Fundamentals of Statistical Thermodynamics

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Lecture – 34

Vibrational Partition Function-II

Welcome back to the next lecture on Vibrational Partition Function. In the previous lecture, we have talked about what is the expression for the vibrational energy and then we discussed about how to set the ground state vibrational energy equal to 0 and then how to account for if we want to overall calculate the internal energy. So, let us take a look at what we have discussed earlier. We talked about this is the overall expression for the vibrational energy levels where V which is the vibrational quantum number is 0, 1, 2, etcetera. And E_v is equal to V h c ν bar where when you set V equal to 0 energy levels for the ground state are set to 0. So, let us now discuss further. q^V is equal to summation V from 0 to infinity. You have exponential minus V I will put β h c ν bar which you can write as is written above or if you do not want you can leave it as such. So, I have now q_v is equal to when V is equal to 0 exponential 0 is equal to 1 plus exponential minus β h c ν bar plus exponential minus 2 β h c ν bar plus exponential minus 3 β h c ν bar plus so on. Now you remember let me just give a background we had E v is equal to V h c ν bar.

So, that means E_0 is equal to 0, E_1 is equal to h c ν bar, E_2 is equal to 2 h c ν bar, E_3 is equal to 3 h c ν bar, etcetera, etcetera. And if you look at the difference, difference between this and this is h c ν bar, difference between this and this is h c ν bar, difference between this and this is h c ν bar. So, that means difference between the successive energy levels is h c ν bar. That means this difference is h c ν bar, each one is h c ν bar. And if you set this h c ν bar if I just write this to be equal to E then you have E_2, E_3, E_4, E etcetera.

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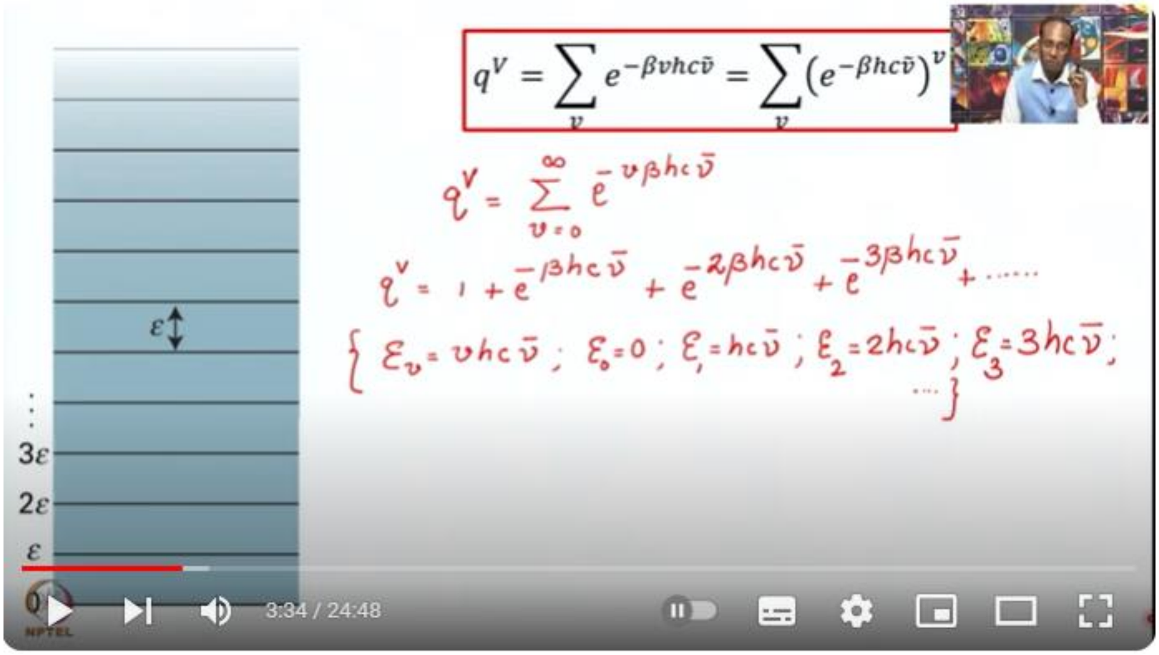

$$q^V = \sum_v e^{-\beta v hc\bar{\nu}} = \sum_v \left(e^{-\beta hc\bar{\nu}}\right)^v$$

$$q^V = \sum_{v=0}^{\infty} e^{-v\beta hc\bar{\nu}}$$

$$q^V = 1 + e^{-\beta hc\bar{\nu}} + e^{-2\beta hc\bar{\nu}} + e^{-3\beta hc\bar{\nu}} + \ldots\ldots$$

$$\left\{ \varepsilon_v = vhc\bar{\nu};\ \varepsilon_0 = 0;\ \varepsilon_1 = hc\bar{\nu};\ \varepsilon_2 = 2hc\bar{\nu};\ \varepsilon_3 = 3hc\bar{\nu};\ \ldots \right\}$$

So, this becomes a uniform ladder of energy levels. Remember the approximation here, we are considering that the vibrational excitation is not too large. Therefore, we are using the harmonic oscillator approximation. So, therefore, this is the same case as that we have discussed earlier when we talked about uniform ladder of energy levels. So, let me come back to this discussion and if you look at the sum it is 1 plus exponential minus β E plus exponential minus 2 β E plus exponential minus 3 β E which can be written as q_v is equal to 1 plus exponential minus β h c ν bar.

For v equal to 1 for v equal to 2 this second term I can write minus β h c ν bar square plus exponential minus β h c ν bar cube plus so on so on. And if I just represent this as x this whole as x then q^v is equal to 1 plus x plus x square plus x cube plus so on so on so on. This is sum of a GP and sum of a GP as we have earlier discussed when we were discussing uniform ladder of energy level it is 1 over 1 minus x β h c ν bar. This is the expression that you are going to use to calculate or to determine the value of vibrational contribution to partition function. Remember that we have used only one approximation here and that approximation is that we have considered the system to be harmonic oscillator which has led to this uniform ladder of energy level and we have not used any other approximation.

So, for a given vibrational wave number you will have a vibrational partition function. If the vibrational wave number changes you will have another value of vibrational partition function. The overall value of vibrational partition function will be equal to q_v 1 into q_v 2 into q_v 3 etcetera etcetera as we have discussed earlier. So, within the approximation of harmonic oscillator or uniform ladder of energy level we can use this expression exclusively at any temperature and we can now discuss the conditions you know what happens when the temperature is very high, what happens when the temperature is very low can we further modify this expression. So, just a recap as I discussed in the previous slide that you can treat within the harmonic oscillator approximation, you can treat the system like a uniform ladder of energy levels which gives rise to equally spaced infinite array of energy levels as shown over here and a harmonic oscillator has the same spectrum of levels that is what I have been discussing.

And our discussion of expanding this I will just quickly once again write for the benefit of all when v is equal to 0 then it is 1 plus exponential minus β h c ν bar plus exponential minus β h c ν bar square plus exponential minus β h c ν bar cube plus so on so on that is what it leads to and this leads to this result that is what we discussed in the previous lecture. That means this expression now we are going to use for calculation for determination of vibrational contribution with this background let us move further. Now there can be different conditions for example, if we consider the vibrational wave number which are very very high that is if β v h c ν bar is much much higher than 1. Let me make a simple correction over here this v is not there. So, treat this as 1 over 1 minus exponential minus β h c ν bar v is not there.

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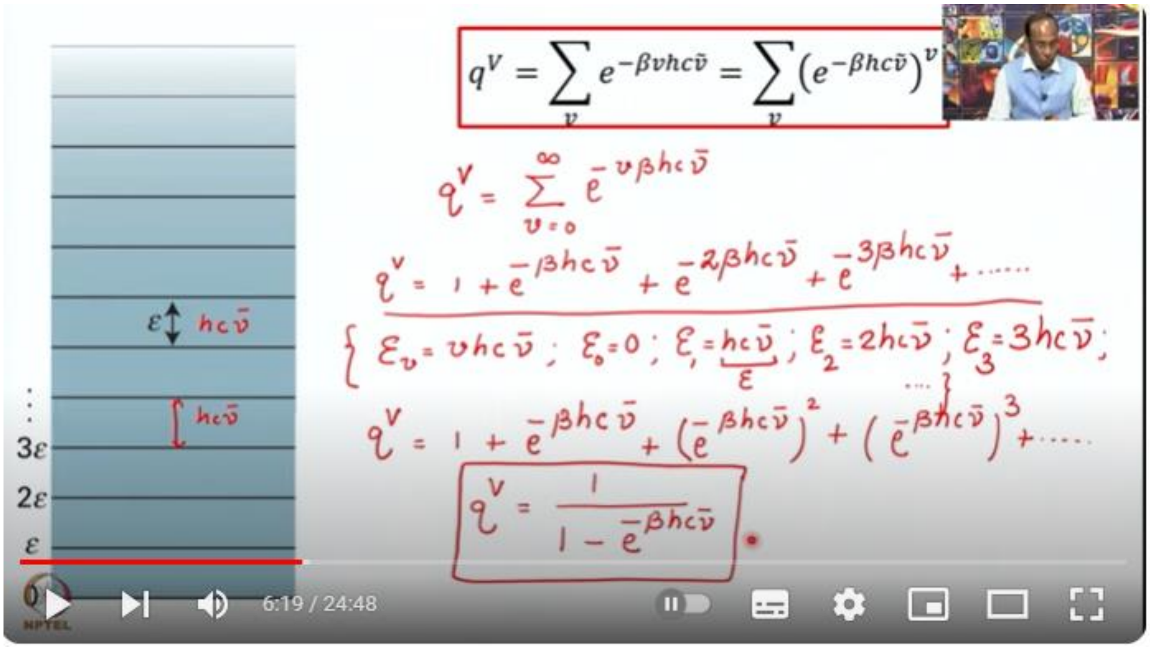

$$\boxed{q^V = \sum_v e^{-\beta v hc\bar{\nu}} = \sum_v \left(e^{-\beta hc\bar{\nu}}\right)^v}$$

$$q^v = \sum_{v=0}^{\infty} e^{-v\beta hc\bar{\nu}}$$

$$q^v = 1 + e^{-\beta hc\bar{\nu}} + e^{-2\beta hc\bar{\nu}} + e^{-3\beta hc\bar{\nu}} + \cdots$$

$$\left\{ \varepsilon_v = v hc\bar{\nu} ;\ \varepsilon_0 = 0 ;\ \varepsilon_1 = \underbrace{hc\bar{\nu}}_{\varepsilon} ;\ \varepsilon_2 = 2hc\bar{\nu} ;\ \varepsilon_3 = 3hc\bar{\nu} ;\ \ldots \right\}$$

$$q^v = 1 + e^{-\beta hc\bar{\nu}} + \left(e^{-\beta hc\bar{\nu}}\right)^2 + \left(e^{-\beta hc\bar{\nu}}\right)^3 + \cdots$$

$$\boxed{q^v = \frac{1}{1 - e^{-\beta hc\bar{\nu}}}}$$

So, make that correction. So, same thing I will put over here which is equal to 1 over 1 minus exponential minus β h c ν bar. So, if β h c ν bar is much much greater than 1 then what happens if this is much much greater than 1 then exponential minus very high quantity you can ignore that. That means in that case q_v is going to be approximately equal to 1. That means we are talking about if the separation is very very high in that case you will have mostly the contribution due to ground state only.

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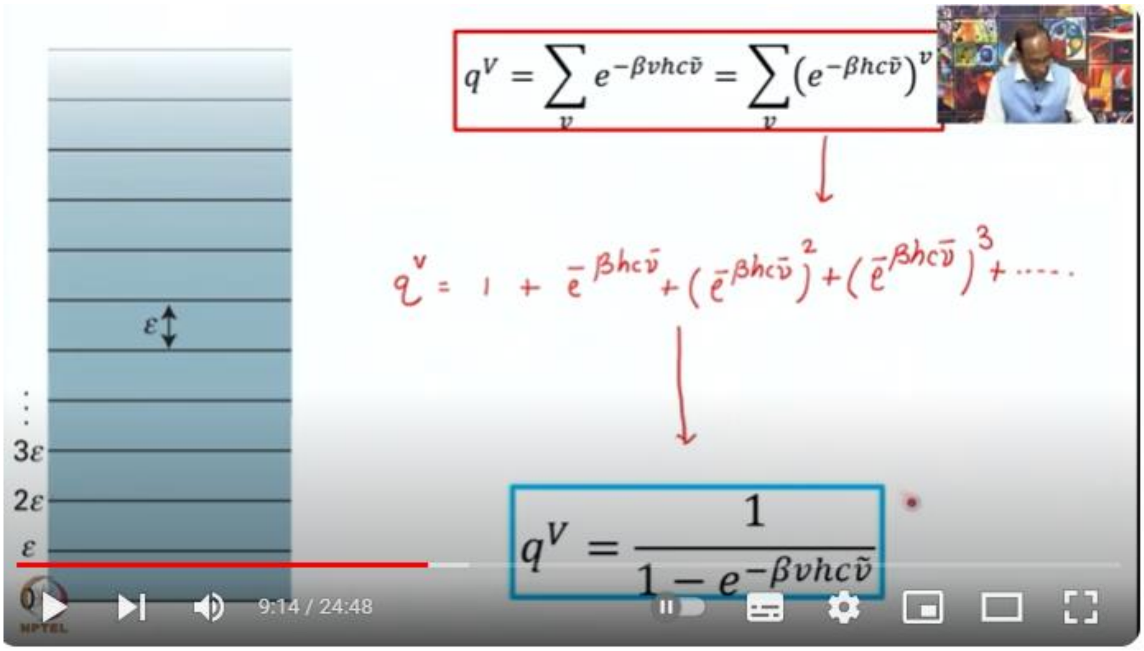

$$\boxed{q^V = \sum_v e^{-\beta v hc\tilde{\nu}} = \sum_v \left(e^{-\beta hc\tilde{\nu}}\right)^v}$$

$$q^v = 1 + e^{-\beta hc\bar{\nu}} + \left(e^{-\beta hc\bar{\nu}}\right)^2 + \left(e^{-\beta hc\bar{\nu}}\right)^3 + \cdots$$

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

That means when you talk about vibrational levels most of the molecules will be there in the ground state only and in that case the vibrational contribution is going to be 1. So, when I put this condition that means I am talking k T is much much less than h c ν bar right β is equal to 1 over k T. That means we are talking about here temperatures which are very very low compared to the h c ν bar or k T is much much lower compared to h c ν bar. Example for example take methane molecule and in the methane molecule the lowest vibrational wave number is 1306 cm^{-1} and when you use room temperature let us say 25 degree centigrade then the value of β h c ν bar you can put the number h is Planck's constant c is speed of light and ν bar is the wave number and when you put the numbers it turns out to be 6 and exponential minus 6 is 0.002.

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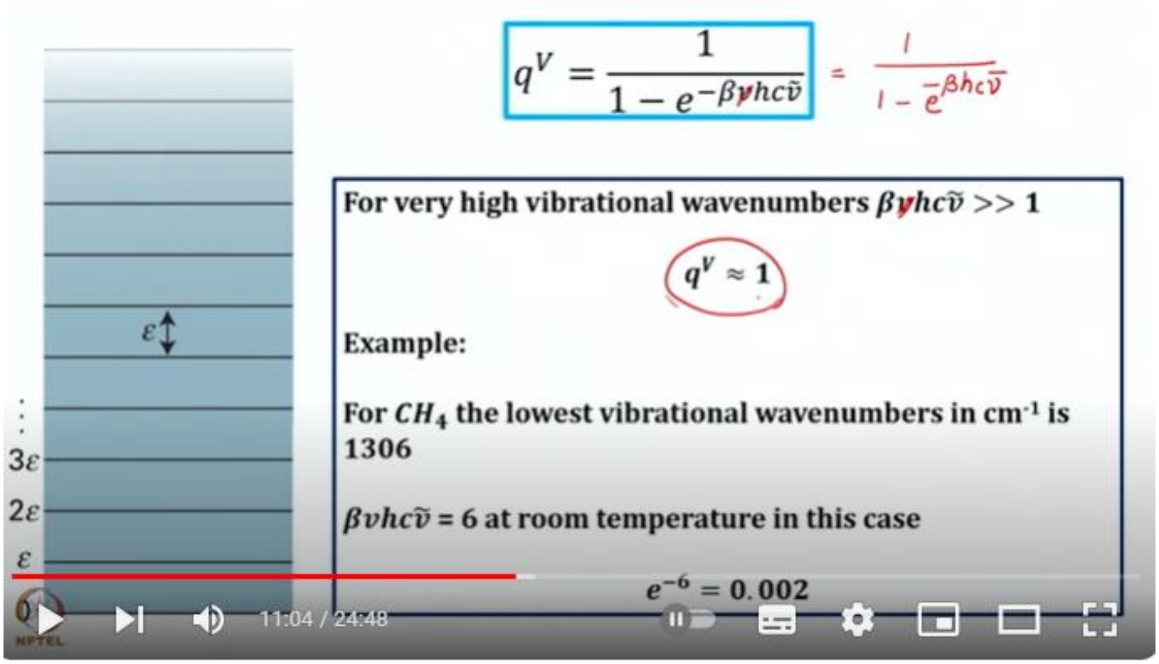

$$\boxed{q^V = \frac{1}{1 - e^{-\beta \cancel{\nu} hc\tilde{\nu}}}} = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}}$$

For very high vibrational wavenumbers $\beta \cancel{\nu} hc\tilde{\nu} >> 1$

$$q^V \approx 1$$

Example:

For CH_4 the lowest vibrational wavenumbers in cm^{-1} is 1306

$\beta \nu hc\tilde{\nu} = 6$ at room temperature in this case

$$e^{-6} = 0.002$$

So, that means 1 over 1 minus 0.002 is approximately 1 ok. So, therefore, if the temperature is very low or if the wave numbers are very very large in that case it is understood that the value of vibrational contribution to partition function for that normal mode of vibration is going to be close to 1 and the reason is given over here just in the form of a short calculation. Now what happens if β h c ν bar is much much less than 1 or k T is much much higher than β h c ν bar that means we are talking about high temperature now. When the temperature is very high then I have q_v is equal to 1 over 1 minus exponential minus β h c ν bar this is very small right and if you treat this β h c ν bar as x 1 over exponential minus x if x is very very small then you can expand this 1 minus with this exponential minus x in this form $1 - x + x^2 - x^3/3!$ ……etcetera etcetera it will come the squared terms cube terms because it is anyway small the square of small is further small cube of small is further small.

So, all these higher values can be ignored. So, what you are left with 1 minus 1 minus β h c ν bar. So, in that case what I have is here 1 over 1 and 1 get cancelled I have β h c ν bar only and β is equal to 1 over k T and β is 1 over k T. So, when you put β is 1 over k T you have vibrational contribution ask T over h c ν bar. I want to highlight two results over here one is this one where we wrote q_v is equal to 1 over 1 minus exponential minus β h c ν bar this can be used at any temperature there is no need to worry about whether the temperature is low temperature is high wave number is low wave number is high nothing to worry about you can go ahead and use this expression.

However, when the temperature is high or when the temperature is low you need to worry about if the temperature is low you cannot ignore if you cannot ignore that and anyway, we have shown if the temperature is low or if ν bar is very very high then q^v is approximately coming to be 1. However, if the temperature is high compared to energy separation in that case we show that q_v can be approximated by k T over h c ν bar when we can use this result and when we can use this result. This result can be used anyway as we just discussed at any temperature, but this result when can be used in order to use that we will come to that what temperature can be used over here, but you see if I write q^v is equal to 1 over 1 minus exponential minus β h c ν bar. If the temperature is very very low for your simplicity, I will write this also 1 minus exponential minus h c ν bar by so if the temperature you see is very very low when the temperature is very very low then exponential minus very high number can be ignored in that case q_v is approximated by a value of 1. I hope it is clear temperature low this number is high exponential minus high number can be ignored so q_v is approximately equal to 1.

If the temperature is high if the temperature is high, what did we have we had the result we just derived which is q^v is approximately k T over h c ν bar. So, k T over h c ν bar that means it is when k T is much much higher than h c ν bar this is what was the condition that is k T is much much higher than. Let me correct this k T is much much higher than h c ν bar alright.

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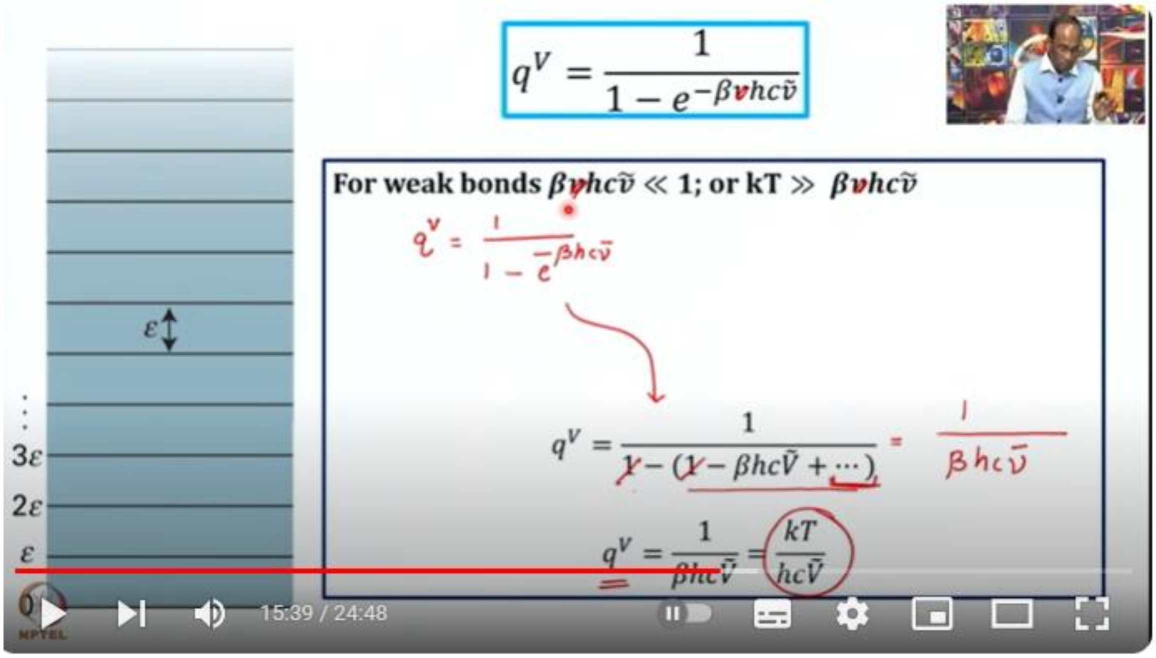

$$\boxed{q^V = \frac{1}{1-e^{-\beta\nu hc\tilde{\nu}}}}$$

For weak bonds $\beta\nu hc\tilde{\nu} \ll 1$; or kT $\gg$ $\beta\nu hc\tilde{\nu}$

$$q^v = \frac{1}{1-e^{-\beta hc\tilde{\nu}}}$$

$$q^V = \frac{1}{\cancel{1}-(\cancel{1}-\beta hc\tilde{V}+\underline{\cdots})} = \frac{1}{\beta hc\tilde{\nu}}$$

$$q^V = \frac{1}{\beta hc\tilde{V}} = \boxed{\frac{kT}{hc\tilde{V}}}$$

So, look at the comment the vibrational partition function of a molecule in the harmonic approximation note that partition function is linearly proportional to temperature when the temperature is high. When temperature is high you use this result and this result basically you know q_v is directly proportional to temperature k is constant h is constant c is constant ν bar is constant for a given mode and then it is almost linearly dependent on temperature right.

This is expressed in terms of k T over h c ν, but then again you know bringing back the same issue that at what temperature or under what conditions of temperature we can use this approximation. For that it is a good idea to introduce a temperature which is called characteristic vibrational temperature. How to introduce characteristic vibrational temperature? We had q^v is equal to k T over h c ν bar. So, you can mathematically show whatever I am going to discuss that now. Characteristic vibrational temperature is introduced by writing this equation k times θ_v is equal to h c ν bar where θ_v is the characteristic vibrational temperature.

That means, write θ_v is equal to h c ν bar by k. We can calculate this you know you can work out the units of this it will turn out to be temperature limit. You calculate this θ_v and on the other hand we have let us say experimental temperature experimental temperature which is T. Now, if temperature T experimental temperature is higher than θ_v then you can use this approximation. So, that is the utility of characteristic vibrational temperature that is it is the temperature above which this approximation is valid.

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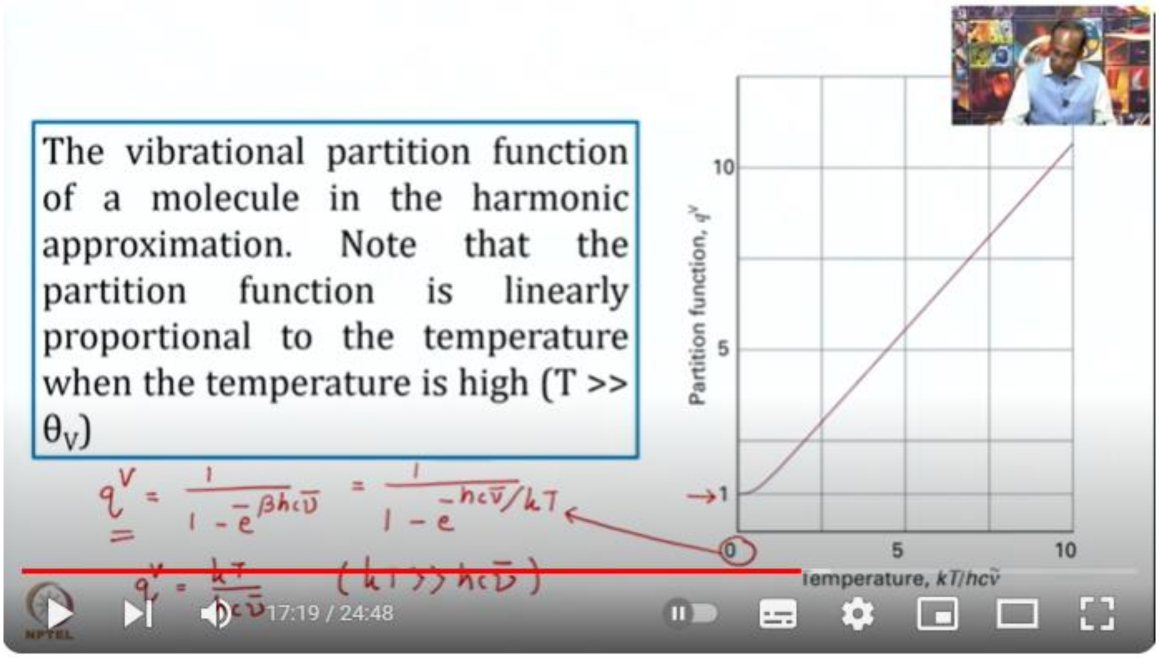

The vibrational partition function of a molecule in the harmonic approximation. Note that the partition function is linearly proportional to the temperature when the temperature is high (T >> θ_V)

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

$$q^V = \frac{kT}{hc\bar{\nu}} \quad (kT >> hc\bar{\nu})$$

And since we have defined the characteristic vibrational temperature θ_v as h c ν bar by k then I can write for h c ν bar by k I can write θ_v. That means, the vibrational partition function then becomes T by θ_v. So, now, we have three forms of vibrational contribution to partition functions. One form is let me write down again v dot q^v is equal to 1 over 1 minus exponential minus β h c ν bar. Second form we write 1 over β h c ν bar or is equal to k T over h c ν bar.

Third form we had basically a modified form of this which is T by θ_v and we have discussed in details under what conditions to use this under what conditions to use any of these. This one can be used at any temperature can be used at any temperature at any wave number. The only approximation in deriving this was we have used harmonic oscillator approximation that is the vibrational is not too much vibrational excitation is not too much. And then when the temperature is high or weak bonds in that case, we got this expression which can be used. However, in order to use this expression what you need is to find out the characteristic vibrational temperature and see if the experimental temperature is much higher than the characteristic vibrational temperature then only you can use this approximation.

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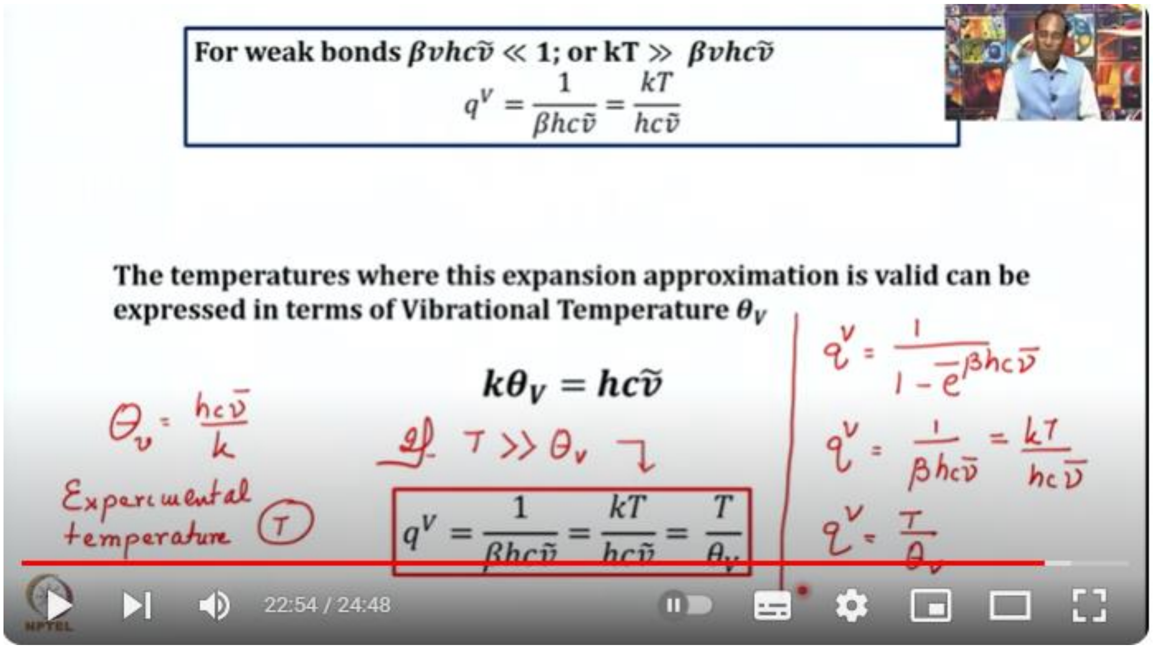

For weak bonds $\beta\nu hc\tilde{\nu} \ll 1$; or $kT \gg \beta\nu hc\tilde{\nu}$

$$q^V = \frac{1}{\beta hc\tilde{\nu}} = \frac{kT}{hc\tilde{\nu}}$$

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

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

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

Experimental temperature $\textcircled{T}$

If $T \gg \theta_v$ ↓

$$\boxed{q^V = \frac{1}{\beta hc\tilde{\nu}} = \frac{kT}{hc\tilde{\nu}} = \frac{T}{\theta_V}}$$

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

$$q^v = \frac{1}{\beta hc\bar{\nu}} = \frac{kT}{hc\bar{\nu}}$$

$$q^v = \frac{T}{\theta_v}$$

And then by using the definition of characteristic vibrational temperature we define that q_v is also equal to T by θ_v. So, therefore, these are the different means these are the different ways of evaluating of calculating or of measuring the vibrational contribution to partition function. So, what we have discussed in this lecture and the previous lecture is how to calculate how to measure the value of vibrational contribution to partition function. First, we discussed that there can be more than one normal modes of vibration. The overall value of vibrational contribution to partition function will be equal to multiplication of each mode of vibration.

Then how to evaluate each normal mode of vibrations contribution to partition function you can use any of these three equations depending upon the temperature. So, now, we are equipped with evaluating the partition function for translational degree of freedom, for rotational degree of freedom and for vibrational degree of freedom. We will make the things more clear by solving numerical problems for each case before we switch over to electronic contribution to overall partition function and that we will do in the next lecture. Thank you very much. Thank you.