Statistical Thermodynamics for Engineers
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Lecture 54
Specific heats, Internal Energy through Vibrational and Ro-vibrational Energy Modes

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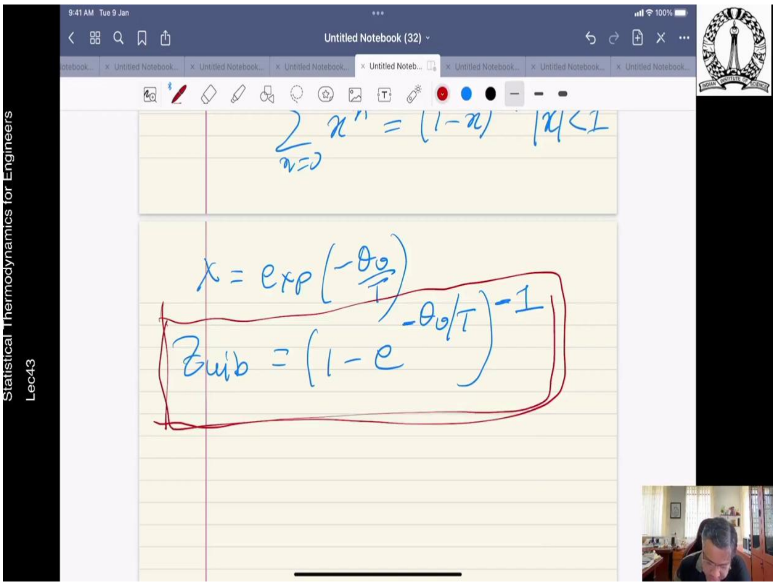

$$\sum_{n=0} x^n = (1-x) \quad |x|<1$$

$$x = \exp\left(-\frac{\theta_0}{T}\right)$$

$$\boxed{Z_{vib} = \left(1-e^{-\theta_0/T}\right)^{-1}}$$

Welcome to lecture number 43 of the Statistical Thermodynamics course, now, in this previously if you recall that we wrote that in the case of vibrational transition, the vibrational partition function is written in this particular form.

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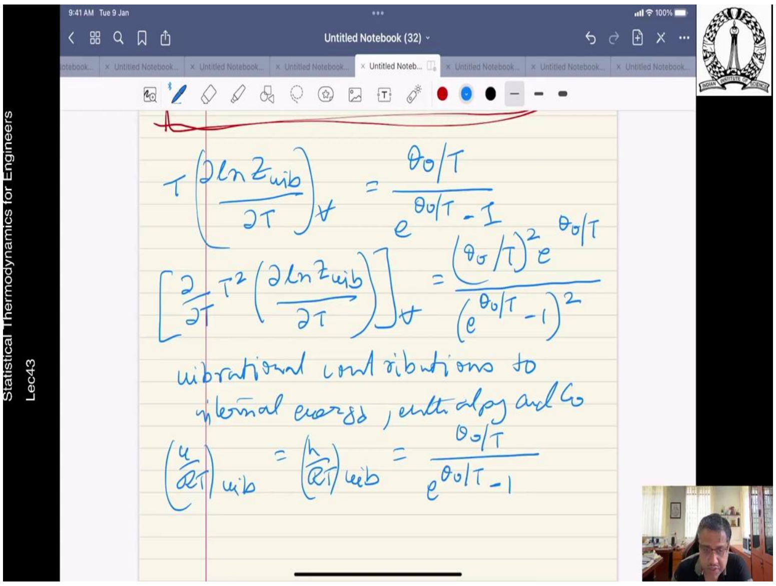
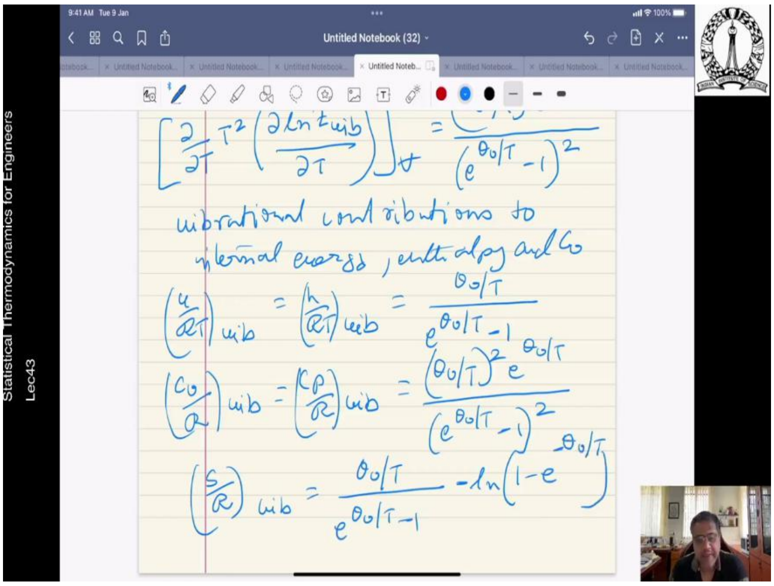


$$T\left(\frac{\partial \ln Z_{vib}}{\partial T}\right)_V = \frac{\theta_0/T}{e^{\theta_0/T}-1}$$

$$\left[\frac{\partial}{\partial T} T^2\left(\frac{\partial \ln Z_{vib}}{\partial T}\right)\right]_V = \frac{(\theta_0/T)^2 e^{\theta_0/T}}{\left(e^{\theta_0/T}-1\right)^2}$$

vibrational contributions to internal energy, enthalpy and C_v

$$\left(\frac{u}{RT}\right)_{vib} = \left(\frac{h}{RT}\right)_{vib} = \frac{\theta_0/T}{e^{\theta_0/T}-1}$$



$$\left[\frac{\partial}{\partial T} T^2\left(\frac{\partial \ln z_{vib}}{\partial T}\right)\right]_v = \frac{}{(e^{\theta_v/T}-1)^2}$$

vibrational contributions to internal energy, enthalpy and C_v

$$\left(\frac{u}{RT}\right)_{vib} = \left(\frac{h}{RT}\right)_{vib} = \frac{\theta_v/T}{e^{\theta_v/T}-1}$$

$$\left(\frac{C_v}{R}\right)_{vib} = \left(\frac{C_p}{R}\right)_{vib} = \frac{(\theta_v/T)^2 e^{\theta_v/T}}{(e^{\theta_v/T}-1)^2}$$

$$\left(\frac{S}{R}\right)_{vib} = \frac{\theta_v/T}{e^{\theta_v/T}-1} - \ln\left(1-e^{-\theta_v/T}\right)$$

Now, we can now to the two standard partial derivatives that we are will customed with right now on his T ln that vibrational T Constant v theta v by T exponential theta v T minus 1 then you have T square ln (())(00:59) by dt v theta v y T square T divided theta v by T minus 1 square. So, on this particular basis these are the two standard partial derivatives for the partition function. So, on the basis of this we can now calculate the vibrational contributions to internal energy, enthalpy and heat capacity to Cv.

So, u by RT the vibrational contribution is h by RT vibrational is equal to theta v by T divided by e theta v by T minus 1 then Cv by R vibrational is equal to CP by R vibrational is equal to theta v by T Square e theta v by T divided by e theta v by T minus 1 whole square. So, for the vibrational contributions to entropy, we have S by R vibrational is equal to theta v by T divided by e theta v by T minus 1 minus ln by 1 minus exponential theta v by T.

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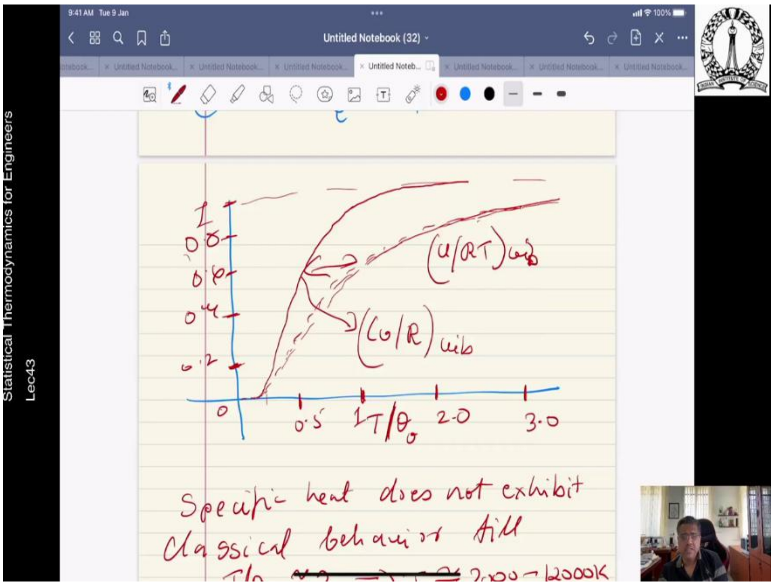
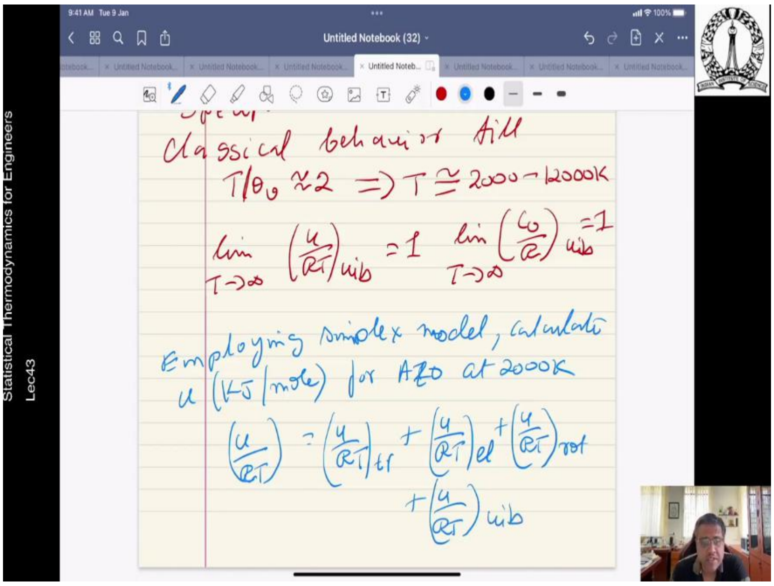


Specific heat does not exhibit classical behavior till



Classical behavior till

$T/\theta_v \approx 2 \Rightarrow T \cong 2000-12000K$

$\lim_{T\to\infty} \left(\frac{u}{RT}\right)_{vib} = 1 \quad \lim_{T\to\infty} \left(\frac{c_v}{R}\right)_{vib} = 1$

Employing simplex model, calculate u (KJ/mole) for AZO at 2000K

$$\left(\frac{u}{RT}\right) = \left(\frac{u}{RT}\right)_{tr} + \left(\frac{u}{RT}\right)_{el} + \left(\frac{u}{RT}\right)_{rot} + \left(\frac{u}{RT}\right)_{vib}$$

The significance so, the significance you can see this vibrational significance of this vibrational contribution. So, thermodynamic properties can be seen in which if you plot if I generate a plot which actually would show this in a little bit more details, so, this is a T by theta v and this will be the vibrational contributions to whatever let us say internal energy or specific heat. So, initially the contribution so, you can mark certain things like 0.5, 1 let us say 2 doing something like that. So, initially for a part there is no contribution. So, then it starts to pick up a little bit and then of course, this goes like this.

So, this is like u by RT vibrational they can see the upswing and if we mark the scale if this is 0, so, this is about 0.2 0.4 0.6, 0.8 about 1 so, it is below 1 of course, so, it is like that, Cv is shows a little bit of a faster rise like this excessive dose, so, this is like Cv, by R vibration, so, as you can see that specific heat does not display classical behaviour until at least we have specific heat does not exhibit classical behaviour till T by theta v is equal to 2 which basically corresponds to T almost equal to 2000 to 12000 kelvin in other words smooths excitation of the vibrational mode to replicate the classical results will be in the limit T approaches infinity u by RT vibrational is equal to 1 and then limit T approaches infinity Cv by R vibrational is equal to 1.

So, it requires very high temperature. So, as you can see from this particular figure that you know the classical limit of internal energy internal energy is delayed compared to the specific heat this is the delay. Hence, in contrast to translational and rotational mode vibrational mode is typically only partially are excited near room temperature. So, waiting two partition prints while the two partition principle applies at sufficiently high temperatures. So, these predictions will be completely inappropriate for vibrating molecules at 300 to say it with 500 Kelvin.

So, exceptions are of course there but so, you can understand that this is what it is, this is what it is it is only activated closer to about 3000 Kelvin. So, let us do a simple math problem now. So, employing simplex model, calculate internal energy u kilo joule by mole for AlO at 2000 kelvin. So, now we know already what the internal energy will be composed off. So, it will be like u by RT is equal to u by RT translational plus u by RT electric electronic plus u by RT rotational plus u by RT vibration.

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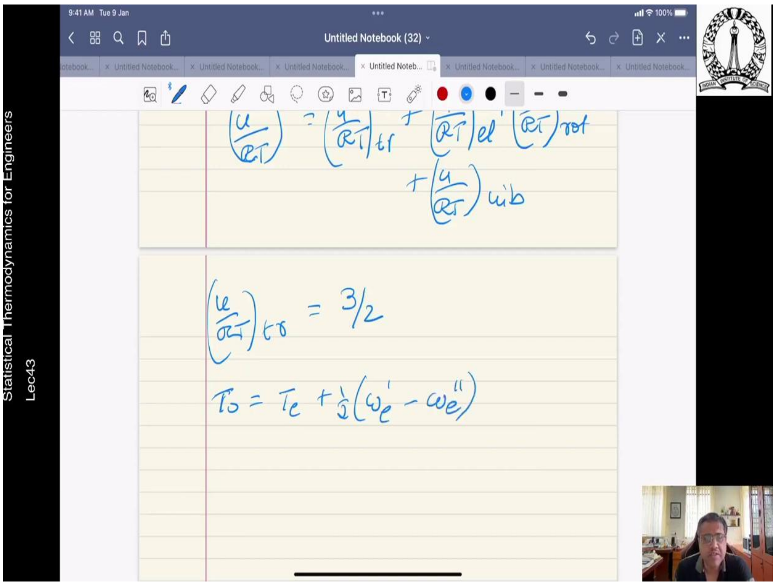
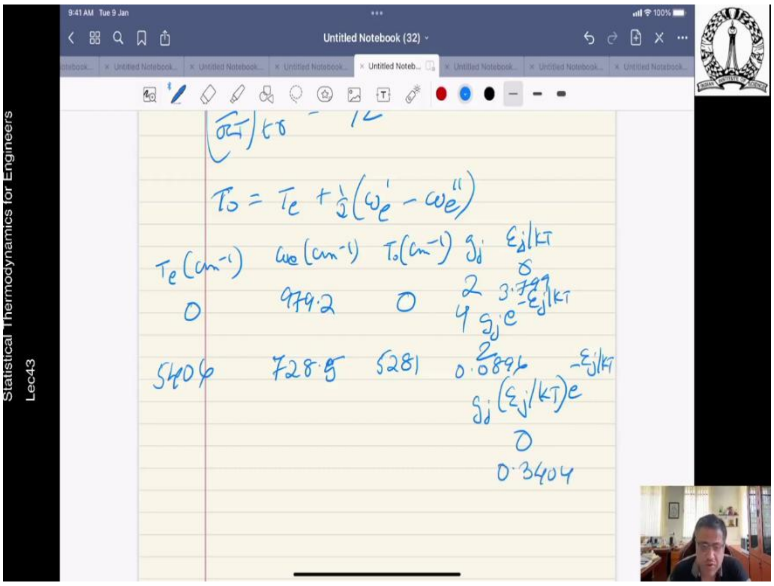


$$\left(\frac{u}{RT}\right) = \left(\frac{u}{RT}\right)_{tr} + \left(\frac{u}{RT}\right)_{el} + \left(\frac{u}{RT}\right)_{rot} + \left(\frac{u}{RT}\right)_{vib}$$

$$\left(\frac{u}{RT}\right)_{tr} = 3/2$$

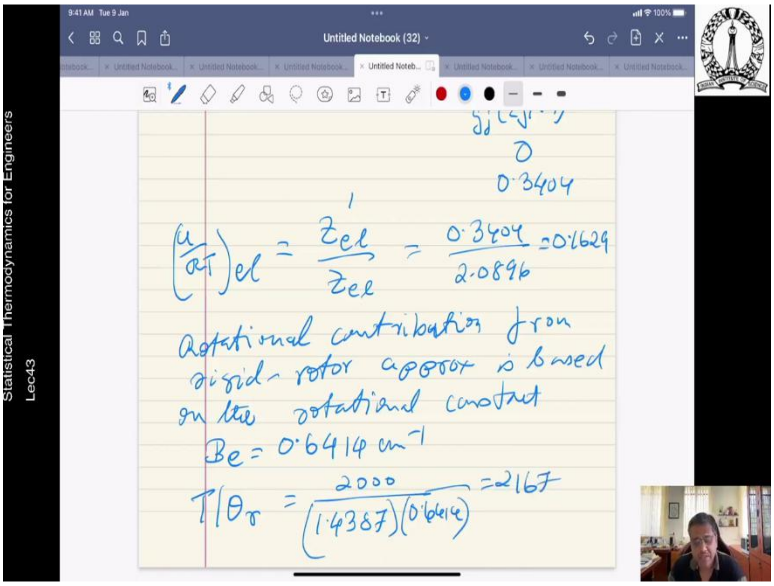
$$T_0 = T_e + \frac{1}{2}(\omega_e' - \omega_e'')$$



$\left(\frac{u}{RT}\right)_{tr}$

$$T_0 = T_e + \frac{1}{2}(\omega_e' - \omega_e'')$$

T_e (cm^{-1})	ω_e (cm^{-1})	T_0 (cm^{-1})	g_j	ε_j/kT	$g_j e^{-\varepsilon_j/kT}$	$g_j(\varepsilon_j/kT)e^{-\varepsilon_j/kT}$
0	979.2	0	2	0	2	0
5406	728.5	5281	4	3.799	0.0896	0.3404



$$\left(\frac{u}{RT}\right)_{el} = \frac{z_{el}'}{z_{el}} = \frac{0.3404}{2.0896} = 0.1629$$

Rotational contribution from rigid-rotor approx is based on the rotational constant

$B_e = 0.6414$ cm^{-1}

$$T/\theta_r = \frac{2000}{(1.4387)(0.6414)} = 2167$$

So, the translational component as we all know that u buy RT translational is equal to 3 by 2. The Electronic contribution obviously requires that you evaluated from the data. So, there is an appendix k2 for example, k dot 2 where you can calculate the first two energy levels. And again the next energy level is very high as a result of that you do not evaluate, we do not go up to that level. And because of our choice of 0 of energy, we convert from the T formulation to the T naught formulation. So, recall that T naught is equal to Te plus half omega e prime minus omega e double prime.

So, if we now look at a table this is a sample table, so say Te given a centimetre inverse, omega e centimetre inverse once again T naught centimetre inverse gj, then Ej by kT, then gj e to Ej by kT and then of course, gj into Ej by kT. Exponential Ej by kT. So, this is 0. This is 979.2. T naught 0, the DeGeneres is equal to 1 Ej is equal to 0 and then gj by this is equal to 2 and this is equal to 0 once again then of course the second one is 5046. So, now you convert this is a 728.5 T naught now will be equal to 5281 gj on the other hand is 4 this Ej by kT is 3.799 and then gj into this is.0896 And lastly, this will be 0.3404.

So, employing this table now we can obtain the corresponding electronic contribution. So, therefore, r RT by el the next energy level is too high so, we are neglecting it essentially it is not activated or the probability is very low as you can see it kind of gets down it kind of decreases in an abnormal way as we go higher and higher. So, let us look at it. So, this is el. So, that is 0.3404 divided by 2.0896 which is equal to 0.1629 this is what we get the rotational contribution from the rigid rotor approximation the rotational contribution from you know, rigid rotor approximation is based on the rotational constant which is Be which is given as 0.6414 centimetre inverse as a result of that T by theta r remember this this is 2000 is the temperature divided by 14387 multiplied by 0.6414 which is given as 2167.

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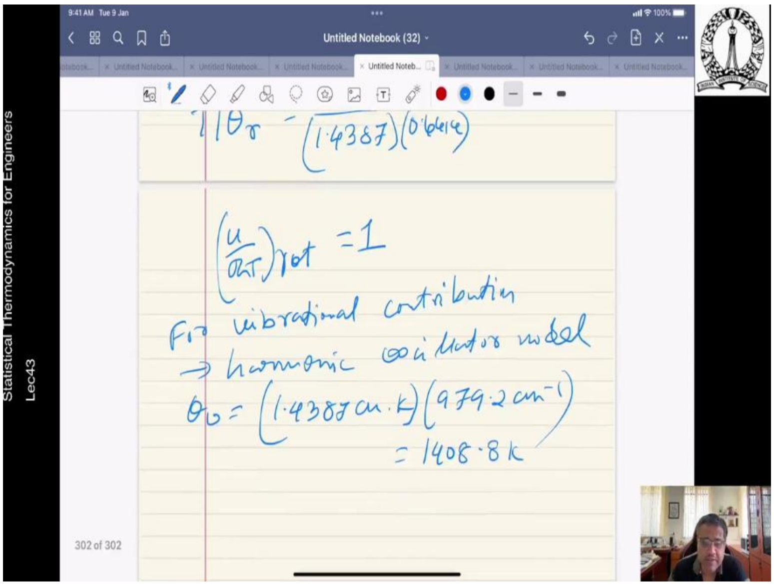


$T/\theta_r = \frac{}{(1.4387)(0.6414)}$

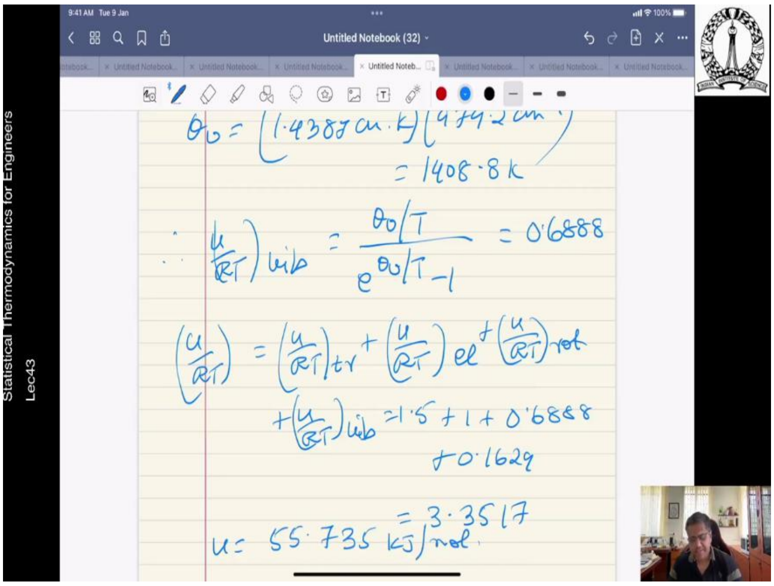
$\left(\frac{u}{RT}\right)_{rot} = 1$

For vibrational contribution

→ harmonic oscillator model

$\theta_v = (1.4387 \text{ cm}\cdot\text{K})(979.2 \text{ cm}^{-1})$

$= 1408.8 \text{ K}$



$$\theta_v = (1.4387\ \text{cm}\cdot\text{K})(979.2\ \text{cm}^{-1}) = 1408.8\ \text{K}$$

$$\therefore \left(\frac{u}{RT}\right)_{vib} = \frac{\theta_v/T}{e^{\theta_v/T}-1} = 0.6888$$

$$\left(\frac{u}{RT}\right) = \left(\frac{u}{RT}\right)_{tr} + \left(\frac{u}{RT}\right)_{el} + \left(\frac{u}{RT}\right)_{rot} + \left(\frac{u}{RT}\right)_{vib} = 1.5 + 1 + 0.6888 + 0.1629 = 3.3517$$

$$u = 55.735\ \text{kJ/mol}$$

So, that is the corresponding this. So, we find now that u by RT rotation is equal to 1 employ all these things, finally, the vibrational contribution we again use the harmonic oscillator to for which theta v is equal to 1.4387 let me do kelvin 979.2 centimetre inverse, which is 1408.8 Kelvin. So, now, therefore, u by RT vibrational equal to theta v by T divided by theta e exponential of theta v minus 1 which is equal to 0.6888 Now, if we back all these things together u by RT visible to u by RT translational plus u by RT electronic plus u by RT rotational plus u by RT vibration. So, this is given as in our summation 1.5 plus 1 plus 0.6888 plus 0.1629 given us 3.3517. So, the final calculation of internal energy therefore will be multiplied by RT it will be 55 735 kilojoules per mole.

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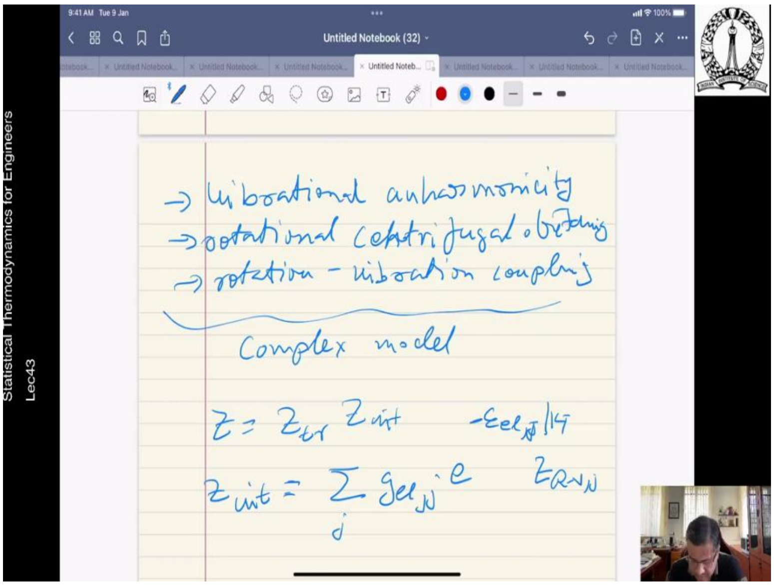
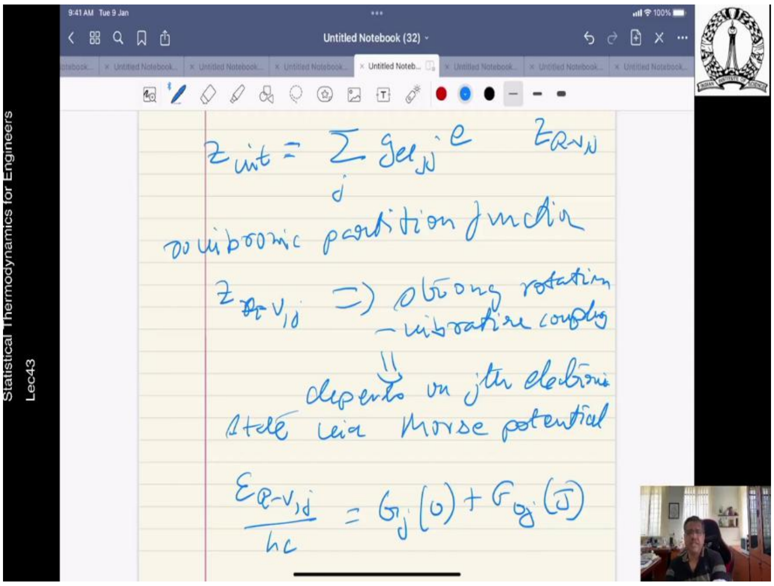


→ vibrational anharmonicity
→ rotational centrifugal stretching
→ rotation - vibration coupling

Complex model

$$Z = Z_{tr} Z_{int}$$

$$Z_{int} = \sum_j g_{el,j}\, e^{-\varepsilon_{el,j}/kT}\, Z_{R-V,j}$$



$$Z_{int} = \sum_j g_{el,j} \, e \quad Z_{R-V,j}$$

ro vibronic partition function

$$Z_{R-V,j} \Rightarrow \text{strong rotation -vibration coupling}$$

$\Downarrow$ depends on jth electronic state via Morse potential

$$\frac{\varepsilon_{R-V,j}}{hc} = G_j(0) + F_{0j}(J)$$

So, that is interesting. So, this gives you a nice insight on how to calculate the whole thing. So, far what we have done is that we have been calculating the thermodynamic properties of a diatomic molecule, we have assumed complete separation of the energy modes and in reality of course, accurate calculations will be required that a simplex model is replaced by the more complex combined rotation and vibration in other words, we should compare the effect of vibrational and harmonicity. So, what we are missing vibrational and harmonicity then rotational centrifugal stretching then of course rotation vibration coupling in other words we need what we call a single complex model of its model.

Furthermore, the controlling mode parameters might not be associated solely with ground electronic states especially for molecules with low lying upper electronic levels. So, in this case a rigorous more rigorous expression for the partition function is given as Z, Z translation into Z internal the internal partition function is now translational part of this the same it is j gel j exponential minus el j by kT to ZRv comma j. So, this is the electronic part and that is the row vibrational part. So, now, what we what we see over here is that the Ro-vibromic partition function which is given as a little capital Rv comma j implies strong rotation vibration coupling it explicitly depends on the jth electronic state via the influence of its nodes potential on both the vibrational and rotational energy nodes.

So, it depends on jth electronic level electronic state via the Morse potential which affects both the rotational and the vibrational modes. In other words, the Ro-vibrational energy that ERv the Ro-vibromic energy rather j by hc would be equal to something like that it depends on the which electronic state you are in and the electronic state is important therefore, this is J see it is always affected by the identity of its associated electronic energy mode. As a result, this invariably requires numerical computations to probably evaluate the partition functions, there are many numerical strategies which are listed in the gen of tables appendix e of the book.

So, the idea is now this is a rigorous model because it depends on that associated electronic state. So, the thermodynamic properties would be considered to be simplified if the couple rotational modes to be separated from electronic energy.

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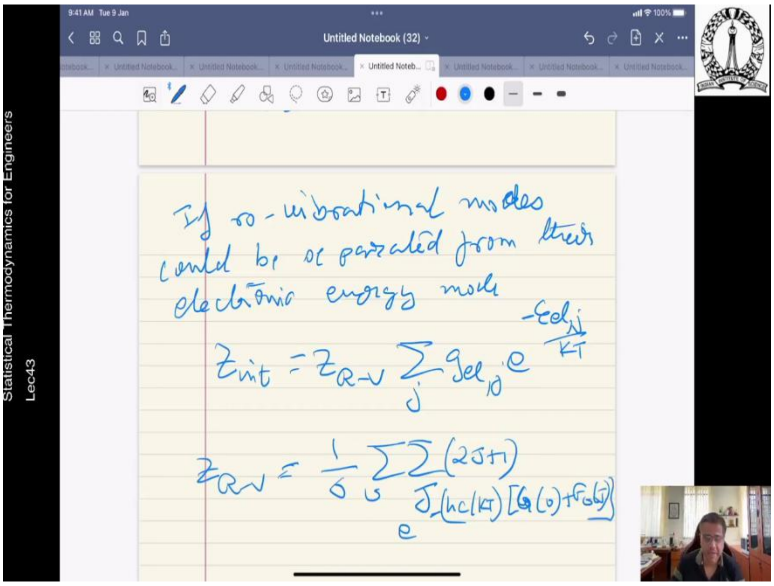
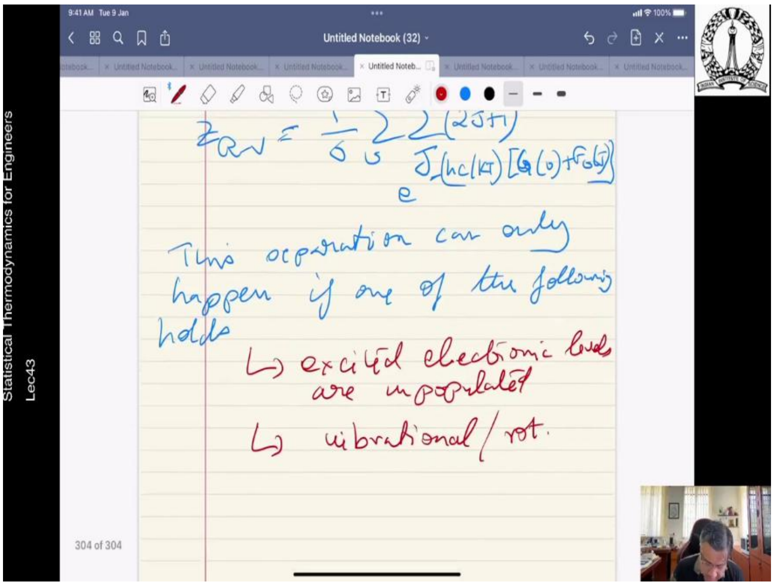


If ro-vibrational modes could be separated from their electronic energy mode

$$Z_{int} = Z_{R-V} \sum_j g_{el,j} \, e^{-\epsilon_{el,j}/kT}$$

$$Z_{RV} = \frac{1}{\sigma} \sum_v \sum_J (2J+1) \, e^{-(hc/kT)[G(v)+F_v(J)]}$$

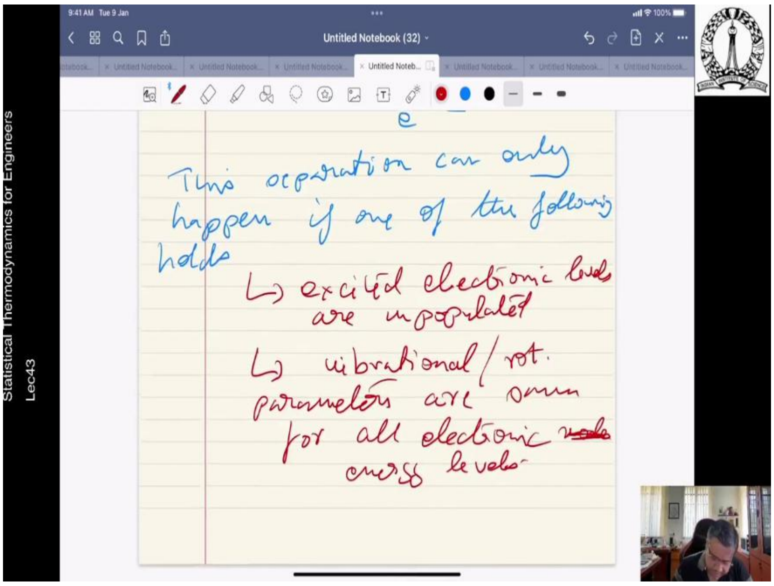


$$Z_{RV} = \frac{1}{\sigma} \sum_v \sum_J (2J+1) \, e^{-(hc/kT)[G(v)+F_v(J)]}$$

This separation can only happen if one of the following holds

↳ excited electronic levels are unpopulated

↳ vibrational / rot.



e

This separation can only happen if one of the following holds

↳ excited electronic levels are unpopulated

↳ vibrational / rot. parameters are same for all electronic ~~mode~~ energy levels.

So, if the rotational the Ro-vibrational modes if Ro-vibrational modes would be separated from their electronic modes electronic energy mode. So, this gives you this is internal This is R Ro-vibrational and it is summed over all j electronics j exponential electronic j divided by kT whether now the Ro-vibrational counterpart will be given as 1 over sigma summing over b and j, 2j plus 1 now let me write all these are within the summation still minus hc by kT and multiplied by G, v plus fv j depends on the vibrational that this separation could be affected if this separation can only happen if to one of the following holds this separation and only happen if one of the following holds.

So, these will be like the excited electronic levels are unpopulated basically you are taking out which electronic mode out of the picture and the second one is that the vibrational rotational parameters are essentially the same and one of the two vibrational slash rotational parameters are letters are same all electronic modes either one of these two all-electronic energy levels, so, the most common scenario first is the presumption of sufficiently low temperature. So, that the entire molecular population is really the ground in a trust.

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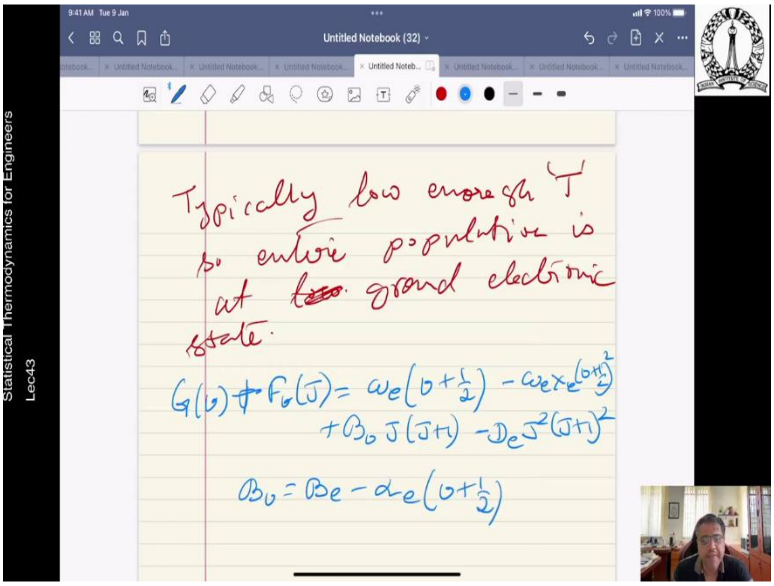
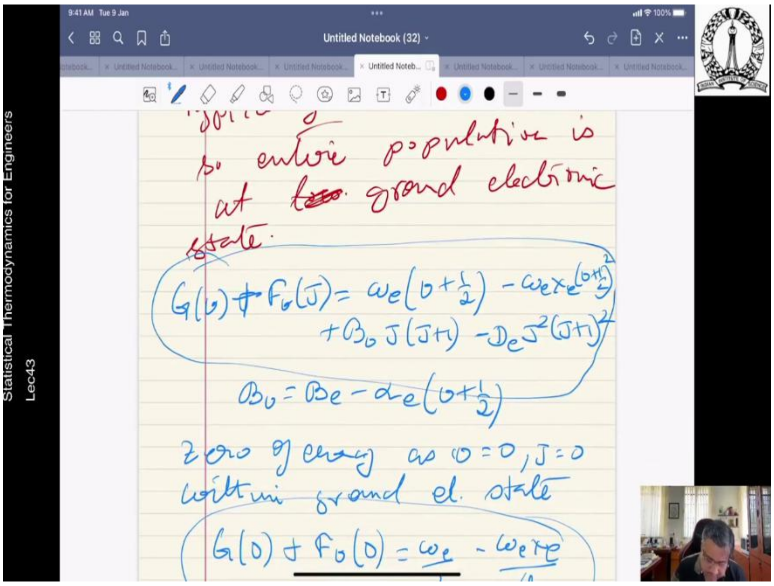


Typically low enough 'T'
so entire population is
at ~~the~~ ground electronic
state.

$$G(v) + F_v(J) = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + B_v J(J+1) - D_e J^2(J+1)^2$$

$$B_v = B_e - \alpha_e\left(v+\frac{1}{2}\right)$$



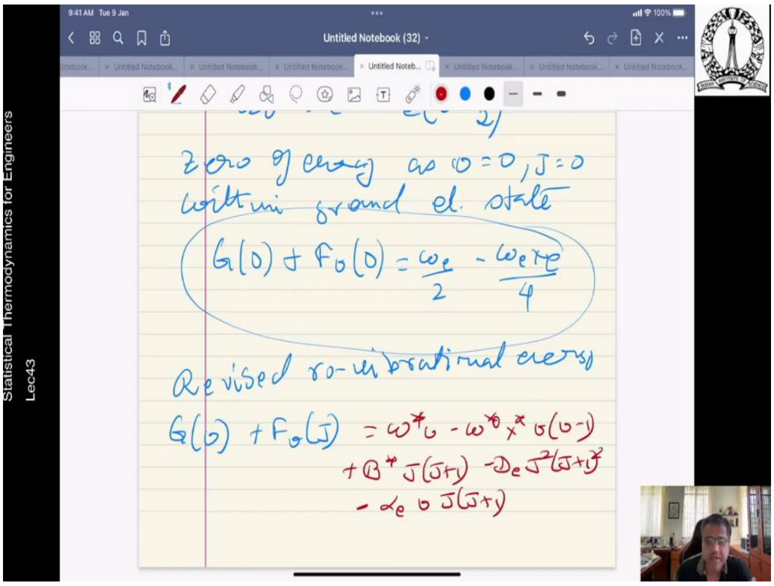
so entire population is
at ~~the~~ ground electronic
state.

$$G(v) + F_v(J) = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + B_v J(J+1) - D_e J^2(J+1)^2$$

$$B_v = B_e - \alpha_e\left(v+\frac{1}{2}\right)$$

Zero of energy as $v = 0, J = 0$
within ground el. state

$$G(0) + F_0(0) = \omega_e - \omega_e x_e$$



Zero of energy as $v = 0, J = 0$
within ground el. state

$$\boxed{G(0) + F_0(0) = \frac{\omega_e}{2} - \frac{\omega_e x_e}{4}}$$

Revised ro-vibrational energy

$$G(v) + F_v(J) = \omega^* v - \omega^* x^* v(v-1) + B^* J(J+1) - D_e J^2 (J+1)^2 - \alpha_e v J(J+1)$$

So, this happens typically if we choose typically low enough temperature so, entire population is at on ground electronic state for some unstable molecules. It is may be a little bit different. So, if we combine now, all of these things together constitute the semi-rigorous model for the partition function, translation and electronic contributions follow the follow those for the simplex model evaluation of the Ro-vibrational contribution is more complicated and this is what we can write. Therefore, G what we need to do is G v plus F v J equal to omega e plus half omega xe plus half square plus Bv J, J plus 1 minus De J square J plus 1 whole square. Bv is equal to Be minus alpha e plus half.

So, you taking the 0 of energy if we take the 0 energy and 0 of energy as equal to 0 j equals to 0 within ground electronic state we have G naught 0 plus F v 0 omega e by 2 omega xe by 4 now if we subtract this from the previous version which is subtract this side from this side we yield the revised Ro-vibrational energy and which is G v plus F v J is equal to omega star make a star omega star, omega star, x star v into minus 1 plus B star J to J plus 1 e squared J plus 1 whole squared alpha e v J into J plus 1.

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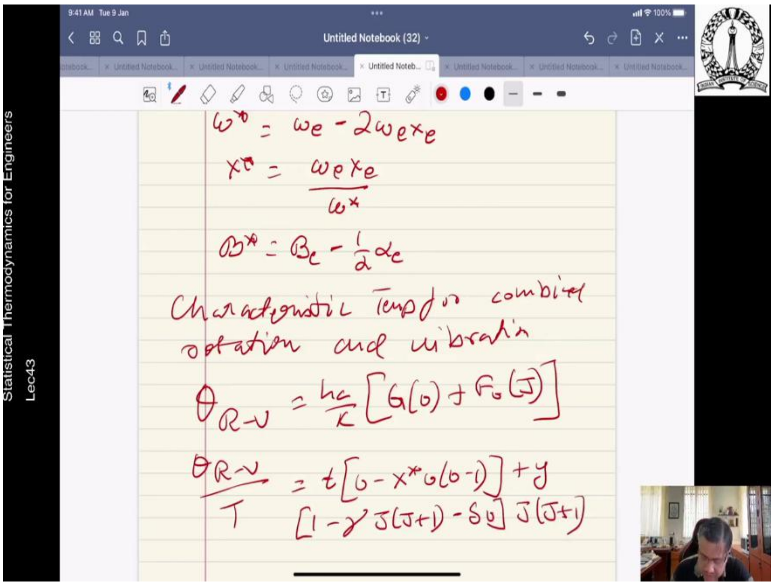


$$\omega^* = \omega_e - 2\omega_e x_e$$

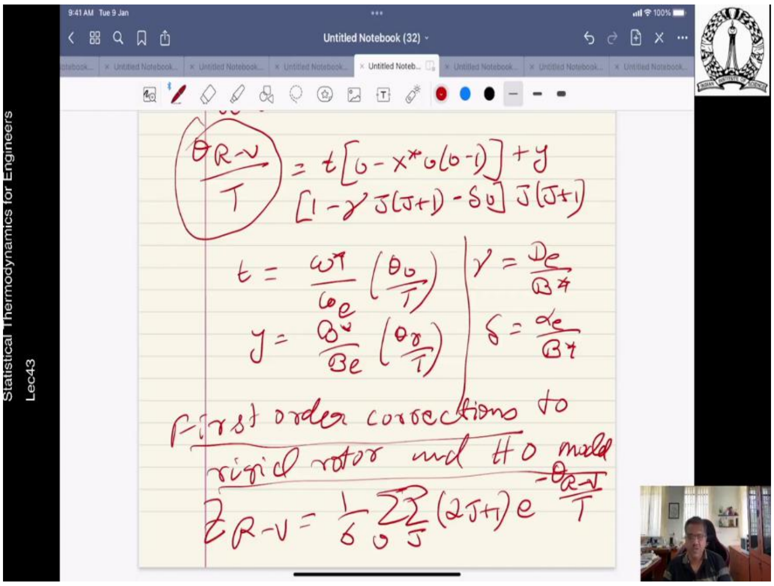
$$x^* = \frac{\omega_e x_e}{\omega^*}$$

$$B^* = B_e - \frac{1}{2}\alpha_e$$

Characteristic Temp for combined rotation and vibration

$$\theta_{R-V} = \frac{hc}{k}\left[G(v) + F_v(J)\right]$$

$$\frac{\theta_{R-V}}{T} = t\left[v - x^* v(v-1)\right] + y\left[1 - \gamma J(J+1) - \delta v\right] J(J+1)$$



$$\boxed{\frac{\theta_{R-V}}{T}} = t\left[v - x^* v(v-1)\right] + y\left[1 - \gamma J(J+1) - \delta v\right] J(J+1)$$

$$t = \frac{\omega^*}{\omega_e}\left(\frac{\theta_v}{T}\right) \qquad \gamma = \frac{D_e}{B^*}$$

$$y = \frac{B^*}{B_e}\left(\frac{\theta_r}{T}\right) \qquad \delta = \frac{\alpha_e}{B^*}$$

First order corrections to rigid rotor and HO model

$$z_{R-V} = \frac{1}{\sigma}\sum_v \sum_J (2J+1) e^{-\frac{\theta_{R-V}}{T}}$$

So, omega star equal to omega e minus 2 omega e into xe, x Star is equal to omega e xe by omega star and B star is equal to Be minus half alpha e. So, we can also define a characteristic temperature for a row by combined and rotation and vibrating which means so, that we can write it as R v equal to hc by K, G v plus Fv J. So, now, if you write it in a proper form divided by T this will be t v minus x star v into v minus 1 plus y into So, this comes with y gamma change to J plus 1 minus delta v we will write all about all the symbols are in a bit this what it is and you write that t is equal to omega star omega e theta v by T and y is equal to a Star Be, theta r by T you can understand that these all comes from rotation on the vibrational.

So, gamma is equal to De by B star delta is equal to alpha e by B star. So, these equations that we found are basically first order corrections to the rigid rotor and the harmonic oscillator model. So, these are first order corrections to rigid rotor and harmonic oscillator model equals as usual Omega e Omega e x e d e alpha e and D are obtained from spectroscopic data. So, using this you can now calculate what will be the theta R v by T.

Now, using all these things you can now evaluate the partition function or you can evaluate the partition function which is written as this finish this by writing this R v 1 over sigma double summation v J, 2 J plus 1 exponential theta R v by T that is the partition function we will in the next class we will see that how this partition function can be broken up into two using the Euler fashion Euler Maclaurin fashion, but this is what it is.

So, these are all first order corrections to the rigid rotor and the harmonic oscillator model and this is what we are going to use to calculate the remainder of the parameters. So, and we will see that how this can be applied to find out maybe you know, stuff like entropy and once again, internal energy and stuff like that. But this is the process this is the procedure that one should follow when you go for a rigorous model.