Fundamentals of Statistical Thermodynamics

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Lecture: 41

Mean Energies (Applications)

Welcome back. We have been discussing Mean Energies and follow-up of Mean Energies; we started discussing Heat Capacities. Basically, we discussed the applications of Mean Energies in further discussing Heat Capacities because we connected Heat Capacity at constant volume with the temperature derivative of Mean Energy. Mean Energy, which we discussed a couple of lectures before, is given by minus 1 by q^M del q by del β at constant volume. Where this m mode represents translational, rotational, vibrational, and electronic. And then we discussed in detail how to connect Heat Capacity at constant volume with the temperature derivative of Mean Energies.

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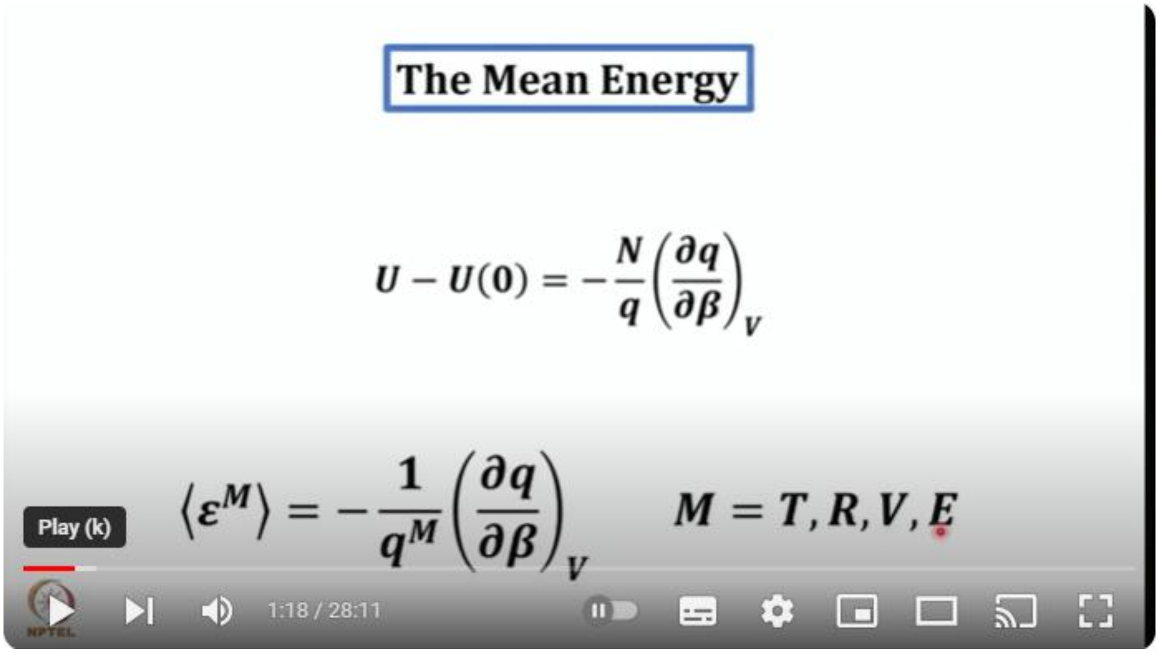

The Mean Energy

$$U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$\langle \varepsilon^M \rangle = -\frac{1}{q^M}\left(\frac{\partial q}{\partial \beta}\right)_V \qquad M = T, R, V, E$$

And we concluded that for a gas at room temperature, the translational contribution to constant volume Heat Capacity is 3 by 2 R. And then we discussed rotational contribution for a linear rotor is equal to R, and for a non-linear rotor, it is 3 by 2 R. For each normal mode of vibration, the contribution is R provided all the modes are fully active. And based upon that discussion, we came up with this expression that is the constant volume molar Heat Capacity is represented by 1 by 2 into 3 plus ν_R^* plus 2 ν star R.

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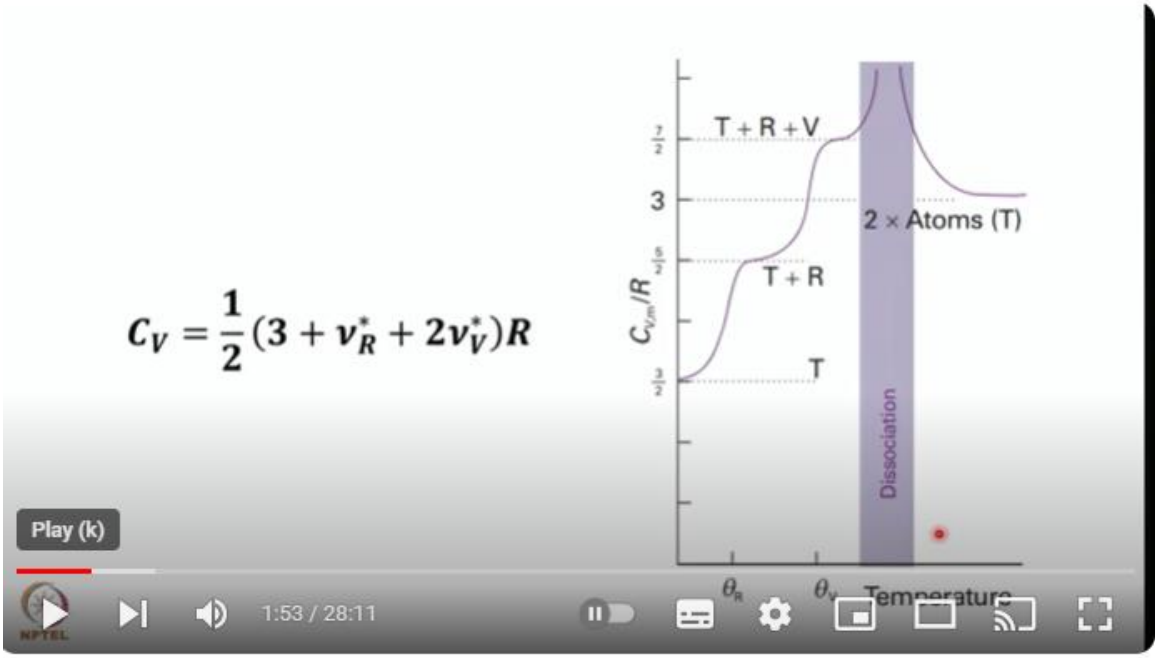

$$C_V = \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$$

And just to revisit that ν_R^* is equal to 2 when the rotor is linear, and it is equal to 3 when the rotor is non-linear. And ν_V^* is equal to 1 for each normal mode of vibration. This equation gives a very good estimate of constant volume Heat Capacity as long as the temperature is much above its relevant or related characteristic rotational temperature or vibrational temperature. And if the temperature difference is very huge, for example, if the vibrational mode is not active, that means if the experimental temperature is much lower than the characteristic vibrational temperature, then you can even put ν_V^* equal to 0. After that, we discussed this plot that initially 3 by 2 R contribution is there, and for a linear rotor as the temperature increases, the full R contribution is added.

So, 3 by 2 plus 1 is 5 by 2 R, and then you further increase the temperature, and when the temperature is much higher than the characteristic vibrational temperature, another R will add up. So, you have 7 by 2 R further increase in temperature leads to dissociation of the molecule, and after dissociation, a diatomic molecule will form 2 atoms, and each atom will have translational degree of freedom which is 3 by 2 R. So, 3 by 2 into 2 is equal to 3 R, this I have shown for a very simple diatomic molecule. Now, suppose if you are given an exercise to make a similar plot for a linear triatomic molecule or a non-linear triatomic molecule, you should be able to make similar plots. You have to take into account whether the molecule is linear or the molecule is non-linear because the rotational contribution will be decided by that, and then after the dissociation again you have to explain your answer with justification. Now, let us discuss an application: estimate the molar constant volume heat capacity of water vapor at 100 °C.

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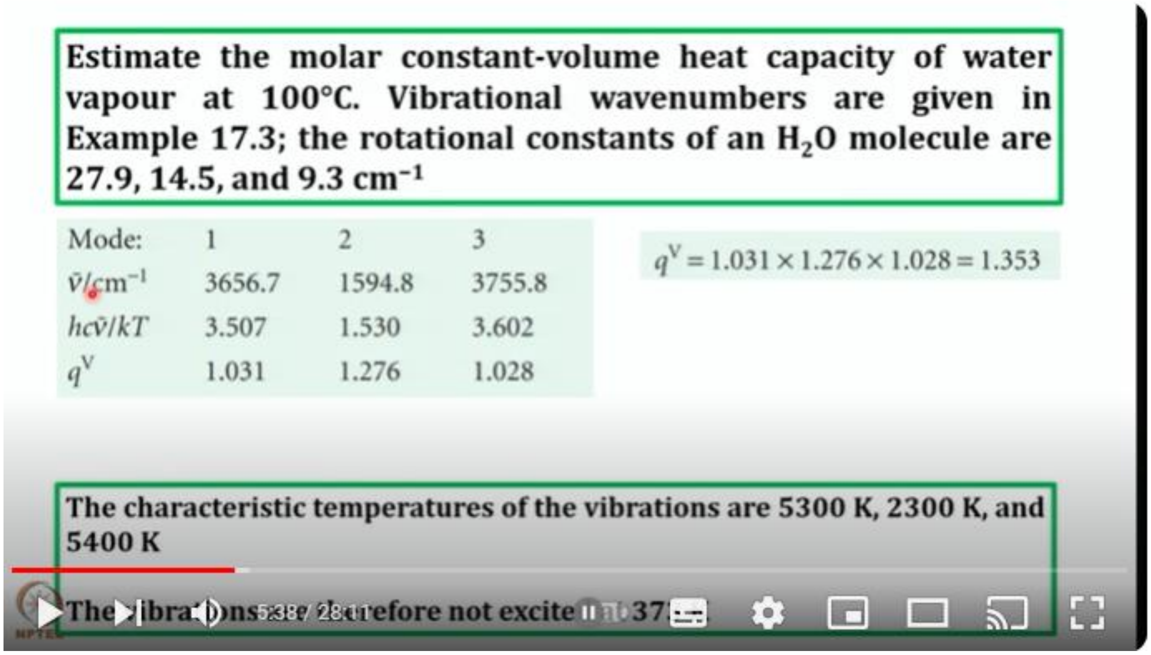

Estimate the molar constant-volume heat capacity of water vapour at 100°C. Vibrational wavenumbers are given in Example 17.3; the rotational constants of an H_2O molecule are 27.9, 14.5, and 9.3 cm^{-1}

Mode:	1	2	3
$\tilde{\nu}/\text{cm}^{-1}$	3656.7	1594.8	3755.8
$hc\tilde{\nu}/kT$	3.507	1.530	3.602
q^V	1.031	1.276	1.028

$q^V = 1.031 \times 1.276 \times 1.028 = 1.353$

The characteristic temperatures of the vibrations are 5300 K, 2300 K, and 5400 K

The vibrations [illegible] therefore not excite [illegible] 37

Vibrational wave numbers are given which is some example, but these vibrational wave numbers you can see here I have included that in the table. Now, once the vibrational wave numbers are there, as I will discuss with you, you can calculate the vibrational temperature. Rotational constants are also given: 27.9, 14.5, and 9.3 cm^{-1}, all right. Now, if you carefully look at the problem statement, it says estimate; it does not say calculate. It's just an estimation, that means, an approximate number for constant heat capacity, and if I go back, you can use this expression to estimate. What you need to know is ν_R^* , what should be the value of ν_R^* , and what should be the value of ν_V^* , ok. So, what we have is CV_m is equal to 1 by 2 into 3 plus ν_R^* plus 2 ν_V^* multiplied by R.

So, this is the constant volume heat capacity per mole. Now, first of all, we need to judge what will be the values for ν_R^* and what will be the values for ν_V^* . Let us talk about first vibration because generally, we say that the vibrational energy levels are far separated. So, their contribution may be very less. First of all, the first step is to calculate the characteristic vibrational temperature.

How do you calculate characteristic vibrational temperature? Use h c ν bar is equal to k theta v. We are interested in finding out the value of theta v. From the knowledge of Planck's constant, speed of light, wave number, and Boltzmann constant. Now, you can look at this table, the wave numbers: first one 3656.7, second one 1594.8, and third, this is water. Water is a non-linear molecule. So, therefore, normal modes of vibration are 3n minus 6, which is 3 into 3n is 3 9 minus 6 is equal to 3. And these 3 normal modes of vibration take place at 3656.7, 1594.8, and 1594.8.

Now, by using this expression, we can calculate 3 vibrational temperatures. The characteristic vibrational temperatures by using this method turn out to be 5300, 2300, and 5400 K. These are roundabout figures. So, you see 5300 correspond to 3656.7. Now, 5400 correspond to 3755.8. The higher the value of the wave number, the higher is the vibrational temperature. But if you look at the lowest wave number 1594.8 is the lowest wave number corresponding to that the characteristic vibrational temperature is 2300 K and the experimental temperature is 373 K, 100 °C. 2300 is much much higher than 373 K. So, I can write that the temperature which is 373 K is much much less than the vibrational temperature, even for the normal mode which is the lowest in wave number. So, automatically then the wave numbers which are higher that those are ruled out.

So, that means vibrations are not excited at 373 K simply because the temperature, which is 373 K, is much much lower than the characteristic vibrational temperature. So, we do not need to worry about the vibrational contribution to constant molar volume heat capacity. Now, that means I can write ν_V^* I will put to be 0 because the vibrations are not active. Now, we also have rotational constants given water non-linear molecule it can, it is a triatomic molecule it can undergo rotational motion and use h c b is equal to k theta r. That means this rotational temperature theta R is h c B upon k b is h cross by 4 pi c I this all we have discussed earlier. And now if you look at the rotational constants given 27.9, 14.5, 9.3 what I will do is I will first calculate the rotational temperature for the highest rotational constant. Because if the characteristic rotational temperature corresponding to the highest rotational constant is much lower than the experimental temperature then the other two rotational constants are automatically covered. So, the strategy here should be first you calculate corresponding to 27.9 when you calculate corresponding to 27.9 the rotational temperature comes to 40 k. So, that means if I put 40 k experimental temperature is 373 K of course, this is much higher. That means t is much higher than theta R this is corresponding to the highest rotational constant. That means rotations are fully active all three rotational constants will give a characteristic rotational temperature which is much lower than the experimental temperature. That means all these rotational modes are fully excited. So, that means what value should I put ν_R^* it is a non-linear molecule I will put a value of 3. We are using this expression CV_m is equal to 1 by 2 3 plus ν_R^* plus 2 ν_V^* into R. As we just discussed vibrations are not active at all at that temperature right the vibrational contribution will be 0 ν_V^* is equal to 0 ν_R^* we just discussed all three rotations or rotational motions around three axis is fully active therefore, this value ν_R^* will be equal to 3.

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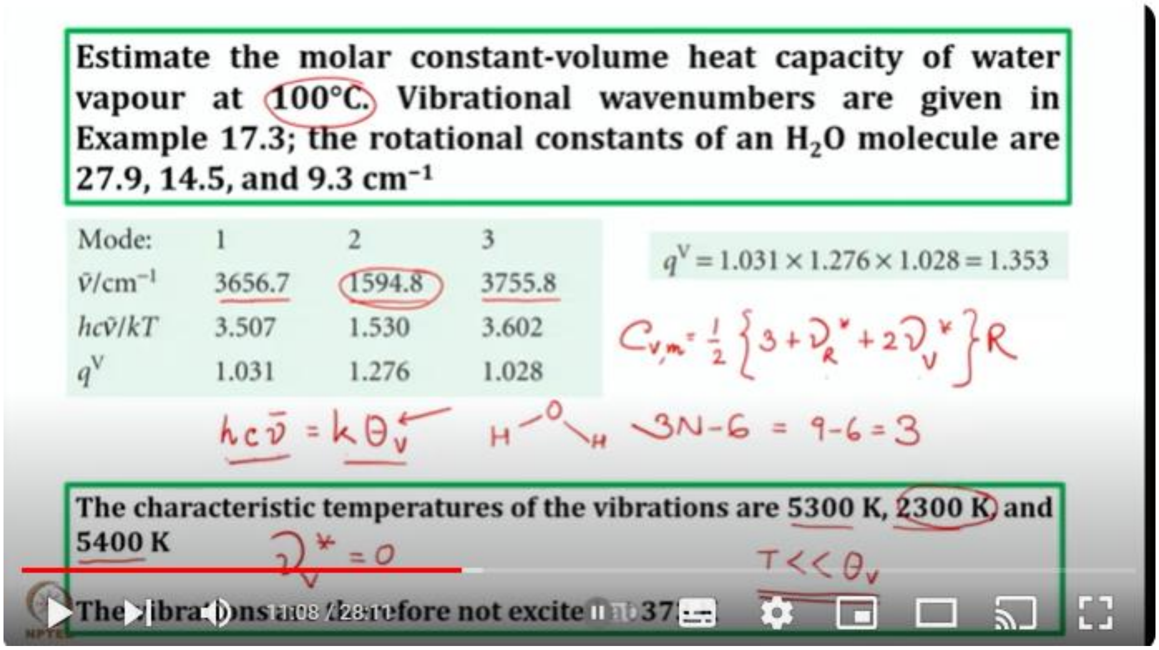

Estimate the molar constant-volume heat capacity of water vapour at 100°C. Vibrational wavenumbers are given in Example 17.3; the rotational constants of an H_2O molecule are 27.9, 14.5, and 9.3 cm^{-1}

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$C_{V,m} = \frac{1}{2}\{3 + \nu_R^* + 2\nu_V^*\}R$

$hc\bar{\nu} = k\theta_V$ H–O–H $3N-6 = 9-6 = 3$

The characteristic temperatures of the vibrations are 5300 K, 2300 K and 5400 K

$\nu_V^* = 0$ $T << \theta_V$

The vibrations are therefore not excite... 37

So, therefore what we have this will be CV$_m$ will be equal to 1 by 2 3 plus 3 R which is equal to 3 R, R is gas constant. So, R is 8.3145 joules per K per mole once you put that number you are going to get a value close to 25 joules per K per mole translational contribution 3 by 2 R rotational contribution 3 by 2 R. So, 12.5 plus 12.5 is 25 joules per K per mole this is predicted the experimental value is 26.1 joule per K per mole. So, there is a difference if you compare there is a difference of about 1.1 joule per K per mole which is not very large, but we should be able to assign some reason to this discrepancy the discrepancy is probably due to deviations from perfect gas behavior what we are considering here water molecule like a perfect gas water vapors, but water vapors are not actually like an ideal gas. So, therefore, this deviation from ideality could be one reason for this discrepancy in the theoretical as well as the experimental value. So, what is important here it is important to know what value we should put for ν_R^* and what value we should put for ν_V^* and for that what we need to do is to know characteristic rotational temperature and characteristic vibrational temperature. So, that we can decide whether to put ν_r^* equal to 3 or 0 or 2 or 0 and ν_V^* equal to 1 or 0 that is by the comparison of experimental temperature and characteristic temperature of that mode of motion, but remember that this expression can only be used to estimate the molar constant volume heat capacity it is not an actual calculation it is simply an approximation it is simply an estimation of the value.

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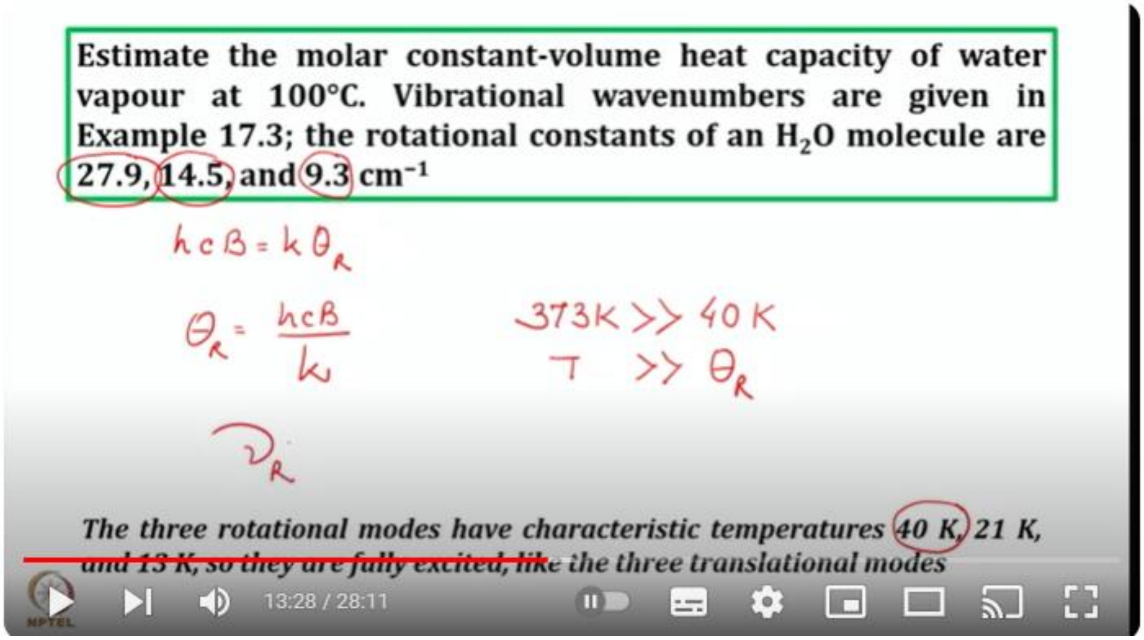

Estimate the molar constant-volume heat capacity of water vapour at 100°C. Vibrational wavenumbers are given in Example 17.3; the rotational constants of an H_2O molecule are 27.9, 14.5, and 9.3 cm^{-1}

$hcB = k\theta_R$

$\theta_R = \frac{hcB}{k}$

$373K \gg 40K$

$T \gg \theta_R$

$\tilde{\nu}_R$

The three rotational modes have characteristic temperatures 40 K, 21 K, and 13 K, so they are fully excited, like the three translational modes

Now, let us discuss a relevant numerical problem. So, that we can understand these derivations more importantly and more clearly consider a system with energy levels E_j is equal to j times E and there are n molecules question part 1 question part a is show that if mean energy per molecule is a E, then the temperature is given by this β is equal to 1 over E log 1 plus 1 by a. Let us go step by step first we will solve this part.

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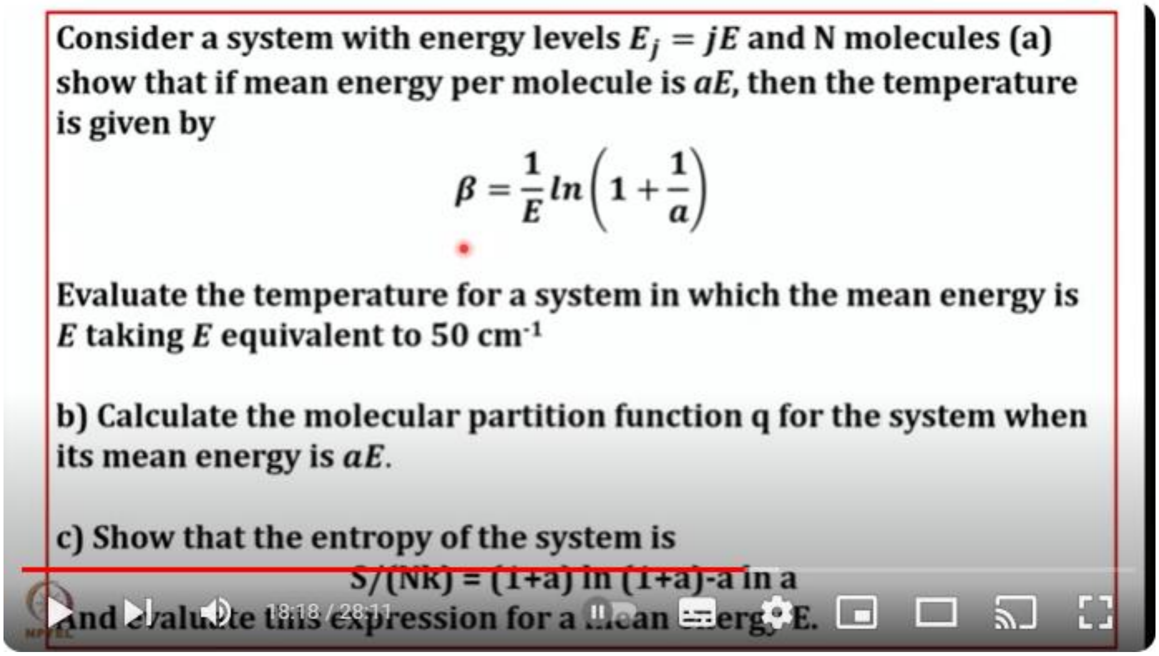

Consider a system with energy levels $E_j = jE$ and N molecules (a) show that if mean energy per molecule is aE, then the temperature is given by

$$\beta = \frac{1}{E} ln\left(1 + \frac{1}{a}\right)$$

Evaluate the temperature for a system in which the mean energy is E taking E equivalent to 50 cm^{-1}

b) Calculate the molecular partition function q for the system when its mean energy is aE.

c) Show that the entropy of the system is

S/(Nk) = (1+a) ln (1+a)-a ln a

And evaluate this expression for a mean energy E.

What is given to us is that the energy levels are given by E_j is equal to j times E and if the mean energy per molecule is a E, then the temperature should be given by this expression of β fine. Let us try to solve this first another parts we will come to them later. Parts we will come to them later. So, what is given to us is E what is given to us is E_j is equal to j times E that means, Q will be equal to summation j exponential minus βE_j which is equal to summation j exponential minus β_j times E because E_j is equal to jE this is equal to when start putting now j from 0 onwards 0 1 2 3 4. So, 1 plus exponential minus β E plus exponential minus 2 β E plus 1.

So, this is equal to 1 plus exponential minus β E plus 1 plus exponential minus 2βE plus exponential minus 3 β E and so on which I can simplify to q is equal to 1 plus exponential minus β E plus exponential minus β E square plus so on. This reminds you of uniform ladder of energy levels you remember harmonic oscillator when we discussed this. This is like a uniform ladder of energy level and this is a series geometric progression series G P series and sum of the G P series is equal to 1 over 1 minus exponential minus β E. This is the expression for the molecular partition function, but what is our problem statement we have to show that this β is given by 1 by E into log 1 by A provided the mean energy per molecule is A times E.

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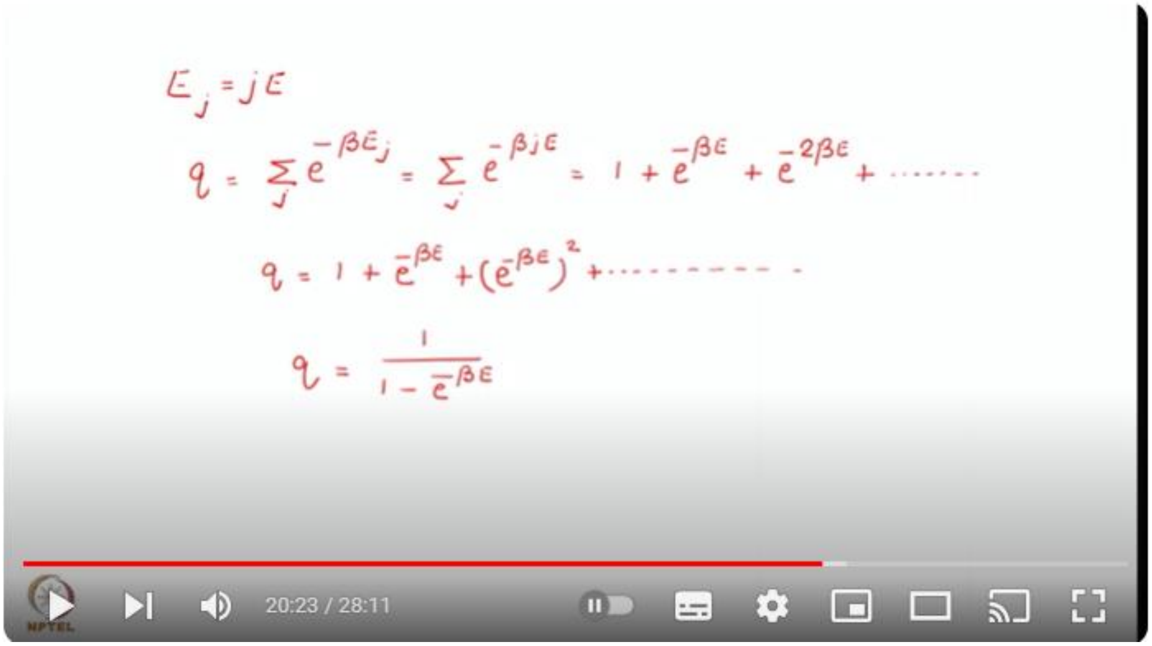

$$E_j = j\varepsilon$$

$$q = \sum_j e^{-\beta\varepsilon_j} = \sum_j e^{-\beta j\varepsilon} = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + \cdots\cdots$$

$$q = 1 + e^{-\beta\varepsilon} + (e^{-\beta\varepsilon})^2 + \cdots\cdots\cdots$$

$$q = \frac{1}{1 - e^{-\beta\varepsilon}}$$

So, let us write down an expression for mean energy, mean energy per molecule is equal to will be equal to U - U (0) by N this is mean energy and U - U (0) is equal to minus N by Q del Q del β at constant volume. This is mean energy per molecule and this is mean energy this is U - U (0) and there is 1 by N factor here already there.

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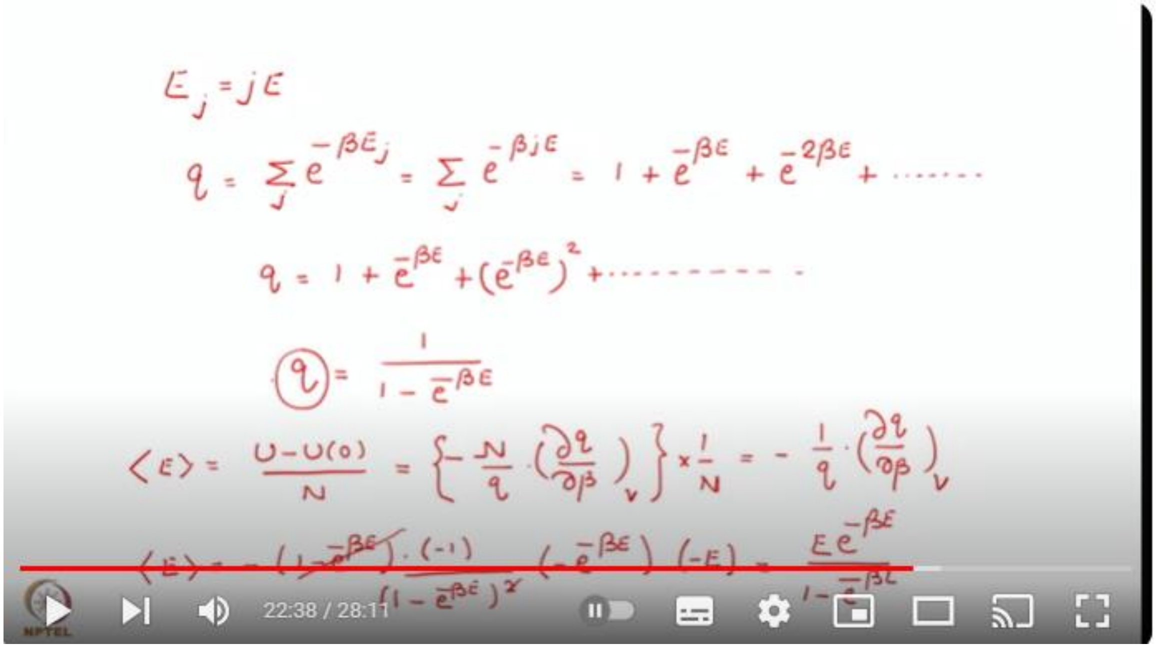

$$E_j = j\varepsilon$$

$$q = \sum_j e^{-\beta E_j} = \sum_j e^{-\beta j\varepsilon} = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + \cdots\cdots$$

$$q = 1 + e^{-\beta\varepsilon} + (e^{-\beta\varepsilon})^2 + \cdots\cdots\cdots$$

$$\boxed{q} = \frac{1}{1 - e^{-\beta\varepsilon}}$$

$$\langle\varepsilon\rangle = \frac{U - U(0)}{N} = \left\{-\frac{N}{q}\cdot\left(\frac{\partial q}{\partial\beta}\right)_V\right\}\times\frac{1}{N} = -\frac{1}{q}\cdot\left(\frac{\partial q}{\partial\beta}\right)_V$$

$$\langle\varepsilon\rangle = -\cancel{(1 - e^{-\beta\varepsilon})}\cdot\frac{(-1)}{(1 - e^{-\beta\varepsilon})^2}(-e^{-\beta\varepsilon})(-\varepsilon) = \frac{\varepsilon e^{-\beta\varepsilon}}{1 - e^{-\beta\varepsilon}}$$

So, what we have is minus 1 by q del q del β at constant volume. So, mean energy per molecule is equal to minus 1 by q minus 1 minus exponential minus βE this is minus 1 by q. I am using this into derivative of this q with respect to β. This will be minus 1 over 1 minus exponential minus β E square into minus exponential minus βE into minus E this and this can cancel and there are four negatives which become positive. So, you have E exponential minus β E over 1 minus exponential minus β E.

Let us carry it forward mean energy per molecule what we are getting is equal to E times exponential minus β E over 1 minus exponential minus βE this is what we get. So, this is what w$E_j$ust got this one. Now, let us further try to solve this mean energy will be equal to I can write this as exponent E divided by exponential βE minus 1 I multiply and divide the numerator and denominator by exponential βE. So, I have come up now with this expression for mean energy. Let us go back to the problem statement now.

Now we are told that treat mean energy to be equal to A times E mean energy per molecule treat it equal to A times E let us do that I will write this to be equal to A times E. So, what I have now E and E cancel and I have exponential β E minus 1 is equal to 1 over A. So, exponential β E is equal to 1 plus 1 by A that means β E is equal to log 1 plus 1 by A in other words now I have β is equal to 1 by E log 1 plus 1 by A. So, this is what I have done. Now, I have β is equal to 1 by E into log 1 plus 1 by A. So, therefore, I have β is equal to

1 by k T, which means the temperature, whether you express it in terms of T or you express it in terms of β, we should be able to get this from the knowledge of the value of E, which is the energy separation, and the number A. So, as you might have noted, we started with the definition of the partition function since we were given a scheme that E_j is equal to j times E. We used that, and we found that the overall expression for the partition function was coming to be equal to the sum of a G P. So, by using that, we got an expression for the partition function, and by using that partition function, we put that expression into the expression for mean energy. That is by using internal energy and then by mathematical manipulations, we were able to get this expression for temperature.

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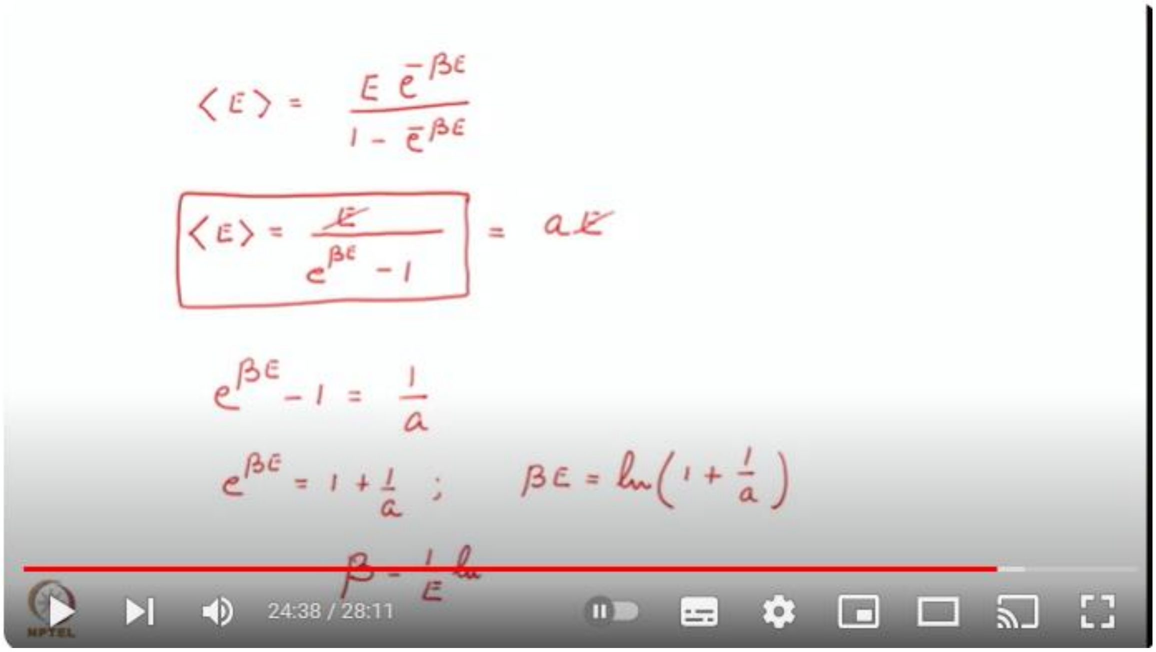

$$\langle E \rangle = \frac{E\, e^{-\beta E}}{1 - e^{-\beta E}}$$

$$\boxed{\langle E \rangle = \frac{\cancel{E}}{e^{\beta E} - 1}} = a\cancel{E}$$

$$e^{\beta E} - 1 = \frac{1}{a}$$

$$e^{\beta E} = 1 + \frac{1}{a} \;; \qquad \beta E = \ln\left(1 + \frac{1}{a}\right)$$

$$\beta = \frac{1}{E} \ln$$

There are still some more parts of the question that is, evaluate the temperature for a system in which the mean energy is E by taking E equal to 50 cm^{-1}. The second part is, calculate the molecular partition function q for the system when the mean energy is a E. And third is, show that the entropy of the system is S over n k is equal to 1 plus a log 1 plus a minus a log a and evaluate this expression for mean energy E. So, there are three or four parts still remaining for this question, but if you look at what is requested, what is asked is the expression for molecular partition function. We already got that. The second one is entropy;

that means, then you have to now think how to connect entropy with the molecular partition function. That is where our previous knowledge will be used when you connect entropy with the canonical partition function or molecular partition function, but we will be discussing all these in detail in the next lecture. Thank you very much. Thank you.