Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

Indian Institute of Technology, Bombay

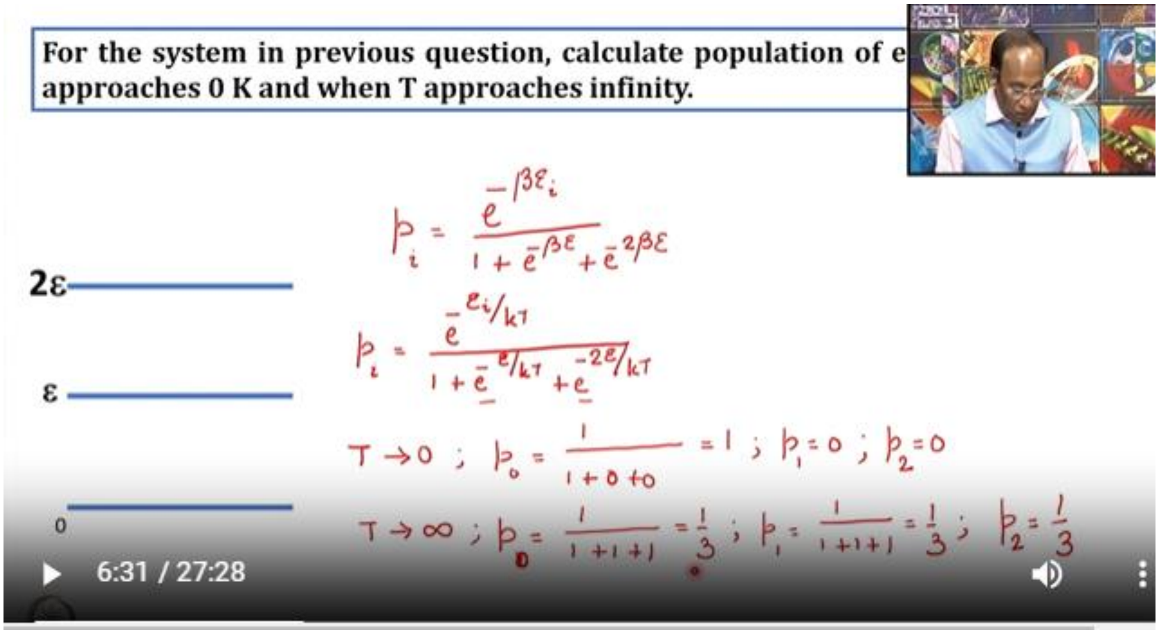
Lecture - 10

Numerical Problems Set-II (based on partition function)

Welcome back to the sessions on solving numerical problems. In the previous session or previous lecture, we discussed this problem that is for a three level system in which different non-degenerate energy states are equally spaced by E, which out of the following expressions is correct for the fractional population of the excited state. We talked in terms of three different states, your ground state, first excited state, and second excited state and then based upon our discussion, we showed that the logarithm of the fractional population is given by this expression. Now, based upon the same question that is for the system in the previous question, that previous question was whether these three energy states 0, E, 2E are equally spaced. Calculate the population of each state when t approaches 0 Kelvin and when t approaches infinity. So, that means now we need to write expressions for populations.

So, populations of i^{th} state are equal to exponential minus beta E_i over partition function here is 1 plus exponential minus beta E plus exponential minus 2 beta E. This is how the fractional population can be calculated. So, let us write down P_i is equal to exponential minus E_i upon kT divided by 1 plus exponential minus E upon k T plus exponential minus 2E upon k T. Note that the numerator has E_i, the denominator which is partition function is written based upon this set of energy levels, energy states. will be because the ground state energy is 0. So, exponential 0 is 1. So, 1 plus exponential minus beta E plus exponential minus 2 beta E and we have to now use the given conditions. Let us say when t approaches 0, when t approaches 0, your p 0 is going to be for 0^{th} energy is 0. So, exponential 0, right, exponential 0 is equal to 1 divided by 1 plus when t approaches 0, it is exponential minus infinity which is 1 by exponential infinity. So, this term is going to be 0. So, 0 plus 0 means p_0 is equal to 1. So, you see when temperature approaches 0, all the molecules are going to be in the ground state. Now, let us calculate p_1. p_1 is going to be when t approaches 0, exponential minus infinity it is 0.

Refer slide time: 6:31



For the system in previous question, calculate population of e
approaches 0 K and when T approaches infinity.

$$p_i = \frac{e^{-\beta\varepsilon_i}}{1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}}$$

$$p_i = \frac{e^{-\varepsilon_i/kT}}{1+e^{-\varepsilon/kT}+e^{-2\varepsilon/kT}}$$

$$T \to 0 \;;\; p_0 = \frac{1}{1+0+0} = 1 \;;\; p_1 = 0 \;;\; p_2 = 0$$

$$T \to \infty \;;\; p_0 = \frac{1}{1+1+1} = \frac{1}{3} \;;\; p_1 = \frac{1}{1+1+1} = \frac{1}{3} \;;\; p_2 = \frac{1}{3}$$

So, p_1 is equal to 0 and similarly p_2 is equal to 0. So, when t is equal to 0, p_0 is 1, p_1 is 0, p_2 is equal to 0. This is the answer to the first part. Now, second is when t approaches infinity. Now, let us say when t approaches a value of infinity. When t approaches infinity, then this becomes exponential 0 which is 1. When t approaches infinity that means exponential minus 0 or exponential 0 which is equal to 1. So, what do we have then? We have p_1 is equal to 1 over 1 plus 1 plus 1 because each term is contributing here 1 which is equal to 1 by 3. I wrote for p_1 or you can also say this is p_0. For p_0, this is 1. For p_1, again the term upper 1 and lower 1 are all going to be 1 over 1 plus 1 plus 1 because each term is contributing 1 which is 1 by 3. And similarly, when you calculate p_2, you also will get 1 by 3, same arguments. So, what do we conclude from this? When temperature approaches infinity, the ground state fractional population is 1 by 3. First excited state fractional population is 1 by 3. The second excited state fractional population is 1 by 3.

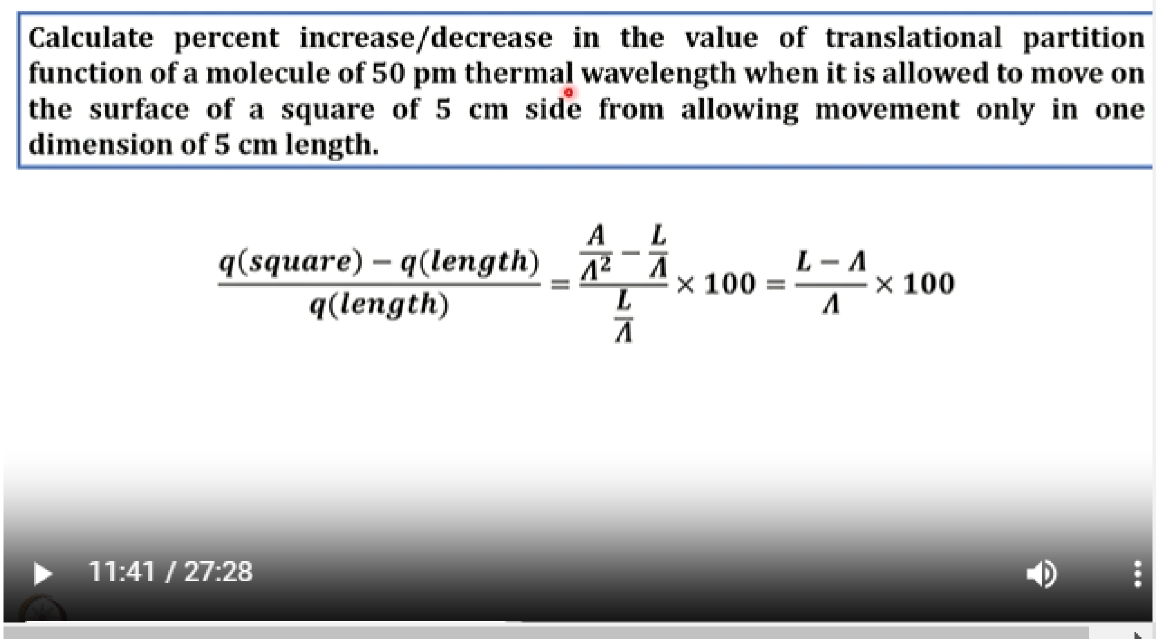
One by three, one by three, one by three. There are three states ground, first excited, second excited and each one is having equal fractional population. So, therefore, you know, let us revisit one of the conclusions that we have drawn in one of the earlier lectures that when the temperature approach is 0, all the molecules are most likely to be found in ground state. When the temperature approach is infinity, all the available energy states are going to be equally populated. It is not that all the molecules from the ground state will be pushed to the upper excited states and the ground state will have 0 occupancy. No. You can see even the calculations here, what do they suggest? When the temperature approaches infinity, each ground state or first excited state or second excited state has equal fractional population. Let me introduce one more aspect here, which is basically similar to this question. For example, now let us take a case not connected with this question. Let us say

I have ground state, I have first excited state, I have second excited state, which is doubly degenerate and this value is 2E. In this case, you should try to find out when the temperature approaches infinity, what is going to be a fractional population of the ground state, first excited state and second excited state.

Remember that in this case, your q is going to be recall your formula g_j exponential minus beta E_j. That means q is going to be 1 plus exponential minus beta E plus 2 exponential minus 2 beta E. Pay attention to how we have written. One comes from the ground state exponential 0 degeneracy is 1, first excited state degeneracy is 1 exponential minus beta E, second excited state degeneracy is 2, 2 times exponential minus beta E. And how do you get a fractional population? N_i upon N is fractional population is equal to exponential minus beta E_i upon q. Now you see in this case q, when the temperature approaches infinity, then all these terms you know exponential minus E upon k T temperature approaches infinity, this well this is going to contribute 1. This factor is going to contribute 1 which means the denominator is going to be 1 plus 1 plus 2 that is 4. In that case, the fractional occupancy here is going to be 1 by 4 here, 1 by 4 here, and 2 by 4 here. One by 4, 1 by 4, and 1 by 4 into 2 because there are 2 states which are corresponding to the same energy. So, therefore, it makes sense that we can introduce something over here which represents the degeneracy of a particular energy level.

We can introduce the degeneracy term even in the fractional population, but that we will discuss in the next numerical problem. Now let us look at a numerical problem that is based upon translational partition function. The question is to calculate percent increase or decrease in the value of the translational partition function of a molecule of 50 picometers thermal wavelength when it is allowed to move on a surface of a square of 5-centimeter side from allowing movement only in one dimension of 5-centimeter length.

Refer slide time: 11:41



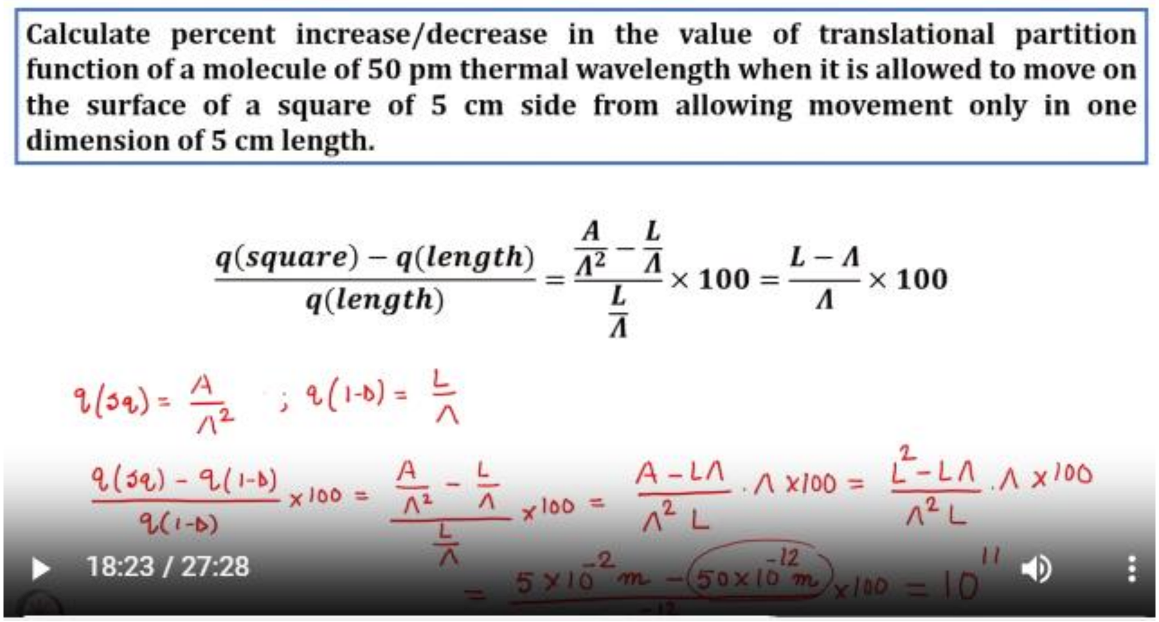
Calculate percent increase/decrease in the value of translational partition function of a molecule of 50 pm thermal wavelength when it is allowed to move on the surface of a square of 5 cm side from allowing movement only in one dimension of 5 cm length.

$$\frac{q(square) - q(length)}{q(length)} = \frac{\frac{A}{\Lambda^2} - \frac{L}{\Lambda}}{\frac{L}{\Lambda}} \times 100 = \frac{L - \Lambda}{\Lambda} \times 100$$

That means we are considering here two scenarios. One scenario is that the molecule is allowed to move only in one dimension that is a length of 5 centimeters. The second scenario is molecule is allowed to move only on the surface, surface of a square and that side is also 5 centimeters. So that means we need to now think about the partition function for a particle for a molecule which is free to move in one dimension and partition function for a molecule which is free to move in two dimensions and of course, at this time we will be concentrating on translational contribution. Let us write down the expressions. q for square let me write square by s cube is equal to area upon lambda square and q for 1-D is going to be length upon lambda. Remember that we have derived expression for the partition function for a particle for a molecule that is free to move in one dimension and it was x upon lambda.

Then we derived an expression for three dimensions it was v upon lambda cube and at that time we said that you can similarly derive expressions for 2-D and that is going to be area a upon lambda square. So we need to now find out how much is the difference when the molecule is allowed to you know move from 1-D movement to 2-D movement and 2-D here is square. So what is the change? Let us try to find out. I am interested in q square minus q 1-D divided by q 1-D and I am interested in knowing the percentage therefore, I will multiply by 100. What is q square? q square is the area divided by lambda square.

Refer slide time:18:23



Calculate percent increase/decrease in the value of translational partition function of a molecule of 50 pm thermal wavelength when it is allowed to move on the surface of a square of 5 cm side from allowing movement only in one dimension of 5 cm length.

$$\frac{q(square) - q(length)}{q(length)} = \frac{\frac{A}{\Lambda^2} - \frac{L}{\Lambda}}{\frac{L}{\Lambda}} \times 100 = \frac{L - \Lambda}{\Lambda} \times 100$$

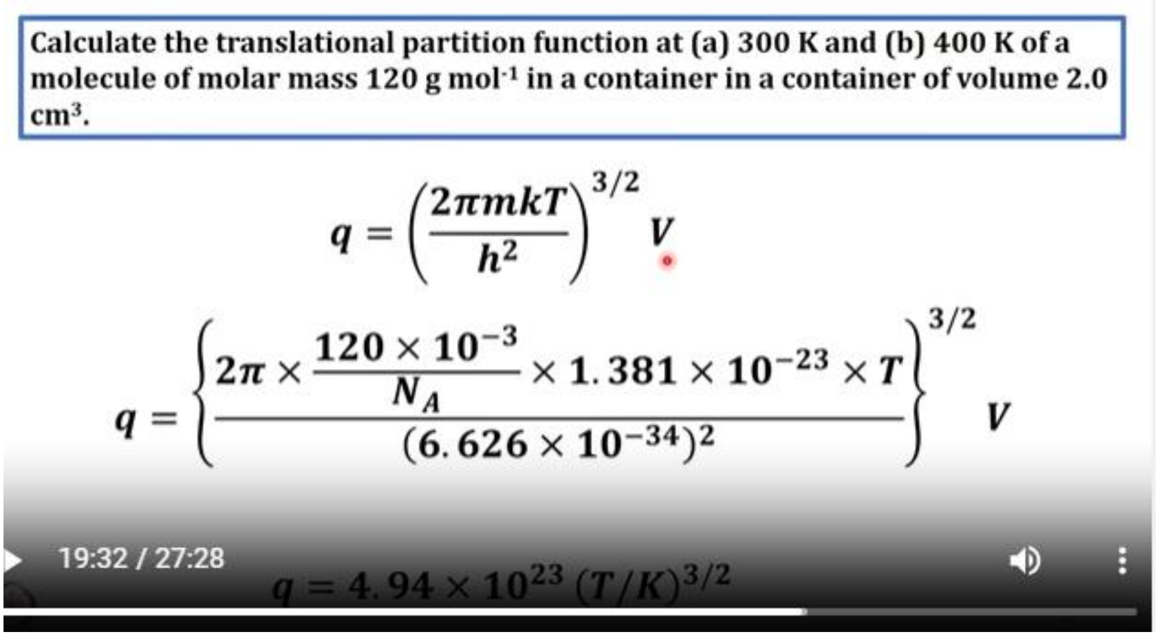
$$q(sq) = \frac{A}{\Lambda^2} \quad ; \quad q(1\text{-}D) = \frac{L}{\Lambda}$$

$$\frac{q(sq) - q(1\text{-}D)}{q(1\text{-}D)} \times 100 = \frac{\frac{A}{\Lambda^2} - \frac{L}{\Lambda}}{\frac{L}{\Lambda}} \times 100 = \frac{A - L\Lambda}{\Lambda^2 L} \cdot \Lambda \times 100 = \frac{L^2 - L\Lambda}{\Lambda^2 L} \cdot \Lambda \times 100$$

$$= \underline{5\times10^{-2}\,m - (50\times10^{-12}\,m)} \times 100 = 10^{11}$$

1-D is L upon lambda and 1-D is L upon lambda into 100. This is equal to what? This is equal to area minus L times lambda divided by lambda square into L into lambda into 100 which is equal to area is nothing but length square minus length times lambda divided by lambda square into length into lambda into 100. So common factor of L and L cancel this lambda and this lambda cancels. So, therefore, what I have is this expression L minus lambda divided by lambda into 100. Now let us substitute the numbers. So this is equal to what now? This is equal to L length is 5 centimeters. So I will put 5 into 10 and raise to the power minus 2 meter minus lambda. Lambda is 50 picometer 50 into 10 raise to the power minus 12 meters divided by lambda 50 into 10 raise to the power minus 12 meters into 100. I can ignore this 50 into 10 raise to the power minus 12 meters. This is much less compared to 5 into 10 raised to the power minus 2 meters. So if I ignore this and then multiply by 100, my answer is going to be this 100 and 10 raise to the power 2 minus 2 cancel. So 5 by 50 is 0.1. This is 5 into 10 raise to the power minus 11. So that means the answer is going to be 10 raised to the power 11. This much you see the increase in the value of translational partition function when a molecule is just allowed to have a transition from movement in one dimension to movement in two dimensions. The point to be noted in this problem is how to write the partition function translational partition function for a particle for a molecule that is free to move on the surface of a square which is A. A is the area over lambda square and the partition function for a molecule which is free to move in one dimension is simply L upon lambda and then simply the next step is simple mathematics and what we find out that the percentage increase when the molecule is allowed to move from one-dimensional movement to two-dimensional movement that see the percentage increase is huge 10 raise to the power 11. Now let us discuss one more problem. The next question is to calculate the translational partition function at 300 Kelvin and 400 Kelvin of a molecule of molar mass 120 gram per mole in a container of volume 2 centimeter cube.

Refer slide time: 19:32



Calculate the translational partition function at (a) 300 K and (b) 400 K of a molecule of molar mass 120 g mol^{-1} in a container in a container of volume 2.0 cm^3.

$$q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

$$q = \left\{\frac{2\pi \times \frac{120 \times 10^{-3}}{N_A} \times 1.381 \times 10^{-23} \times T}{(6.626 \times 10^{-34})^2}\right\}^{3/2} V$$

$$q = 4.94 \times 10^{23}\,(T/K)^{3/2}$$

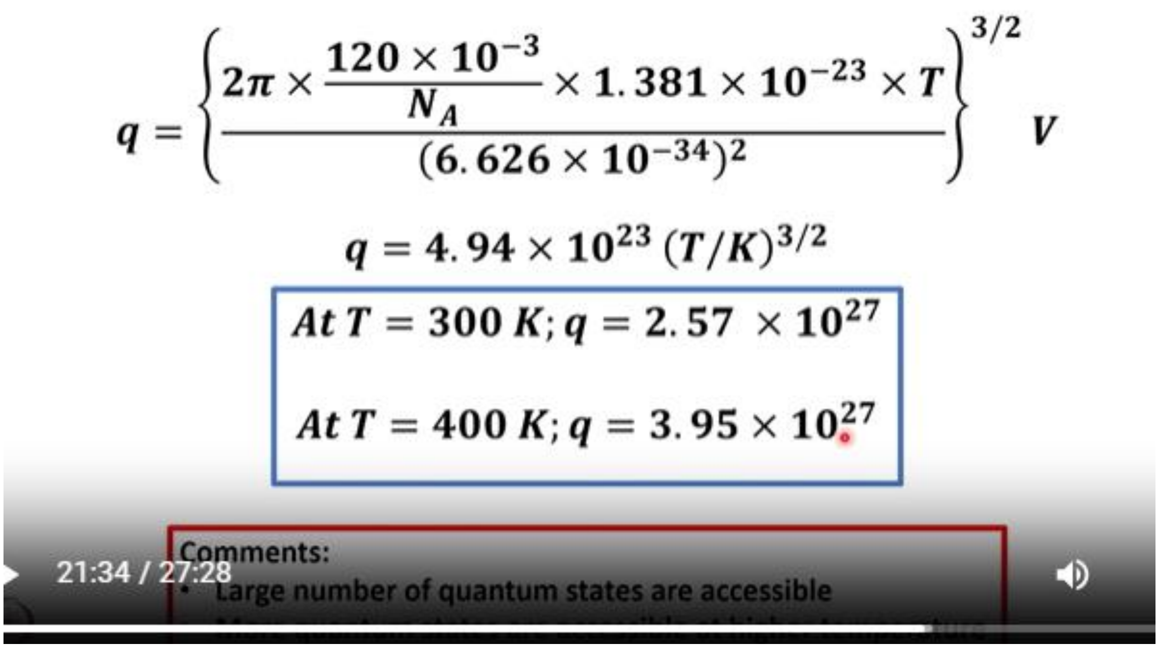
In fact, this is a revisit of a similar problem that I have earlier done but I am deliberately bringing one more problem over here so that everything becomes clear that the various parameters of their units are to be taken care of and for example the mass, mass has to be that of one particle. This is the expression q is equal to 2 pi m k T over h square raise to the power 3 by 2 into V which is basically V upon lambda q where lambda is equal to beta h square of 2 pi m.

$$q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

I am just you know reading for the sake of your connection with the previous lectures. The point to be noted over here m we are given 120 grams per mole. So therefore to convert 120 grams per mole into the mass of one particle you need to divide by Avogadro constant which is 6.023 into 10 raising to the power 23 and to convert gram into a kilogram another factor of 10 is raised to the power minus 3 is required. This is Boltzmann constant and I am keeping T as general and Planck's constant is 6.626 into 10 raising to the power minus 34. So when you calculate this q turns out to be 4.94 into 10 raise to the power 23 multiplied by temperature in Kelvin raised to the power 3 by 2 and now we can look at what we were asked to calculate at 300 Kelvin and 400 Kelvin and you can substitute T here as 300 Kelvin and 400 Kelvin and you can get the result.

Let us take a look at the result. At 300 Kelvin substituting this T equal to 300 over here we see the value is 2.57 into 10 raise to the power 27. When it is 400 Kelvin the value increases to 3.95 into 10 raise to the power 27. So what kind of general conclusions can be drawn here? One conclusion is that look at the order 10 raised to the power 27 both at 300 Kelvin and 400 Kelvin.

Refer slide time: 21:34



$$q = \left\{\frac{2\pi \times \frac{120 \times 10^{-3}}{N_A} \times 1.381 \times 10^{-23} \times T}{(6.626 \times 10^{-34})^2}\right\}^{3/2} V$$

$$q = 4.94 \times 10^{23}\,(T/K)^{3/2}$$

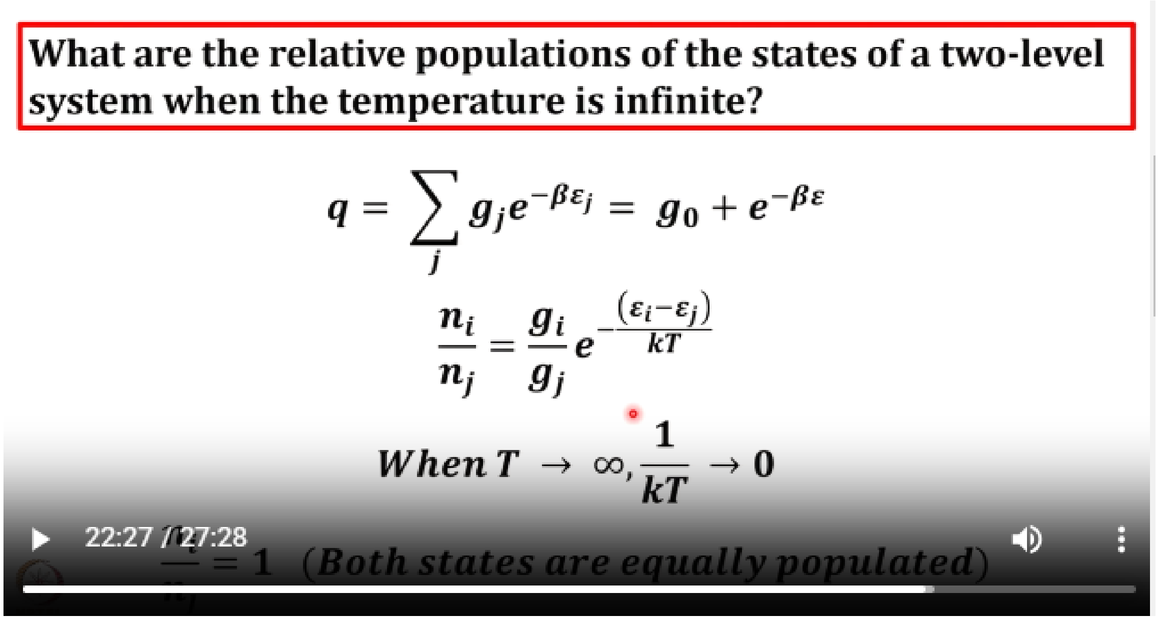
$$\boxed{\begin{array}{l} At\ T = 300\ K;\ q = 2.57 \times 10^{27} \\ At\ T = 400\ K;\ q = 3.95 \times 10^{27} \end{array}}$$

Comments:

- Large number of quantum states are accessible

10 raise to the power 27 quantum states are very high. Therefore first comment large number of quantum states are accessible 10 raise to power 27 and when you compare a 300 versus 400 there is an increase in the number also means more quantum states are accessible at higher temperature. Let us now have another problem discussed. The question is what are the relative populations of the states of a two-level system when the temperature is infinite?

Refer slide time: 22:27



What are the relative populations of the states of a two-level system when the temperature is infinite?

$$q = \sum_j g_j e^{-\beta\varepsilon_j} = g_0 + e^{-\beta\varepsilon}$$

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-\frac{(\varepsilon_i-\varepsilon_j)}{kT}}$$

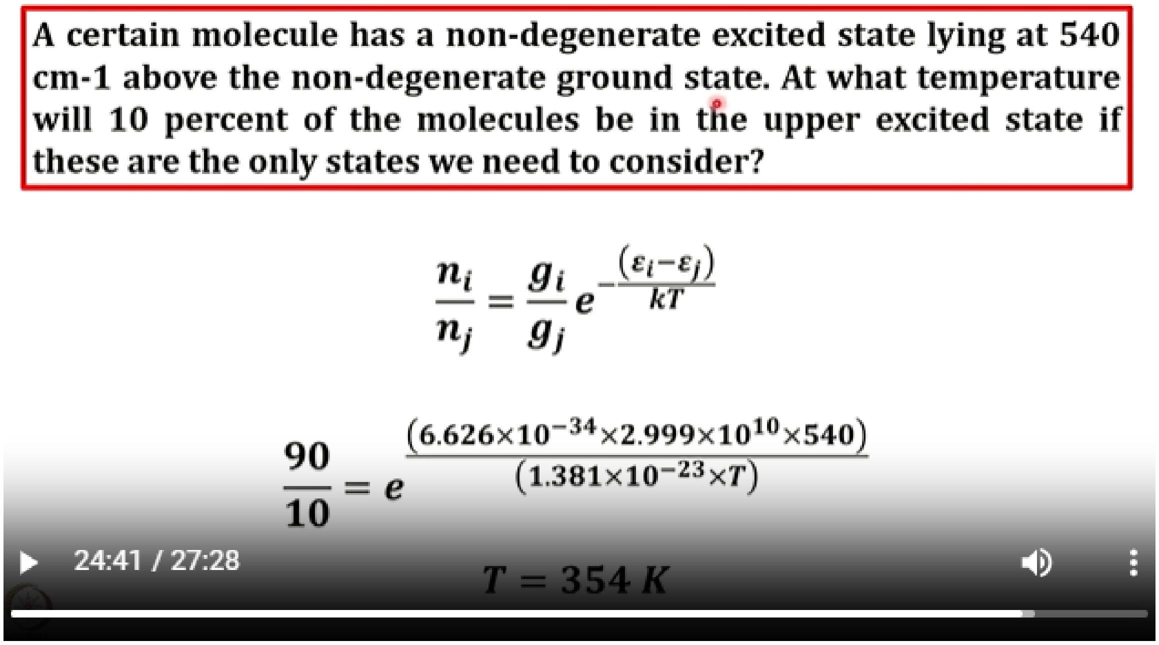
$$When\ T \rightarrow \infty, \frac{1}{kT} \rightarrow 0$$

$$\frac{n_i}{n_j} = 1 \quad (Both\ states\ are\ equally\ populated)$$

In fact, I have already discussed this kind of problems by taking a two level system and by taking a three-level system. But why I am deliberately putting this question again on this slide is that remember that in the previous lecture, I said that if there is a particular level that has a degeneracy that means two or three states have the same energy then that level is degenerate, g fold degenerate.

So, therefore, you remember that I said that you can include a degeneracy into n i upon n. Let us rewrite that. n_i upon n is equal to exponential minus beta E_i upon q. And what I said that if there are more than one state corresponding to one particular energy that will form a level and that degeneracy factor can be included over here. So therefore if I put g i over here and then I write n_i upon n_j I end up with this kind of result. Obviously when temperature approaches infinity one over k T approaches zero n i upon n j is equal to one both states are equally populated. So this again leads to the same conclusion that when the temperature approaches infinity all the available states are equally populated. The only difference that I brought here in the discussion is the inclusion of the degeneracy of the two states. A similar question is being discussed in the next problem which is a certain molecule has a non-degenerate excited state lying at 540 centimeters inverse above the non-degenerate ground state. At what temperature will 10 percent of the molecules be in the upper excited state if these are the only states we need to consider.

Refer slide time: 24:41



A certain molecule has a non-degenerate excited state lying at 540 cm-1 above the non-degenerate ground state. At what temperature will 10 percent of the molecules be in the upper excited state if these are the only states we need to consider?

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-\frac{(\varepsilon_i - \varepsilon_j)}{kT}}$$

$$\frac{90}{10} = e^{\frac{(6.626\times10^{-34}\times2.999\times10^{10}\times540)}{(1.381\times10^{-23}\times T)}}$$

$$T = 354\ K$$

You are considering you are comparing here two states n i and n j. And the question is at what temperature will 10 percent of the molecules be in the upper excited state? That means we need to act upon n i upon n_j and we have just discussed that n i upon n j is equal to g i upon g j into exponential and then we need to just consider the differences in the energies of i th state and j th state. And if we consider i is the ground state which will have 90 percent and upper excited state 10 percent then the corresponding energies when they are put in and you solve this for the temperature you get a value of 354 kelvin. That means at 354 kelvin 10 percent of the molecules will be in the upper excited state where the difference between these two states is 540 centimeter inverse.

So, in this session of solving the numerical problems we have used the expressions for molecular partition function. We have used the expression for translational partition function and we have also used the expressions for the fractional population of i th state. With this knowledge of partition function and translational contribution to partition function now we will discuss about internal energy in the next lecture.

Thank you very much.