Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

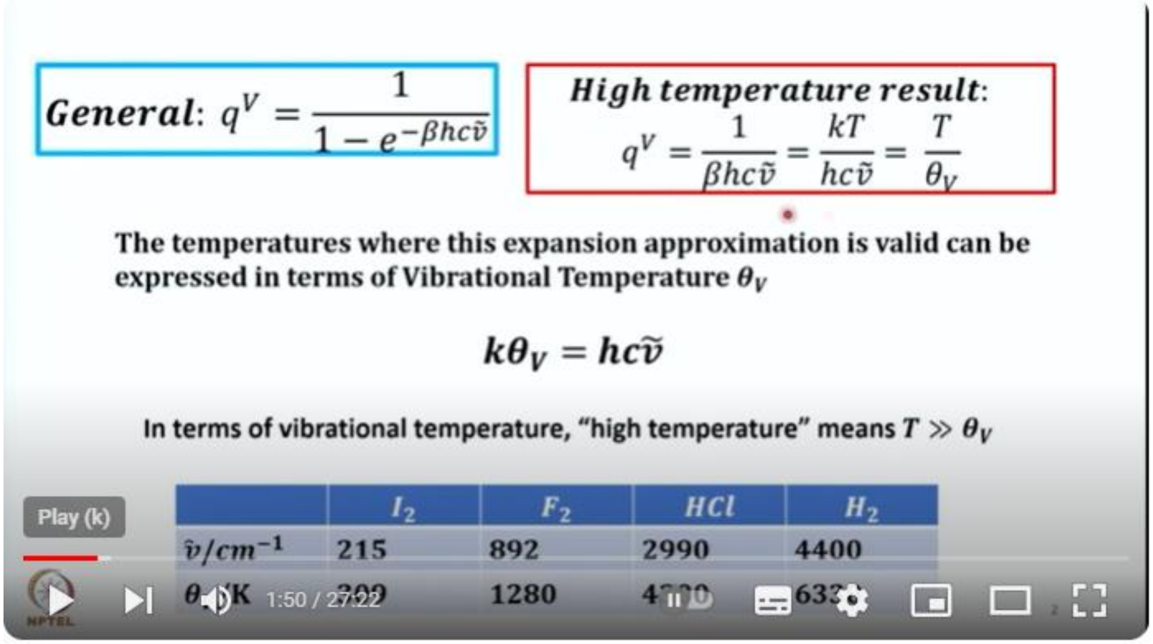
Indian Institute of Technology, Bombay

Lecture – 35

Vibrational Partition Function Applications

Welcome back to the next lecture on Statistical Thermodynamics. After having discussed translational contribution and rotational contribution, we now have been discussing the vibrational contribution to the overall partition function of a molecule. In the previous lecture, we derived certain relations. The only approximation that we made in the discussion of the vibrational partition function is that we treated the vibrator as a harmonic oscillator with an assumption that too many vibrational states are not occupied. And even in that case, when we treated that as a uniform ladder of energy levels, we derived an equation where a general expression for the vibrational partition function was arrived at, and that equation is q^v equal to 1 over 1 minus exponential β h c ν bar. Then we further discussed that if the temperature is low, in that case, you can use this general result, and if the temperature is high, then this result can be used, where the vibrational partition function could be expressed in terms of temperature, that is T is the experimental temperature or the temperature of interest, and θ_v is the characteristic rotational temperature.

See Slide time: 1:50



General: $q^V = \dfrac{1}{1 - e^{-\beta hc\tilde{\nu}}}$

High temperature result:
$q^V = \dfrac{1}{\beta hc\tilde{\nu}} = \dfrac{kT}{hc\tilde{\nu}} = \dfrac{T}{\theta_V}$

The temperatures where this expansion approximation is valid can be expressed in terms of Vibrational Temperature θ_V

$$k\theta_V = hc\tilde{\nu}$$

In terms of vibrational temperature, "high temperature" means $T \gg \theta_V$

	I_2	F_2	HCl	H_2
$\tilde{\nu}/cm^{-1}$	215	892	2990	4400
θ_V/K	309	1280	4[illegible]	633[illegible]

Then we also discussed the significance of this characteristic vibrational temperature. So, what is the significance of this characteristic vibrational temperature? The expression can be used if the temperature is much higher than the vibrational temperature, which we calculate by using this equality, that is k θ_V is equal to h c ν bar, where ν bar is the vibrational wave number for a particular mode of vibration. So, that means when we say high temperature, high temperature result means what is the meaning of high temperature here? The meaning of high temperature is that the temperature of interest should be much much larger than the characteristic vibrational temperature or vibrational temperature. Some typical values of the vibrational temperatures are listed in this table.

This is the wave number in cm^{-1}, and the corresponding vibrational temperature calculated by using this expression. I repeat vibrational temperature calculated by using this expression. Now you see for iodine, the vibrational mode iodine is a linear molecule. So, 3N minus 5 iodine 2 atoms. So, 3 into 2 6 minus 5 1, there is only one mode of vibration and that is 215 cm^{-1}.

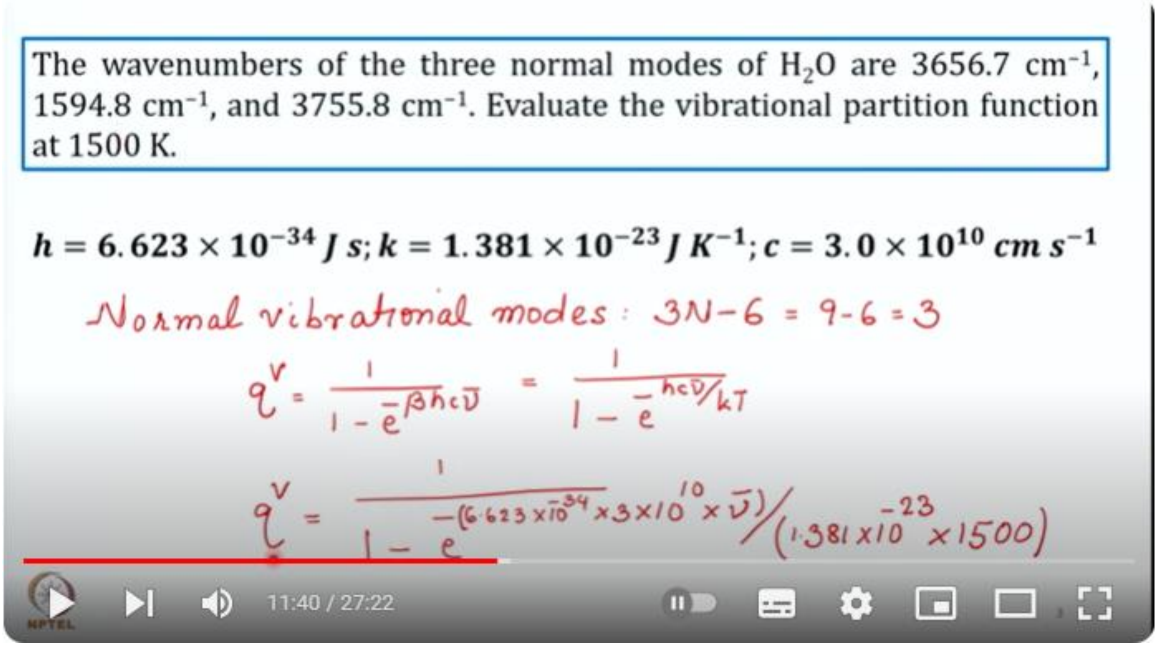
Once you use this 215 cm^{-1} into this equation, you get a vibrational temperature of 309 K. Now you go to fluorine. Fluorine is also a linear molecule diatomic, again one mode of vibration occurring at 892 cm^{-1}. The corresponding characteristic vibrational temperature is 1280. Now you go to H Cl, again a linear molecule, the vibration is at 2990.

The corresponding vibrational temperature is 4300. Now look at hydrogen, very large vibrational wave number 4400 cm^{-1}, and the corresponding characteristic vibrational temperature is 6330 K. So, there are many meanings more than one meaning which you can assign to this value of characteristic vibrational temperature. One is that above this temperature when the temperature is much larger than this vibrational temperature, you can use this expression to calculate q^v. And if the actual temperature is lower than the vibrational temperature, you will be using this expression.

And as we will see soon that if the temperature is low not many upper vibrational levels are significantly populated. Another general trend which you notice in this table look at the molecular weights here the heavier molecule iodine is a heavy molecule, then fluorine is lighter, then HCl you have and then you have hydrogen, a very light molecule. And you can correlate with the vibrational wave numbers that as the molecule is becoming lighter, you have the wave number is increasing. And if the wave number is increasing, that means you require more energy for the more vibrational modes to be active. So, therefore, you need more temperature also.

So, therefore, a correlation with the heaviness or the molecular weight or the bond length can be correlated over here with wave number as well as characteristic vibrational temperature. So, I hope the meaning of this vibrational temperature is clear and the significance of this vibrational temperature is also clear. Let us apply whatever we have discussed in solving some numerical problems. The wave numbers of three normal modes of H_2O are given, which are 3656.7 cm^{-1}, 1594.8 cm^{-1}, and 3755.8 cm^{-1}. Calculate the vibrational partition function at 1500 K; this is the temperature given. So, there are three normal modes of vibration. Now water is a non-linear molecule.

See slide time: 11:40



The wavenumbers of the three normal modes of H_2O are 3656.7 cm^{-1}, 1594.8 cm^{-1}, and 3755.8 cm^{-1}. Evaluate the vibrational partition function at 1500 K.

$$h = 6.623 \times 10^{-34}\, J\, s;\ k = 1.381 \times 10^{-23}\, J\, K^{-1};\ c = 3.0 \times 10^{10}\, cm\, s^{-1}$$

Normal vibrational modes : 3N−6 = 9−6 = 3

$$q^{v} = \frac{1}{1-e^{-\beta h c \bar{\nu}}} = \frac{1}{1-e^{-hc\bar{\nu}/kT}}$$

$$q^{v} = \frac{1}{1-e^{-(6.623\times10^{-34}\times3\times10^{10}\times\bar{\nu})/(1.381\times10^{-23}\times1500)}}$$

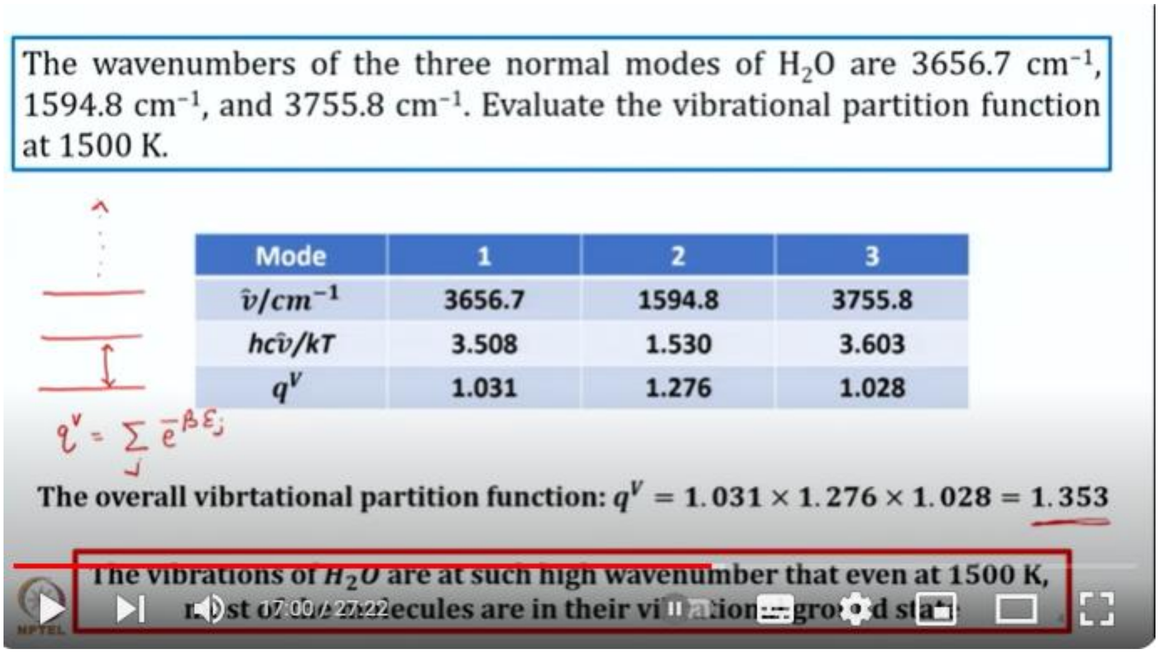
So therefore, normal modes of vibration, normal vibrational modes can be calculated by 3N minus 6 non-linear. There are three atoms in water, so, 9 minus 6 is equal to 3. These three normal modes vibrate at the frequency, which are given, these are normal modes and we need to now find out the vibrational partition function. We know that the vibrational partition function is given by 1 over 1 minus exponential minus β h c ν bar. I can write this as 1 over 1 minus exponential minus h c ν bar upon kT; β is 1 over kT.

So therefore, in order to solve for vibrational contribution, you need the value of h, Planck's constant, which is given over here, 6.623 into 10 to the power minus 34 joules second. C is the speed of light, which is 3 into 10 to the power 8 meters per second or 3 into 10 to the power 10 cm per second, and the Boltzmann constant, 1.381 into 10 to the power minus 23 joules per K. So, note that h is constant, c is constant, and k is constant. So sometimes h c upon k that number itself can be used. Okay. So, once you substitute the values of ν bar here with appropriate substitution for h, c, and k, you can calculate the vibrational contribution. Remember that we have also discussed another result, high-temperature result. Now, whether to use that high-temperature result or not that will depend upon the vibrational temperature.

One can calculate the vibrational temperature and then decide what is to be done. But if you don't want to get into that suppose if you decide that okay, why should I go into the calculation of vibrational temperature, you can directly use this general result. However, as I earlier mentioned if you know if you have an idea of characteristic vibrational temperature, you can actually guess what will be the value of vibrational partition function. We will take those examples. So, therefore, q^v is equal to 1 over 1 minus exponential minus 6.

623 into 10 to the power minus 34 h into c 3 into 10 to the power 10. I am keeping it in centimeters per second because I will use ν bar in cm^{-1}. This one divided by kT, k is 1.381 into 10 to the power minus 23 into 1500. This can be solved. Now remember that you have three values of the vibrational wave numbers, 3656.7 cm^{-1}, 1594.8 cm^{-1}, and 3755.8 cm^{-1}. So, once you have, once you know these three normal modes of vibration, you can calculate the partition function due to each normal mode of vibration.

See slide time: 17:00



The wavenumbers of the three normal modes of H_2O are 3656.7 cm^{-1}, 1594.8 cm^{-1}, and 3755.8 cm^{-1}. Evaluate the vibrational partition function at 1500 K.

Mode	1	2	3
$\tilde{\nu}/cm^{-1}$	3656.7	1594.8	3755.8
$hc\tilde{\nu}/kT$	3.508	1.530	3.603
q^V	1.031	1.276	1.028

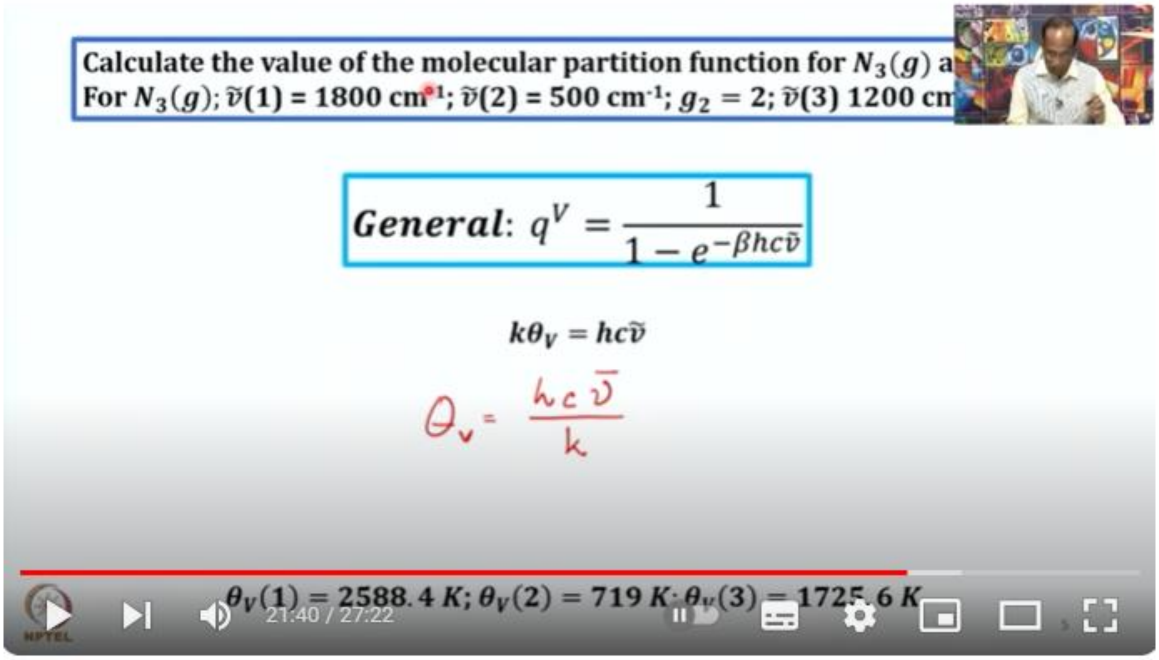
$$q^v = \sum_j e^{-\beta\varepsilon_j}$$

The overall vibrtational partition function: $q^V = 1.031 \times 1.276 \times 1.028 = \underline{1.353}$

The vibrations of H_2O are at such high wavenumber that even at 1500 K, most of the molecules are in their vibrational ground state

Listen to what I am saying carefully due to each normal mode of vibration. That value can be substituted here and you can obtain the value of partition function for each normal mode of vibration. As shown in this table. So, the first normal mode is at 3656.7 here. The corresponding value after calculation of q^v comes to 1.031. The second one at 1594.8 gives a Q value of 1.276. The third value which is at 3755.8, the Q value Q_v value comes out to

1.028. So, what is interesting in this to note? Look at the table carefully. The highest wave number in this case is number 3 and the corresponding q 1.028 is the minimum amongst all these three. The lowest wave number is 1594.8 and the corresponding partition function is 1.276. This is giving an indication and information that if the vibrational normal vibrational mode is at some lower wave number that means energy for that corresponding energy is you know separation is less and therefore, there will be more value of vibrational partition function for that. So, this inverse correlation can be checked in the values reported in this table. So, after having calculated the vibrational partition function for each normal mode of vibration, now we need to calculate overall vibrational partition function and as we have been always discussing earlier that when you talk about overall partition function, it is the multiplication of each partition function. So, energy is additive, but the partition function is multiplicative. So, therefore, the overall contribution to the vibrational partition function is going to be $Q_v(1)$ into $Q_v(2)$ into $Q_v(3)$.



Calculate the value of the molecular partition function for $N_3(g)$ a
For $N_3(g)$; $\tilde{\nu}(1)$ = 1800 cm^{-1}; $\tilde{\nu}(2)$ = 500 cm^{-1}; $g_2 = 2$; $\tilde{\nu}(3)$ 1200 cm

$$\boxed{\textbf{General}:\ q^V = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}}}$$

$$k\theta_V = hc\tilde{\nu}$$

$$\theta_v = \frac{hc\bar{\nu}}{k}$$

$\theta_V(1) = 2588.4\ K$; $\theta_V(2) = 719\ K$; $\theta_V(3) = 1725.6\ K$

So, 1.031 into 1.276 into 1.028, the overall value is 1.353. Even the overall value, you see, is just 1.35, it is not very high. Once again, you know when you compare with the rotational contribution, the translational contributions where the numbers were very very high, the translational contribution number was really high, exceptionally high, but the vibrational contribution you see for water at 1500 K, 1500 K is a high enough temperature where water is in the vapor form under normal conditions of pressure, okay.

So, let us look at the comment. The vibrations of H_2O are at such high wave number that even at 1500 K, most of the molecules are in their vibrational ground state. What it means is if I represent ground state, first excited state, second excited state, and then I will just say it increases in this order, it is like a uniform ladder of energy levels, the value of 1.353, 1.3 is close to 1 and if only the ground state is occupied, then Q vibrational if I just say j exponential minus βE_j, in this case if most of the molecules are in the ground state, then what you have is a value of just one ground state only because the upper-state contribution is going to be negligible because this energy difference is very very large. So, I hope it is clear that is why this comment that the vibrations of H_2O are at such high wave number that even at 1500 K, most of the molecules are in their vibrational ground state.

So, just a quick hint, you know when you come across various numerical problems where you have to evaluate or estimate the vibrational partition function. The overall result in general what you will get is close to 1. That does not mean that you do not solve, you just write a value of 1. We still have to solve and show, but the expected result is not much larger than 1 unless the temperatures are really really exceptionally high. Even in those cases, the value of the overall vibrational partition function is not going to be very very high, alright.

Now, let us look at another application. The question is, calculate the value of the molecular partition function for N_3 and the temperature is 25 °C. For N_3, the wave numbers are given. The first one is 1800 cm^{-1}, the second one is 500 cm^{-1}, but the second one is doubly degenerate. The third one is 1200 cm^{-1}, right.

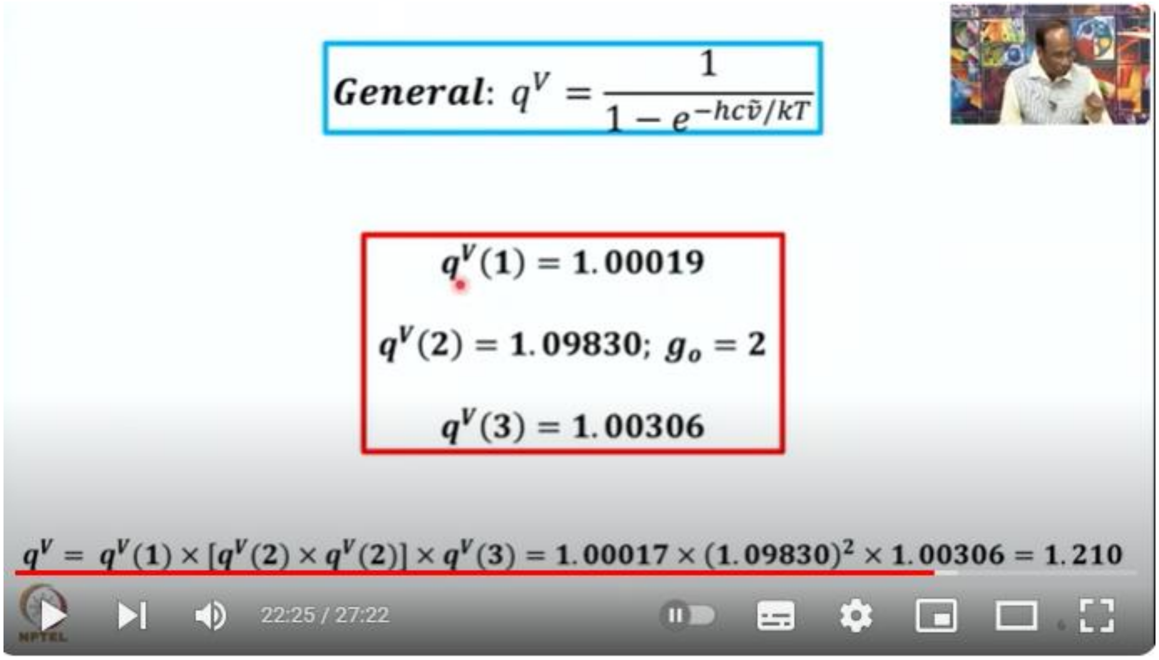
So, again there are 3, N_3. So, there are 1, 2, 3. Actually, there are 4, 4 values of vibrational wave numbers, but 2 of them are the same. Therefore, the second one is doubly degenerate, right. For a linear molecule, you expect the value of 4 vibrational modes. So, how to proceed? This is the general expression for q^V and as I discussed in the previous example, you can substitute the value of 1 by kT into h into c into ν bar for each and get a value.

But let us go a little bit more deeper into the discussion. q^V, which is the vibrational temperature, is h c wave number over k. We all know the values of h c and k. Once you substitute this, you get the following results. For the first one, corresponding to 1800 cm^{-1}, you get a vibrational temperature of 2588. 4 K. The second one, corresponding to 500, you expect 719 K. For the third one, which is 1200, you get 1725.6 K. Again, notice that the one which is largest 1800, the corresponding vibrational temperature is largest and for the smallest, the corresponding vibrational temperature is smallest. But there is another point to note over here and what is that? Your experimental temperature is 298 K and the lowest vibrational temperature is 719 K.

You can focus on the lowest because if the experimental temperature is lower than the lowest vibrational temperature, in that case, you cannot use the high-temperature approximation. You have to go exclusively by this formula. Once again, even for the lowest wave number, first you focus on the lowest wave number. Lowest wave number will give you some vibrational temperature and if that vibrational temperature is higher than the experimental temperature, that means the high-temperature approximation cannot be used because the other vibrational temperatures are anyway higher than 719 K. So therefore, you have to exclusively use this result and once you use this result for each value, then let us see what is to be done next.

The first one which was the highest, let's go back and look at. The first one is the highest wave number, 1800 cm^{-1} and for that highest wave number, the corresponding vibrational partition function is 1.00019. That is what I was just telling you a few minutes ago that if the vibrational wave number is high or if the characteristic vibrational temperature is higher than the experimental temperature, you do not expect the upper vibrational level to be populated. In that case, the q^v value is going to be just 1, approximately 1 and that is what you observe over here.

See Slide time: 22:25



$$\boxed{\textbf{General: } q^V = \frac{1}{1 - e^{-hc\tilde{\nu}/kT}}}$$

$$q^V(1) = 1.00019$$

$$q^V(2) = 1.09830;\ g_o = 2$$

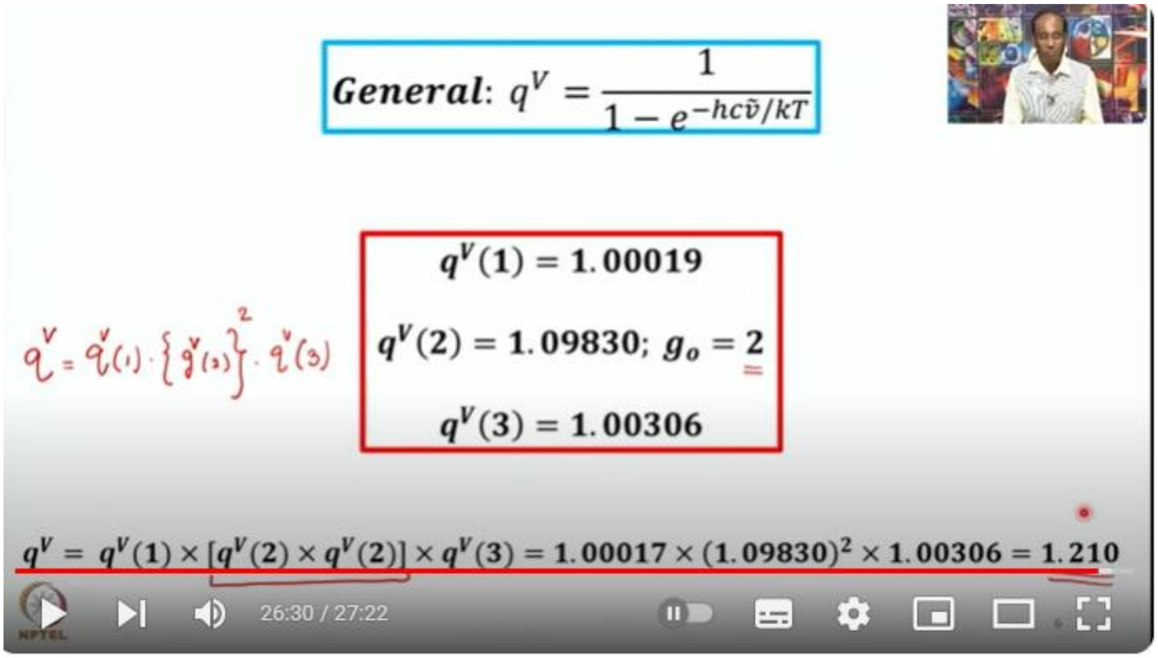
$$q^V(3) = 1.00306$$

$$q^V = q^V(1) \times [q^V(2) \times q^V(2)] \times q^V(3) = 1.00017 \times (1.09830)^2 \times 1.00306 = 1.210$$

Now, the smallest one, even the smallest one, let us look at what was the number. The smallest one was 500 cm^{-1}, but still the vibrational temperature is higher than the experimental temperature. In that case, still the value is coming out to 1.098. This is also not very different from 1. Again, you can assign this reason to the comparison of vibrational temperature with the actual experimental temperature and degeneracy for this is 2. Now the third one which was the second highest, in that case the value is again coming to close to 1. Now we have all the four values. For one normal mode of vibration and for the second which is doubly degenerate, for that normal mode of vibration and for the third one which is non-degenerate, that is the value in each case is close to 1. But in any case, the overall partition function is going to be Q_v of 1 into, second one is doubly degenerate.

So I can write q^v of 2, this will appear twice, so square into q^v of third. So that is what I was saying, this will appear twice, the second one because the degeneracy is 2. So, once you multiply all this, you get a value of 1.210. You have to be little careful when you are dealing with the vibrational partition function because as I discussed in the previous lecture also and I am discussing now also that each normal mode of vibration will give rise to its own partition.

See Slide time: 26:30



$$\boxed{\textbf{General: } q^V = \frac{1}{1 - e^{-hc\tilde{\nu}/kT}}}$$

$$q^V = q^V(1) \cdot \{q^V(2)\}^2 \cdot q^V(3)$$

$$\boxed{\begin{array}{c} q^V(1) = 1.00019 \\ q^V(2) = 1.09830;\ g_o = \underline{\underline{2}} \\ q^V(3) = 1.00306 \end{array}}$$

$$q^V = q^V(1) \times \underbrace{[q^V(2) \times q^V(2)]} \times q^V(3) = 1.00017 \times (1.09830)^2 \times 1.00306 = \underline{\underline{1.210}}$$

And once you know the value of partition function for each normal mode of vibration, then you can use this multiplicative rule to get an overall value of vibrational contribution to partition function. Once again, I have repeated it many times that since the temperature, experimental temperature 298 K in this case is lower than the vibrational temperature for each normal mode, therefore you do not expect the overall number to be much different than 1. In this case, it is 1.2. So, I hope that you should be able to now evaluate, calculate the values of vibrational contribution to partition function.

As a general rule, you expect translational contribution to be highest followed by rotational and now we have discussed the vibrational. This is coming next lower, right. So translational, rotational, vibrational we have discussed and in mind we have that which one will be highest, which one will be lowest. So that is you know in terms of the energy orders and as we discussed here also that vibrational contribution in general, you do not expect to be much different than 1 unless the temperatures are extremely high. The next partition function that we should discuss now is the electronic partition function and we will see that in terms of this order of the values where it falls, but that we will discuss in the next lecture. Thank you very much.