Fundamentals of Statistical Thermodynamics

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Lecture: 42

Problem Solving

Welcome back to the next lecture on Statistical Thermodynamics. By now we have connected molecular partition function with almost all thermodynamic quantities. And in the previous few lectures, we have also connected molecular partition function with mean energy, of course, mean energies were expressed in terms of internal energy divided by the total number of molecules. We also connected the molecular partition function with heat capacities. We have discussed the method of determining heat capacities from molecular partition function and also, we have discussed a method to estimate the constant volume molar heat capacity. With all these discussions, now we should be able to solve a variety of numerical problems.

And today we will be discussing some of those numerical problems. Continuing with what we started with in the previous lecture in which we started discussing this problem. Consider a system with internal energy levels E_j is equal to j times E. N molecules A show that if the mean energy per molecule is a E, then the temperature is given by β is equal to 1 over E log 1 plus 1 by a.

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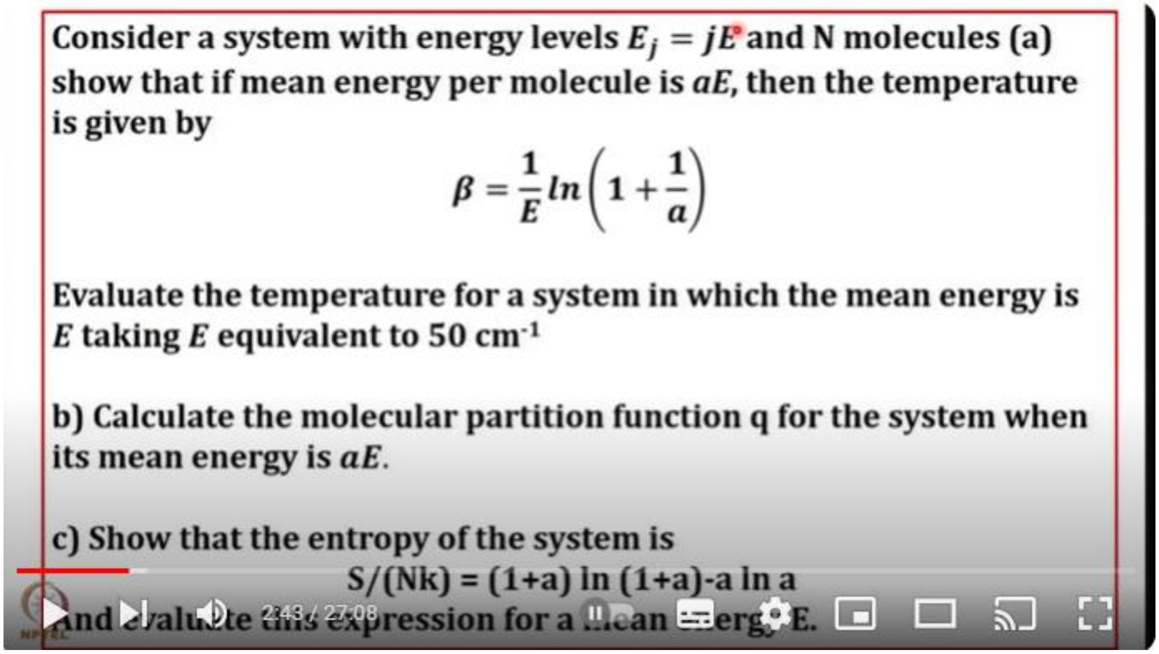

Consider a system with energy levels $E_j = jE$ and N molecules (a) show that if mean energy per molecule is aE, then the temperature is given by

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

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.

This is something we have derived in the previous lecture. The special point of attention in this numerical problem is that E_j is equal to j times E. That means when you put it in the expression for molecular partition function then the molecular partition function becomes like a sum of a GP. Let us rewrite that; what we have is E_j is equal to j times E, and q is equal to summation j exponential minus β E_j starting with j is equal to 0. You will have 1 plus exponential minus β E plus exponential minus 2 β E plus exponential minus 3 β E and plus so on, and this is a G P. So, q is equal to 1 over 1 minus exponential minus β E; this is our q.

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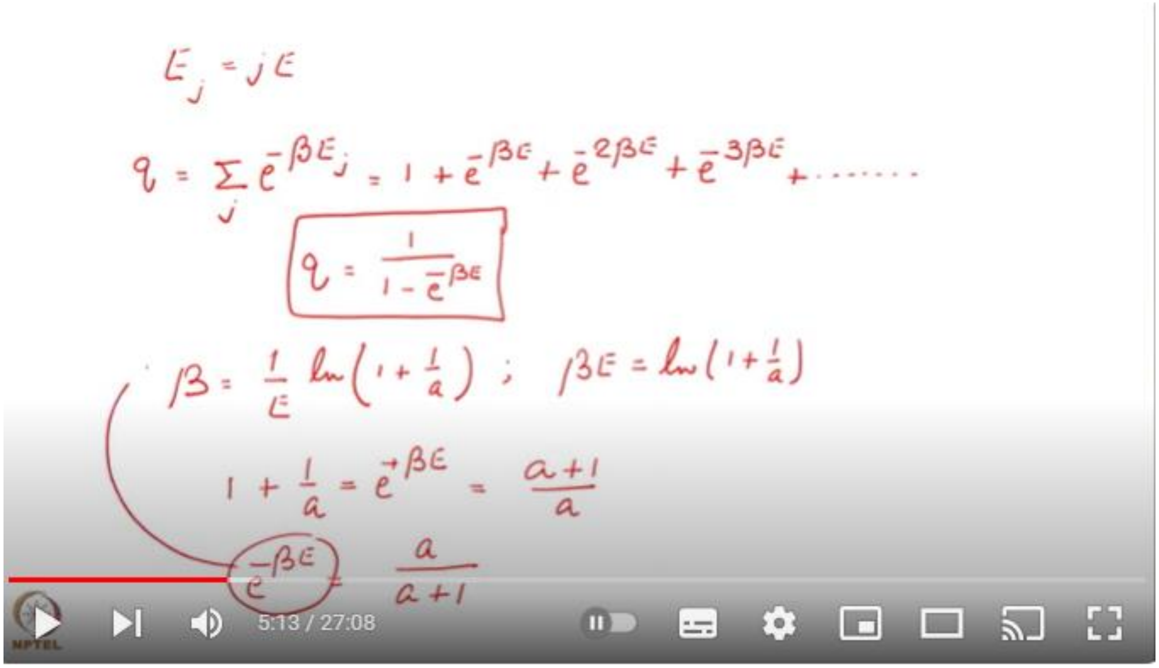

$$E_j = j\varepsilon$$

$$q = \sum_j e^{-\beta E_j} = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} + \cdots\cdots$$

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

$$\beta = \frac{1}{\varepsilon}\ln\left(1 + \frac{1}{a}\right) \; ; \quad \beta\varepsilon = \ln\left(1 + \frac{1}{a}\right)$$

$$1 + \frac{1}{a} = e^{+\beta\varepsilon} = \frac{a+1}{a}$$

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

And then in the previous discussion, what we showed is that β is equal to 1 over E log 1 plus 1 by a. Let me write this as such that β is equal to 1 over E log 1 plus 1 by a. This basically came from β E is equal to log 1 plus 1 by a. That means, I can write this as 1 plus 1 by a is equal to exponential plus β E, or can I write this as A plus 1 by a. That means, exponential minus β E is equal to a over a plus 1.

I can substitute this now here. What will I get? First of all, let us write down again Q is equal to 1 over 1 minus exponential minus β E. And we also showed that exponential minus β E is equal to a over a plus 1. Let us recheck that, yes. So, therefore, what I get now Q is equal to 1 over 1 minus a over a plus 1. So, therefore, what I am going to get here is A 1 plus A divided by 1 plus a minus a is equal to 1 plus a. Let us go back to the question.

It says calculate the molecular partition function q for the system when its mean energy is a times E. Mean energy is a times E. When mean energy per molecular is a times E, we have made use of this expression β is equal to 1 over E into log 1 plus 1 by a and we have come up with an expression for the molecular partition function. What we have come up with is that molecular partition function is equal to 1 plus a. If we have the value of a, then we can easily get the value of q.

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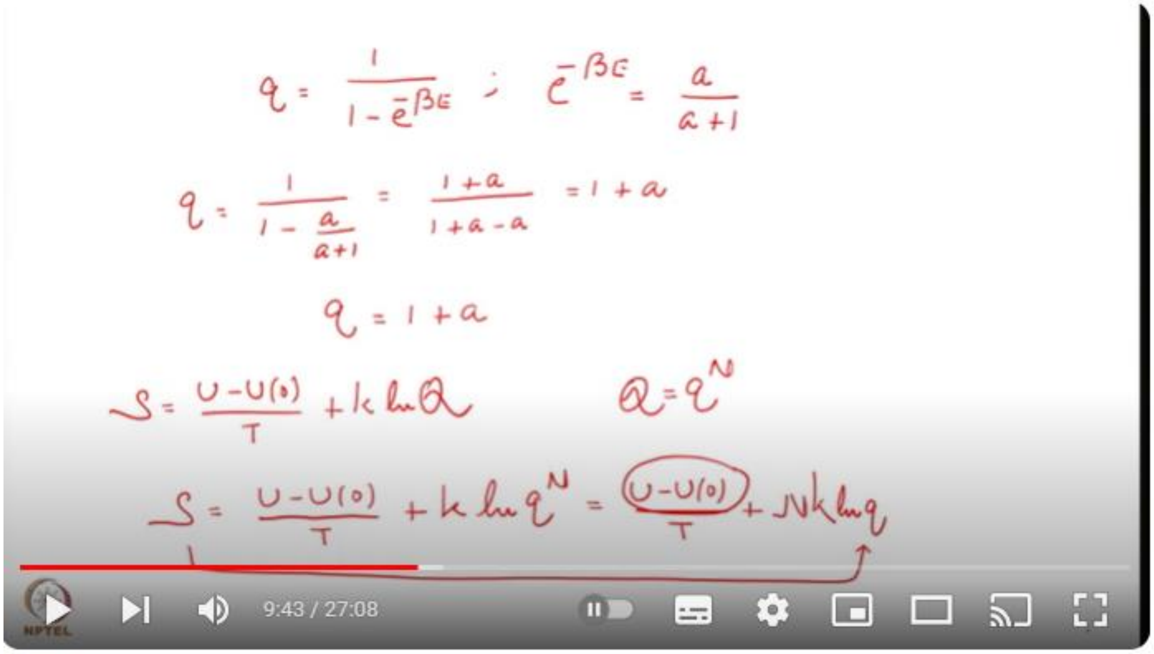

$$q = \frac{1}{1 - e^{-\beta\varepsilon}} \; ; \; e^{-\beta\varepsilon} = \frac{a}{a+1}$$

$$q = \frac{1}{1 - \frac{a}{a+1}} = \frac{1+a}{1+a-a} = 1 + a$$

$$q = 1 + a$$

$$S = \frac{U - U(0)}{T} + k \ln Q \qquad Q = q^N$$

$$S = \frac{U - U(0)}{T} + k \ln q^N = \frac{\boxed{U - U(0)}}{T} + Nk \ln q$$

We have the expression for q now. Let us look at the problem statement again. By now, we have addressed this, we have also addressed this. Now, it says show that the entropy of the system is S by N k is equal to 1 plus a log 1 plus a minus a log a. This is what now we need to show.

Entropy, we have an expression for the molecular partition function. So, therefore, we need to think of a relation which connects the entropy with molecular partition function. We know that relation, and that relation is S is equal to U - U (0) by T plus k log q. Let us apply it to independent molecules; that means q is equal to q raised to the power N. We will apply it to distinguishable molecules.

So, therefore, the expression that I get now is S is equal to U minus U (0) by T plus k log q raised to the power N is equal to U minus U (0) by T plus N k log q. We have an expression now which connects S with q. We can also express U minus U (0) in terms of q; we know the equation. So, what I will do now is we will divide throughout by Nk. What we have got now S is equal to U minus U (0) by T plus Nk log q divide throughout by Nk because this is what the question says you get an expression of S by Nk; this is equal to U minus U (0) by N kT plus log q.

U minus U (0) by N is equal to mean energy. I will take mean energy divided by kT plus log q. What are we supposed to get? We are supposed to get this expression that S by Nk is equal to 1 plus A log 1 plus a minus a log a and we have got now up to this. Now, the mean energy is given to us. If you look back into the problem statement, the mean energy is a times E; we have to use this, let us use this. So, can I write now S by Nk is equal to a times E and this 1 by kT. I can write as β plus log q. We have the expression for β E and we have the expression for q.

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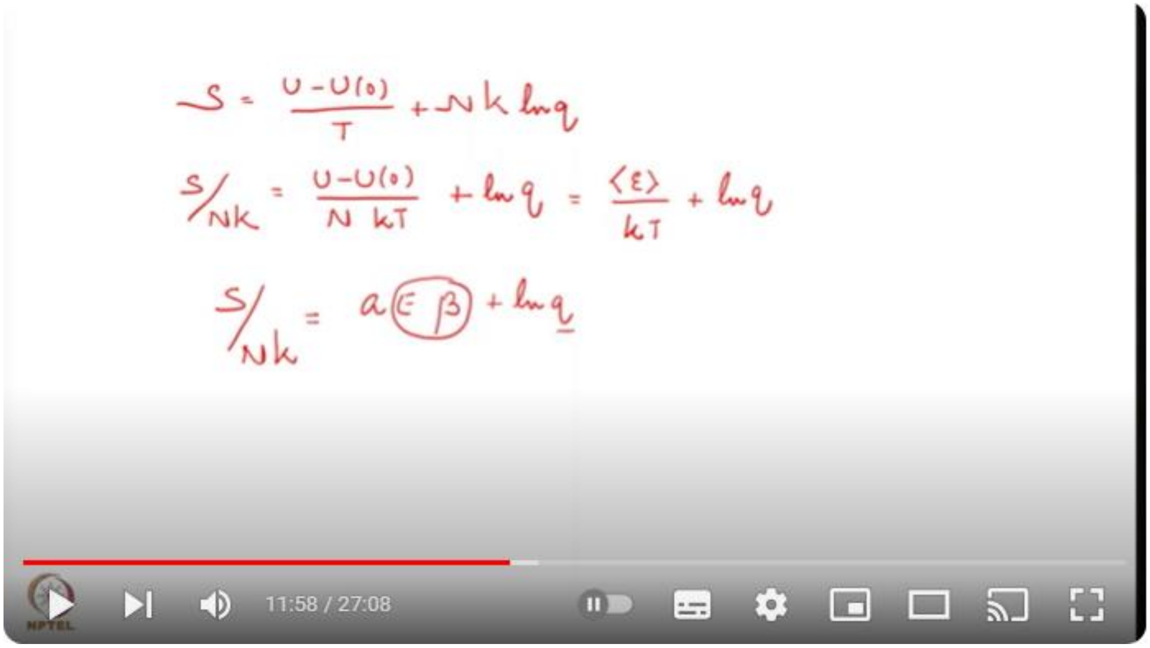

$$S = \frac{U-U(0)}{T} + Nk\ln q$$

$$S/Nk = \frac{U-U(0)}{N\,kT} + \ln q = \frac{\langle E\rangle}{kT} + \ln q$$

$$S/Nk = a\boxed{E\beta} + \ln \underline{q}$$

You remember that β E is equal to log 1 plus 1 by a and Q is 1 plus A; let us substitute that. So, that means S by N k is equal to A log 1 plus 1 by a plus 1 by A which is equal to A log 1 plus a by a plus 1 plus a, and of course, this has to be with log because we have to put for logarithm. So, S by N k is equal to A log 1 plus a minus a log a plus log 1 plus a going further S by N k I can take log 1 plus A is common and then it will be 1 plus A. So, 1 plus A log 1 plus a minus a log a. I have taken log 1 plus a common. So, what I have is now this expression S by N k is equal to 1 plus a log 1 plus a minus a log a; let us look at what was required. S by N k is equal to 1 plus A log 1 plus a minus A log a; this is what was required, and we have got it.

Now it says evaluate this expression for a mean energy of E carefully examine the statement which is given to you; it says evaluate this expression for a mean energy equal to E. So, that means they are saying you treat a E equal to E essentially, they are saying you use a equal to 1, and if you use a equal to 1 what do you have here is 1 plus 1 is 2 2 log 2 and when a is equal to 1 log 1 is 0.

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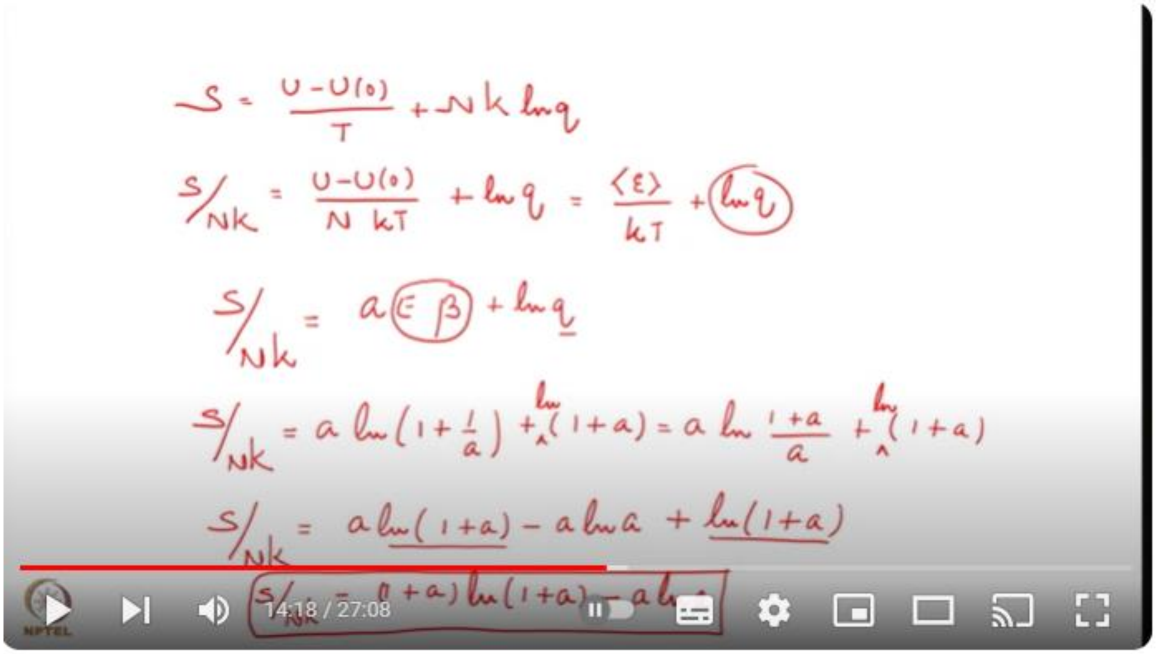

$$S = \frac{U - U(0)}{T} + Nk\ln q$$

$$S/Nk = \frac{U - U(0)}{NkT} + \ln q = \frac{\langle \varepsilon \rangle}{kT} + \boxed{\ln q}$$

$$S/Nk = a\,\boxed{\varepsilon\beta} + \ln \underline{q}$$

$$S/Nk = a\ln\left(1 + \frac{1}{a}\right) + \overset{\ln}{\wedge}(1+a) = a\ln\frac{1+a}{a} + \overset{\ln}{\wedge}(1+a)$$

$$S/Nk = a\underline{\ln(1+a)} - a\ln a + \underline{\ln(1+a)}$$

$$\boxed{S/Nk = (1+a)\ln(1+a) - a\ln}$$

So, therefore, the answer is 2 log 2 and if you want to calculate the entropy then you have to use 2 log 2 multiplied by N multiplied by the Boltzmann constant you know the values of Avogadro constant and Boltzmann constant therefore, the entropy per mole can easily be evaluated. So, through various steps I hope you understood that how to begin from a certain step and take it forward keeping in mind the desired answer. If you look back at the original statement it started with the equation for the energy uniform ladder of energy levels from that knowledge of uniform ladder of energy levels, we knew that what is going to be the expression for the molecular partition function.

Once you have the molecular partition function you know how to connect it with the different thermodynamic quantities, and that is what we did here when we first looked at the energy levels and then first expressed in terms of the molecular partition function and then we got an expression for that molecular partition function and eventually we connected it with the canonical partition function and further we connected it with the entropy. Eventually, what we got is S is equal to 2 log 2 times N times K; this is just an example for the evaluation of entropy. Similarly, you can also develop equations for enthalpy, Gibbs free energy, Helmholtz free energy, pressure, etcetera whatever thermodynamic quantity you are interested in. So, what is the beauty of the discussion that is emerging is that here to determine entropy you are not talking about calorimetric determination. If someone asks you how to determine or how to experimentally measure the entropy of a system in the laboratory, then what equipment is required what kind of equipment is required? Obviously, the answer is that in order to determine entropy in the laboratory for any substance what we need is a calorimeter because entropy is connected to heat capacity and heat capacities can easily be measured by calorimeters.

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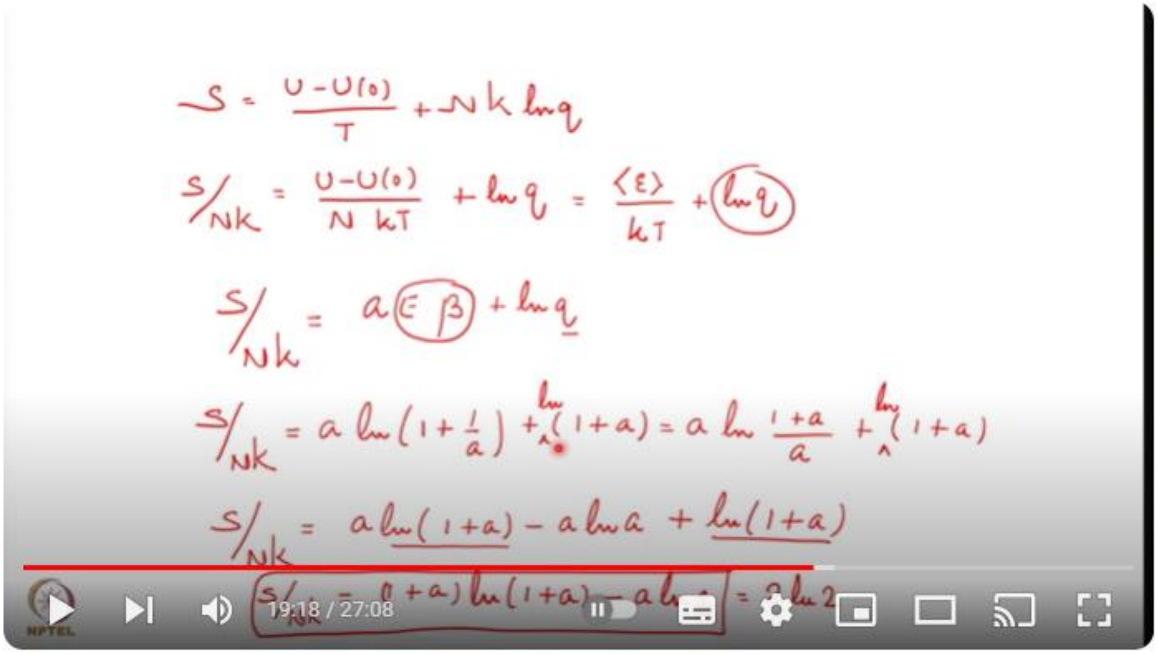

$$S = \frac{U-U(0)}{T} + Nk\ln q$$

$$S/Nk = \frac{U-U(0)}{NkT} + \ln q = \frac{\langle \varepsilon \rangle}{kT} + \boxed{\ln q}$$

$$S/Nk = a\,\boxed{\varepsilon\beta} + \underline{\ln q}$$

$$S/Nk = a\ln\left(1+\frac{1}{a}\right) + \overset{\ln}{\wedge}(1+a) = a\ln\frac{1+a}{a} + \overset{\ln}{\wedge}(1+a)$$

$$S/Nk = a\underline{\ln(1+a)} - a\ln a + \underline{\ln(1+a)}$$

$$\boxed{S/Nk = (1+a)\ln(1+a) - a\ln} = 2\ln 2$$

But here we are not talking about any calorimetry; we are here talking about connecting entropy with the molecular partition function and partition function is further connected with the energy separations various energy levels and the information on energy levels comes from spectroscopic measurements. So, what we are showing here is how to determine the entropy of a system by spectroscopic measurements. When you talk about Q here, here we had some expression so there is no issue, but the overall molecular partition function can also be a product of translational, rotational, vibrational, electronic, etcetera and that has to be properly accounted for.

Let us move forward and discuss another type of problem. Now the question is what electronic energy spacing will contribute to 10 raised to the power minus 6 to q electronic at 1200 K, and then they are asking express the answer in units of J, J/mol and cm^{-1}.

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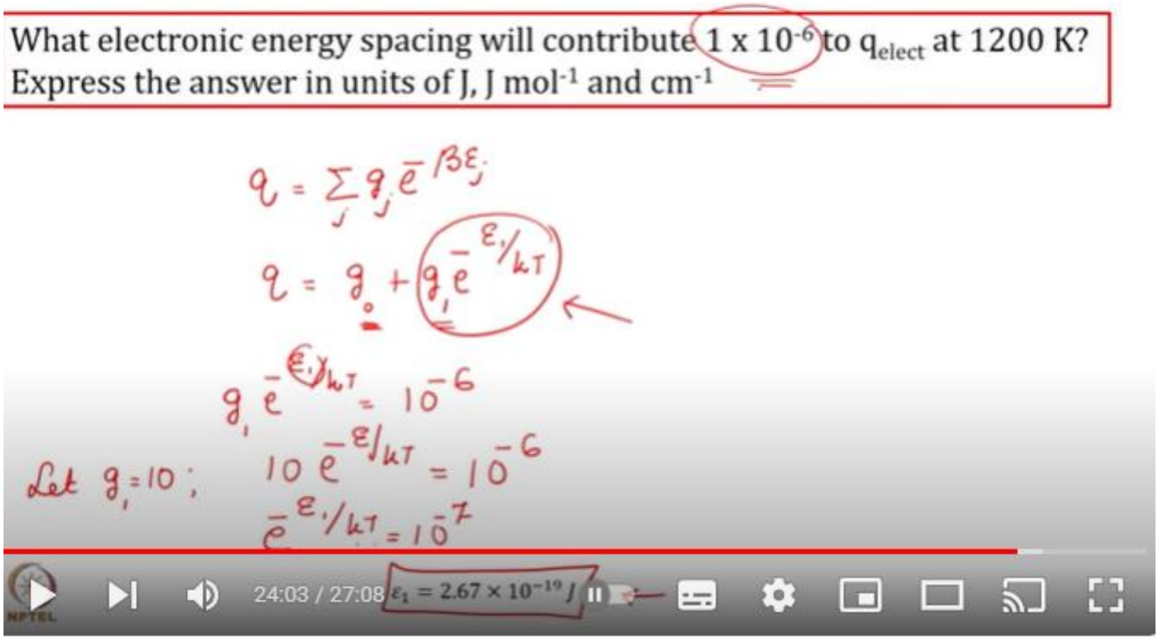

What electronic energy spacing will contribute 1×10^{-6} to q_{elect} at 1200 K? Express the answer in units of J, J mol^{-1} and cm^{-1}

$$q = \sum_j g_j e^{-\beta \varepsilon_j}$$

$$q = g_0 + \boxed{g_1 e^{-\varepsilon_1/kT}} \leftarrow$$

$$g_1 e^{-\varepsilon_1/kT} = 10^{-6}$$

Let $g_1 = 10$; $\quad 10 e^{-\varepsilon/kT} = 10^{-6}$

$$e^{-\varepsilon_1/kT} = 10^{-7}$$

$$\boxed{\varepsilon_1 = 2.67 \times 10^{-19} J}$$

Try to understand the problem; it says what electronic spacing will contribute this much to q electronic at 1200 K. First of all, recognize that the temperature given to us is 1200 K 1200 K it is not very small and it is not very high that many upper states electronic states will start contributing to the molecular partition function. So, when we discuss about the electronic contribution to the partition function, we usually go by the direct subsummation method. So, when we expand because we know that the electronic energy spacing is usually very, very large. So, therefore, when I expand it q is equal to g_0 plus g_1 exponential minus E_1 upon kT β is 1 over kT.

I can also go to plus g_2 into exponential minus β E 2 by kT, but since the electronic energy spacing is large it does not make sense to go to the further higher energy levels. G's this g's g_0, g_1 these are degeneracies of the ground state degeneracies of the upper excited state let us say first excited state g_0 and g_1 respectively. The question is what electronic spacing will contribute this 10 raised to the power minus 6 10 raised to the power minus 6 is also not very large, but that means we need to use this and then calculate what is the value of E_1. So, that the contribution is 10 raised to the power minus 6 so that means we are interested in knowing g_1 exponential minus E_1 upon kT is equal to 10 raised to the power minus 6 this is the problem to be solved and we are supposed to calculate E_1. So, you take a generous value of the degeneracy of the first excited state generous value.

Let us take a generous value of 10 okay let G_1 be 10 and then let us see what happens you have 10 raised to the power minus 6 that means exponential minus E_1 upon kT is equal to 10 raised to the power minus 7. We know the value of Boltzmann constant temperature is given to us 1200 K and we can get the value of E_1 that turns out to be 2.67 into 10 raised to the power minus 19. Since we were asked to find out what electronic energy spacing will contribute 10 raised to the power minus 6 that means we need it to act upon the second term and this series of calculation suggest that E_1 is equal to 2.67 into 10 raised to the power minus 19 J and you can always express in terms of J/mol or you can always express in terms of cm^{-1}.

How to get in terms of cm^{-1} you simply use this E_1 is equal to h c ν bar where h is equal to 6.626 into 10 raised to the power 34 J /s c is equal to, we usually take 3.0 into 10^{10} cm/s d and ν bar in cm^{-1} is given. So, therefore, the energy can be h c ν bar h is blanks constant c is speed of light and ν bar is given to you and since that is per molecule in order to convert per molecule to per mole you need to multiply by Avogadro constant. So, therefore, multiply by Avogadro constant which is n the value of Avogadro constant is 6.

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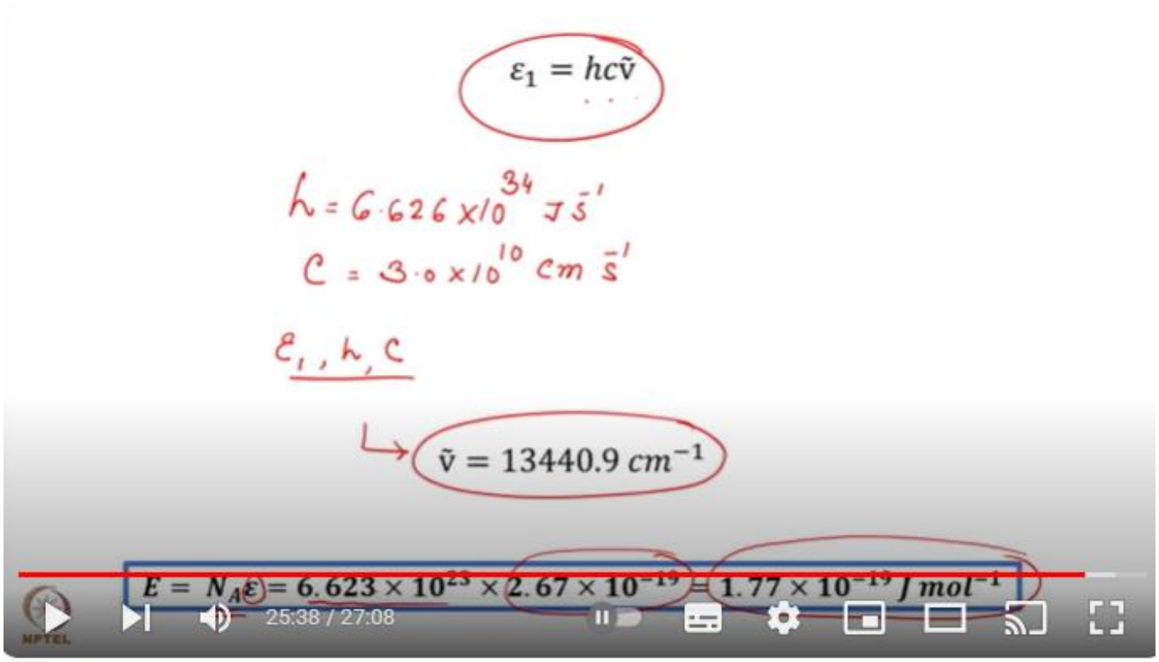
$\varepsilon_1 = hc\tilde{\nu}$

$h = 6.626 \times 10^{34}\ J\ s^{-1}$

$C = 3.0 \times 10^{10}\ cm\ s^{-1}$

$\underline{\varepsilon_1, h, c}$

$\hookrightarrow \boxed{\tilde{\nu} = 13440.9\ cm^{-1}}$

$$\boxed{E = N_A\varepsilon = 6.623 \times 10^{23} \times 2.67 \times 10^{-19} = 1.77 \times 10^{-19}\ J\ mol^{-1}}$$

6.23 into 10^{23} that is per mole and therefore, this per molecule can be converted to per mole by multiplying by Avogadro constant it comes to 1.77 into 10 raised to the power minus 19 J/mol. So, when you are solving these kinds of numerical problems it is a good idea to remember the values of blanks constant speed of light Boltzmann constant. So, that we do not worry about you know if someone gives us those values or not. In statistical thermodynamics h c k these are routinely required proper parameters.

So, therefore, in physical chemistry or as a physical chemist it is a good idea to even memorize these kind of numbers. So, therefore, with the knowledge of various connections between thermodynamic quantities and molecular partition function we should be able to solve a variety of questions some of those questions we have discussed in today's lecture and many more questions are coming up which we will discuss in the lectures ahead. Thank you very much. Thank you.