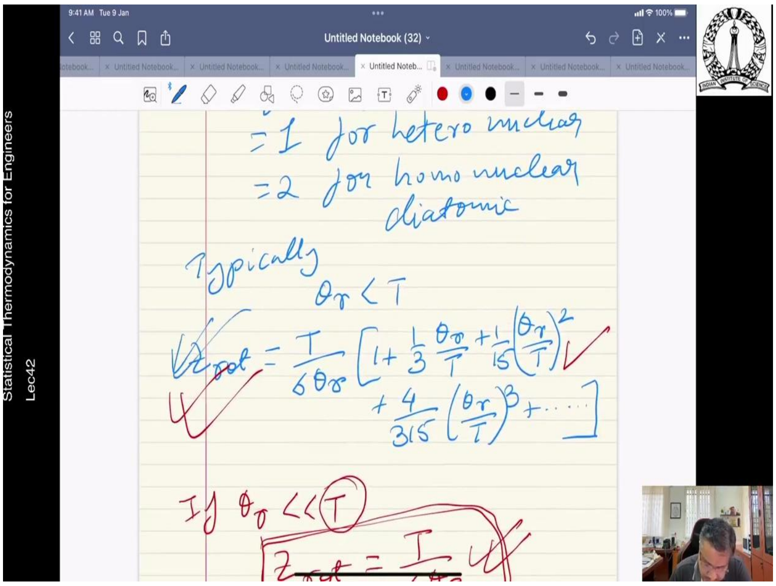


$= 30.1494K$

At $T = 300K$

$\frac{T}{\theta_r} = 9.9505$

$$\left(\frac{S}{R}\right)_{rot} = T\left(\frac{\partial \ln Z_{rot}}{\partial T}\right)_V + \ln Z_{rot}$$



$= 1$ for hetero nuclear

$= 2$ for homo nuclear diatomic

Typically

$\theta_r < T$

$$Z_{rot} = \frac{T}{6\theta_r}\left[1 + \frac{1}{3}\frac{\theta_r}{T} + \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\theta_r}{T}\right)^3 + \cdots\right]$$

If $\theta_r << \boxed{T}$

$Z_{rot} = \frac{T}{\ldots}$

So, therefore, for a given temperature say 300 Kelvins at T equal to 300 Kelvin T by theta r is equal to 9.9505. So, you have to use the expansion terms now the related expressions. So, using that the rotational contribution will be equal to So, the expression will be something like this you have to use this because it is less than 10. So, you can find out this S by R rotation is equal to T is the entropy rotation divided dt constant v plus ln Z rotation. So, Z rotation then you can basically use the expansion and you take the take the first derivative, which needs to be that means the correction terms needs to be evaluated

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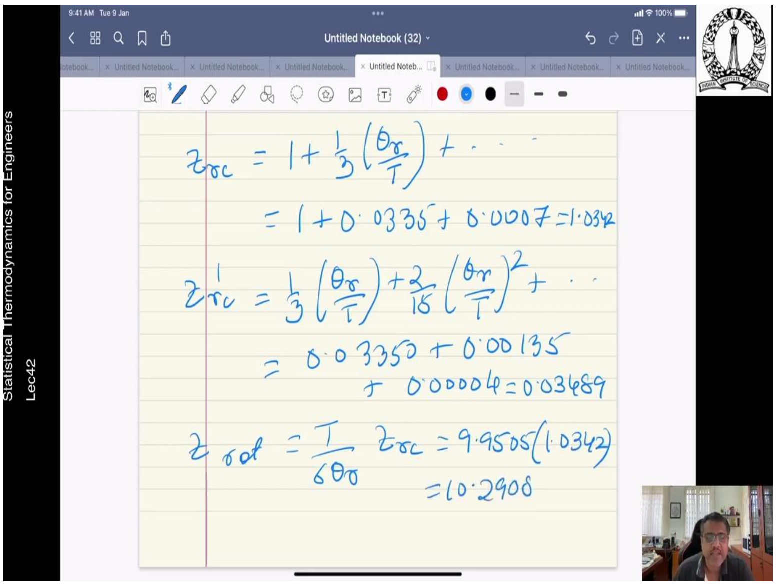

$$Z_{rc} = 1 + \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \cdots$$

$$= 1 + 0.0335 + 0.0007 = 1.0342$$

$$Z'_{rc} = \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{2}{15}\left(\frac{\theta_r}{T}\right)^2 + \cdots$$

$$= 0.03350 + 0.00135 + 0.00004 = 0.03489$$

$$Z_{rot} = \frac{T}{6\theta_r} Z_{rc} = 9.9505(1.0342)$$

$$= 10.2908$$

So, the correction terms for example, Zrc will be 1 plus one third theta r by T… So, it is like 1 plus 0.0335 plus 0.0007 The first two terms are sufficient because it drops off quickly the series drops off quickly. So, Zrc prime is one third theta r by T plus 2 by 15 theta r by T square… again we I mean depending on the situation you evaluate of the terms so, 3350 plus 0.00135 plus 0.00004, which is basically 0.03489. So, this is the term.

So, the rotational Z rotation therefore becomes T by sigma theta r Zrc which is 9.9505 multiplied by 1.0342 which is like 10.2908.

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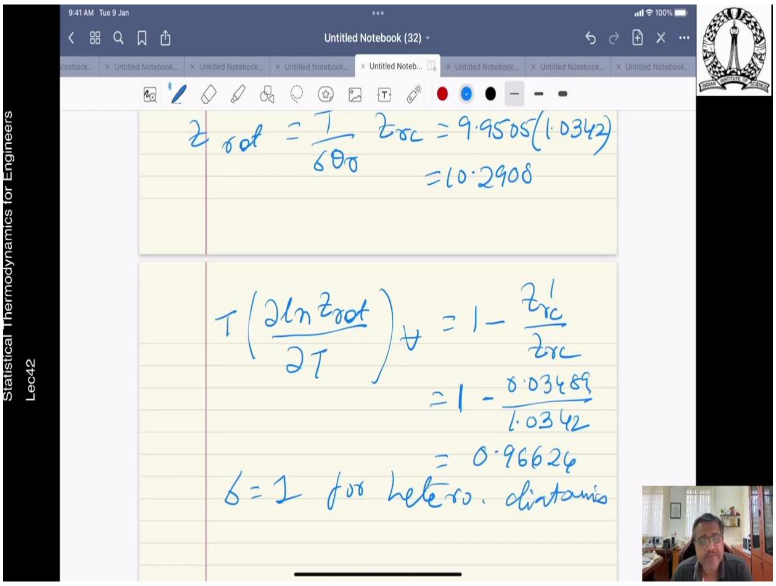

$$z_{rot} = \frac{T}{\sigma\theta_r} z_{rc} = 9.9505(1.0342)$$

$$= 10.2908$$

$$T\left(\frac{\partial \ln z_{rot}}{\partial T}\right)_V = 1 - \frac{z'_{rc}}{z_{rc}}$$

$$= 1 - \frac{0.03489}{1.0342}$$

$$= 0.96626$$

$\sigma = 1$ for hetero. diatomics

And if we now evaluate T the derivatives Z rotation v constant volume, this is 1 minus the first derivative of the correction to Zrc which is equal to 1 minus this is 0.03489 divided by 1.0342 which is equal to 0.96626, so, sigma equal to 1 for hetero nuclear atoms diatomic.

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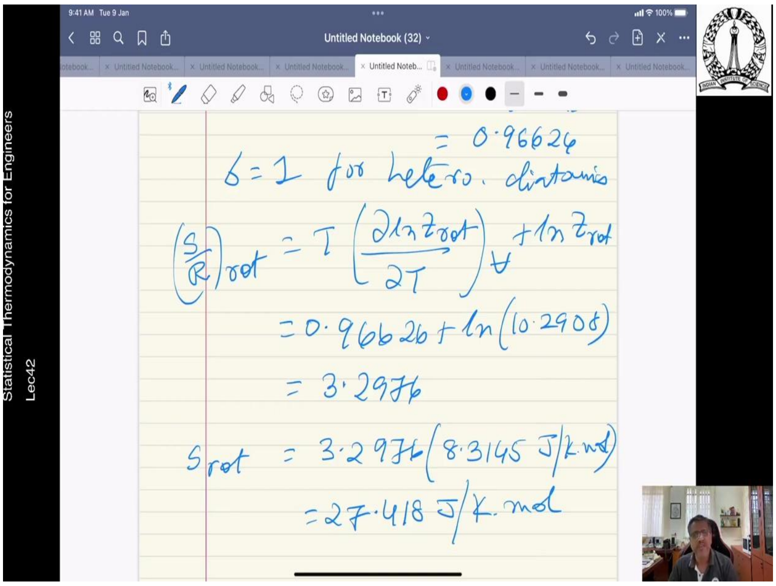

$$= 0.96626$$

$\sigma = 1$ for hetero. diatomics

$$\left(\frac{S}{R}\right)_{rot} = T\left(\frac{\partial \ln z_{rot}}{\partial T}\right)_V + \ln z_{rot}$$

$$= 0.96626 + \ln(10.2908)$$

$$= 3.2976$$

$$S_{rot} = 3.2976(8.3145\ J/K.mol)$$

$$= 27.418\ J/K.mol$$

So, the dimensionless entropy now becomes S by R rotation equal to T Z rotation divided by dt at constant v plus ln Z rotation which is equal to 0.96626 plus ln 10.2908. This gives rise to 3.2976. So, the entropy finally, you get the entropy as 3.2976 into 8.3145 J per kilo mode Kelvin mode which is comes out to the 27.418 joule per Kelvin mole. So, this actually tells you roughly the story of the full thing. So, there are there are more things that 1 can do for the symmetric and anti-symmetric.

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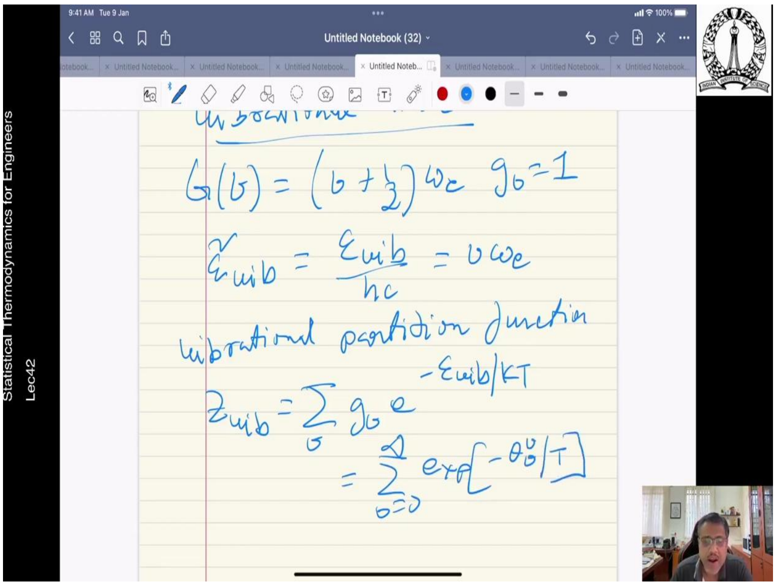

$$G(v) = \left(v + \frac{1}{2}\right)\omega_e \quad g_v = 1$$

$$\tilde{\varepsilon}_{vib} = \frac{\varepsilon_{vib}}{hc} = v\omega_e$$

vibrational partition function

$$Z_{vib} = \sum_v g_v e^{-\varepsilon_{vib}/KT}$$

$$= \sum_{v=0}^{\infty} \exp\left[-\theta_v^v / T\right]$$

Now, we go to the final thing which is the vibrational mode vibration mode, now, the vibrational energy levels of the degeneracies we already know. So, this Gb b plus half omega e where the degeneracy is equal to 1. So, again if we place the 0 of energy the ground vibrational level within the ground electronic state. So, therefore, we express the vibrational energy but harmonic oscillator we call that vibrational energy, harmonic oscillator is this this we have done now, countless number of times this is what it is.

So, the vibrational partition function therefore, becomes a function becomes Z vibrational summing over all the vibrational levels e. E vibrational divided by KT which is equal to summation will go to 0 to infinity exponential minus theta v v by T.

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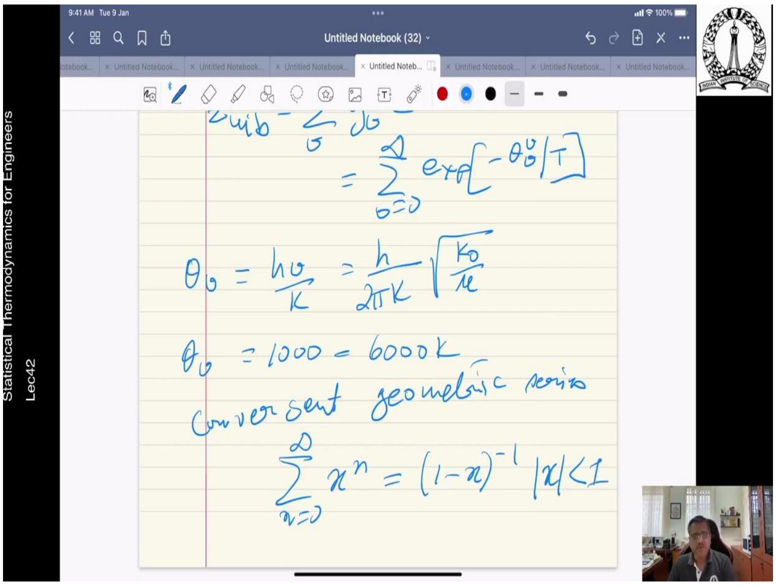

$$Z_{vib} = \sum_{\upsilon} g_{\upsilon}$$

$$= \sum_{\upsilon=0}^{\infty} \exp\left[-\theta_{\upsilon}^{\upsilon}/T\right]$$

$$\theta_{\upsilon} = \frac{h\upsilon}{K} = \frac{h}{2\pi K}\sqrt{\frac{K_0}{\mu}}$$

$$\theta_{\upsilon} = 1000 - 6000\,K$$

Convergent geometric series

$$\sum_{n=0}^{\infty} x^n = (1-x)^{-1} \quad |x|<1$$

So, the characteristic vibrational temperature therefore becomes hv by K which is equal to h by 2pi K K naught by mu. So, this we already know So, theta v (())(24:50) 10,000 to about 6000 Kelvin for full excitation. So, it is very difficult to you know expand this in a series but we can use convergent geometric series in this cases. So if you recall convergent geometric series rather than boiler series, geometric series in this case, which means summation say n equal to 0 to infinity, x to the power of n is 1 minus x 1 so long as the mod of x is less than 1.

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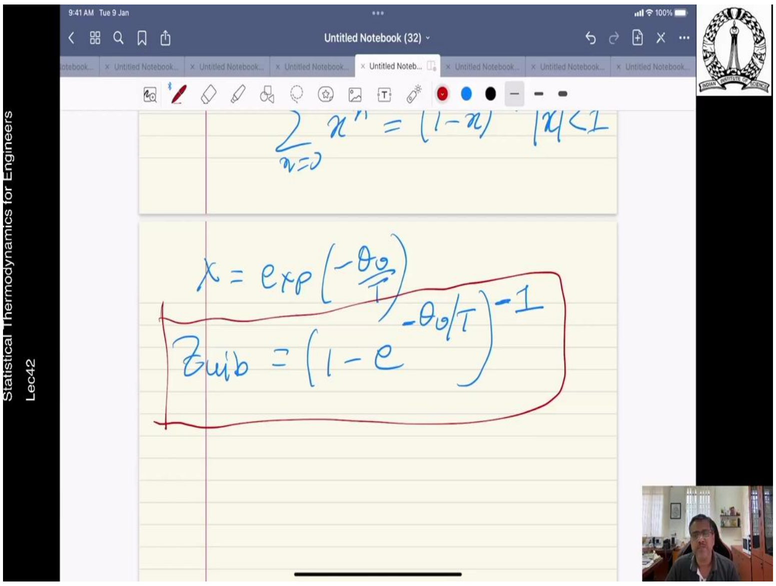
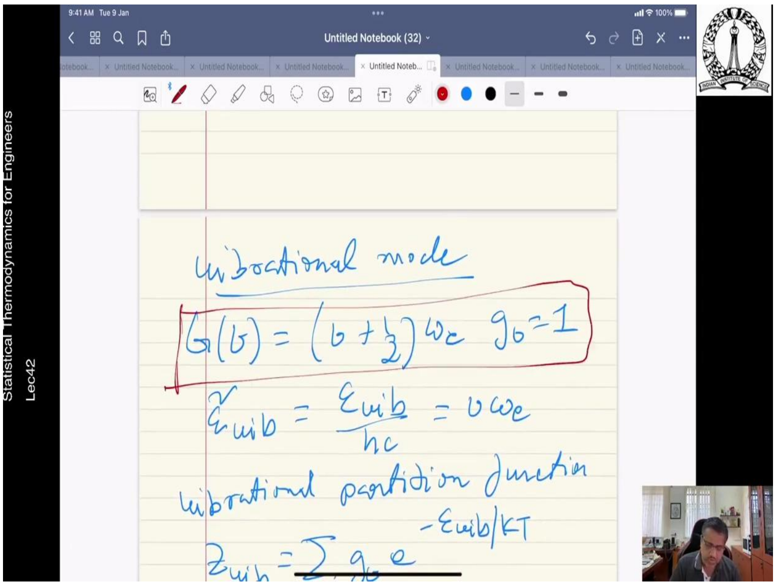


$$\sum_{n=0} x^n = (1-x)^{-1} \quad |x|<1$$

$$x = \exp\left(-\frac{\theta_{\upsilon}}{T}\right)$$

$$\boxed{Z_{vib} = \left(1 - e^{-\theta_{\upsilon}/T}\right)^{-1}}$$



vibrational mode

$$\boxed{G(v) = \left(v+\tfrac{1}{2}\right)\omega_e \quad g_0 = 1}$$

$$\tilde{\varepsilon}_{vib} = \frac{\varepsilon_{vib}}{hc} = v\omega_e$$

vibrational partition function

$$Z_{vib} = \sum g_v e^{-\varepsilon_{vib}/KT}$$

So, here of course, we can assume that our x is nothing but exponential minus theta v by T, because mod x is less than less than modulus of x is actually less than 1. So, from here we can obtain the vibrational partition function as Zv is 1 minus exponential theta v by t. We will look at it in a little bit more detail in the next lecture, then we will do the subsequent partial standard partial derivatives of the partition function with respect to temperature to evaluate the properties.

But so, but this is fairly fairly straightforward. We are now well versed with how to go about doing things only the 0 of energy is particularly important and that is what you need to protect for doing these types of calculations. So, we will finish this vibrational part of the partition function and use it. We well do a sample problem also. And then see basically complete a diatomic part diatomic gas part of this particular course. Thank you.