Fundamentals of Statistical Thermodynamics

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Lecture – 51

Contributions to equilibrium constant (continued) and Problems Solving

Welcome back, we have been discussing Contributions to Equilibrium Construct. We have taken certain examples for discussing insights into different contributions that can go into explaining the equilibrium constant in terms of population of the various energy levels corresponding to reactants and products. In the previous lecture, we were discussing a special case where the reactants R have only one ground state available and the product P has energy states which are like uniform ladder of energy levels. And then by using an expression for equilibrium constant which is equal to the ratio of the molecular partition functions corresponding to products and reactants into exponential minus ΔE° by RT. And then we discussed that since it has only one energy level, soqis 1 and here we used the partition function for a uniform ladder of energy levels and after substitution we got this result. And that result is that equilibrium constant is equal to Boltzmann constant into temperature divided by this energy separation into exponential minus ΔE_0 by RT.

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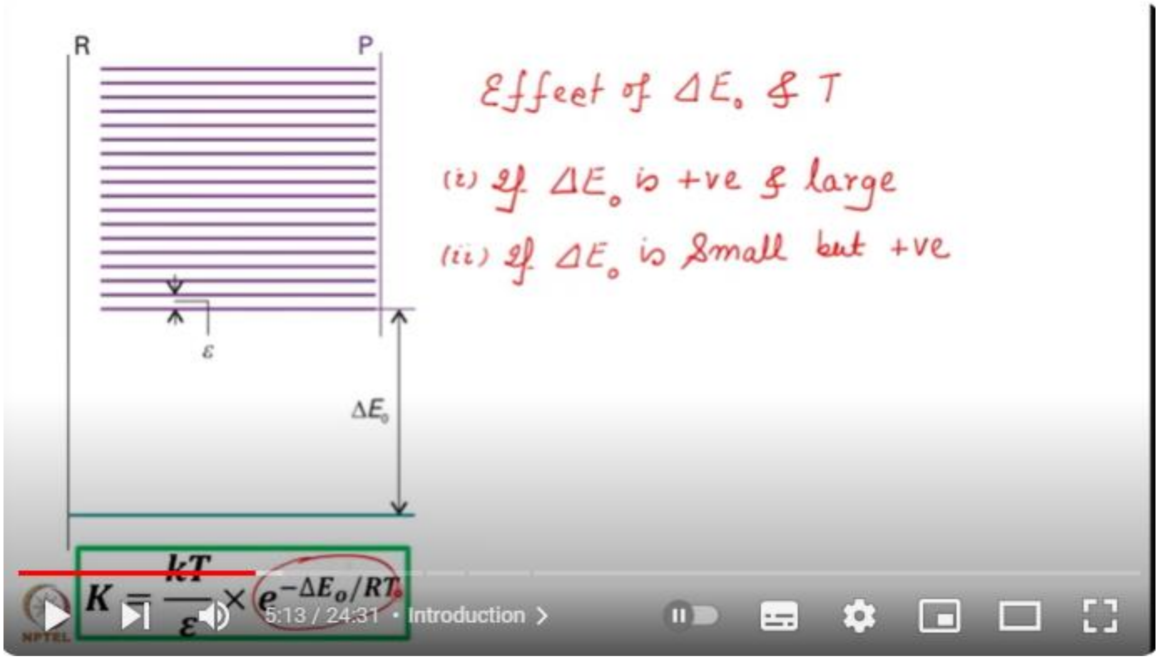

Effect of ΔE_0 & T

(i) If ΔE_0 is +ve & large

(ii) If ΔE_0 is small but +ve

$$K = \frac{kT}{\varepsilon} \times e^{-\Delta E_0/RT}$$

Note that this ΔE_0 is positive, is a positive number here. And then we started discussing Le Chatelier principle. Recognize that this particular example is of an endothermic reaction because the energy corresponding to product is higher than the energy, zero-point energy corresponding to the reactants. Now let us discuss effect of temperature, effect of ΔE_0 and temperature both we will discuss.

First of all case number 1, if $\Delta E_0$is positive and large, what I am trying to say here is that if this distance, this difference is very large, then this exponential term, if ΔE° is very large that means what will happen? If $\Delta E_0$is very large, then the value of equilibrium constant is going to be small. So, if ΔE_0 is large that means exponential minus large quantity which is equal to 1 over exponential large quantity that is going to reduce the value of k, the k is going to be small. If k is small what that means that the population of the various energy levels corresponding to product is also small. It makes a sense because if ΔE_0 is large, most of the molecules will be in the energy state corresponding to R that means k is going to be small. The second example or second case we will choose if ΔE° is small but positive, now you assume that this $\Delta E_0$is very not very large, it is positive but not very large.

Then this is a reasonable number. Remember if we were saying if ΔE_0 is large, then this factor is going to dominate. If $\Delta E_0$is small but still positive, this is a reasonable number but this pre-exponential factor is going to dominate. That means if we increase the temperature, then more and more molecules will occupy the energy levels corresponding to the product. So that means the equilibrium constant is also going to increase.

I repeat if $\Delta E_0$is small but still positive, in that case this is a reasonable number and the overall value of k is going to be dependent upon this temperature. So according to this if you increase the temperature kT by E term is going to increase. So therefore, the equilibrium constant will increase. Isn't it in accordance with the Le Chatelier principle which says that for an endothermic reaction, if the temperature is increased, the value of equilibrium constant is going to increase. Therefore, based upon these considerations, we took only one energy level for reactant and we took uniform ladder of energy levels for product, we derived some equation and based on that equation we have been able to explain the effect of temperature.

Our explanation is consistent with Le Chatelier principle. Remember that ΔG° is equal to minus RT log k. This particular discussion suggests that we cannot explain everything just based upon ΔG°. It is not just ΔG° but its components ΔG° has two components, one is ΔH° and the other is T ΔS°. I would say minus T ΔS°.

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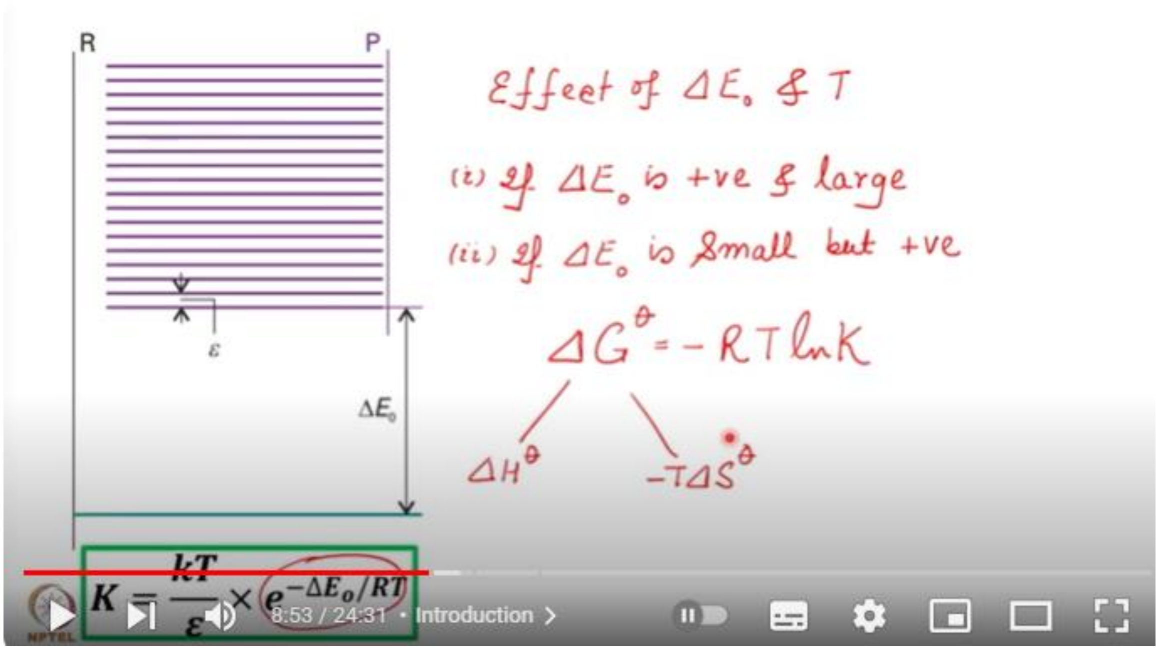

Effect of ΔE_0 & T

(i) If ΔE_0 is +ve & large

(ii) If ΔE_0 is small but +ve

$$\Delta G^\theta = -RT\ln K$$

ΔH^θ $-T\Delta S^\theta$

$$K = \frac{kT}{\varepsilon} \times e^{-\Delta E_0/RT}$$

So these two components are explained by this differences in zero-point energy levels. This particular example belongs to endothermic reaction. So therefore, for the reaction to be spontaneous for an endothermic reaction, there has to be sufficient increase in entropy and that factor will be taken care of if more and more molecules here occupy these densely populated states of the product that will explain the increase in entropy for the process. So it is not just the free energy, its components ΔH° and minus T ΔS° become very very important in providing mechanistic insights into the process under consideration. So, these were the various contributions to equilibrium constant.

It is very important to address these contributions because ΔH° ΔH in other words the enthalpy depends upon the nature of interaction. An entropy change depends upon not only the interaction but also associated with the changes in the surroundings. So it is not only the association between the two reactants, if that association between two reactants lead to release of lot of solvent molecules which were earlier oriented around the reacting groups and that release can increase the entropy. And here in terms of statistical thermodynamics, we are explaining them in terms of the population of various energy states. So not only enthalpy but entropy change is also very important consideration.

By now we have discussed all thermodynamic quantities starting with internal energy, we discussed entropy, we discussed Helmholtz energy, Gibbs energy, enthalpy, heat capacity, mean energy and then we have now discussed the equilibrium constant. We have connected all these thermodynamic quantities with either canonical partition function or molecular partition function. So, in a sense now we have shown that all these thermodynamic quantities can be experimentally measured with the help of spectroscopy. All right. Now a couple of lectures we will spend on solving numerical problems.

One such numerical problem let us take it up today. The question is to calculate the vibrational contribution to molar heat capacity of nitrogen gas at 1000 K. The experimental value is 3.43 joules per K per mole. The question is calculation of vibrational contribution to molar heat capacity.

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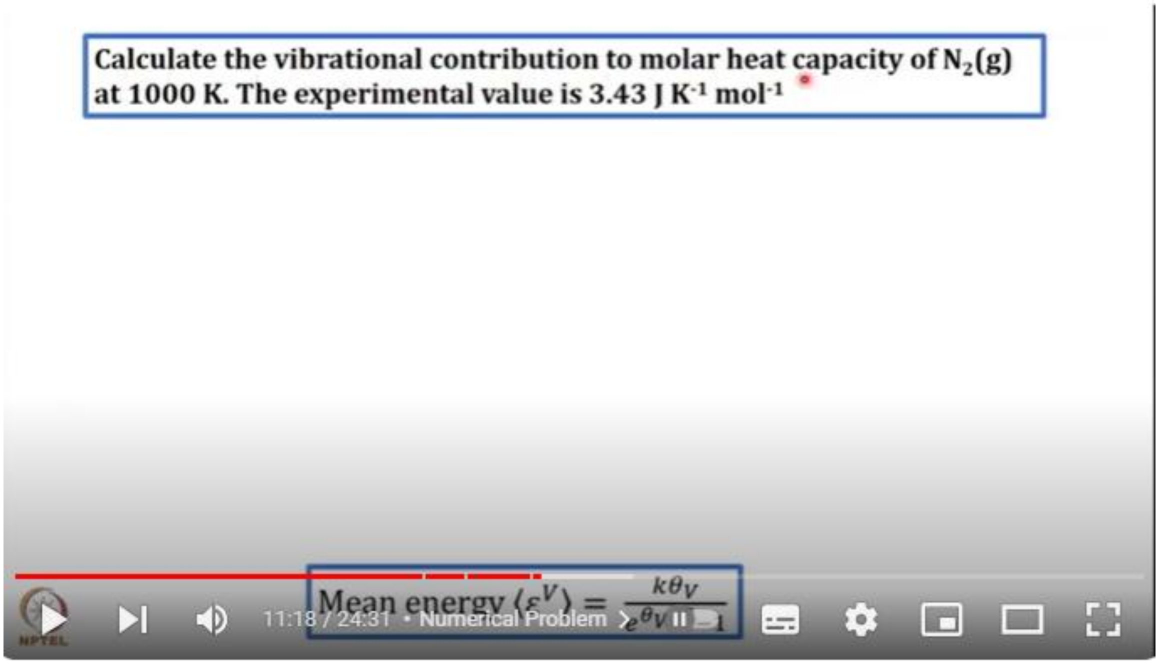

Calculate the vibrational contribution to molar heat capacity of $N_2(g)$ at 1000 K. The experimental value is 3.43 J K^{-1} mol^{-1}

Mean energy $\langle \varepsilon^V \rangle = \frac{k\theta_V}{e^{\theta_V} \quad 1}$

How do we begin answering this question? First of all, we need to first decide that how to connect this molar heat capacity with something which may depend upon the molecular partition function. Molar heat capacity or heat capacity is change in internal energy when 1 °C temperature change occurs in a system at constant volume. So, what we have now is to calculate the vibrational contribution to molar heat capacity of nitrogen gas at 1000 K. The experimental value is given to us and we know that heat capacity C_v is equal to Δ U by Δ T at constant volume.

This we know. We also know that $C_{v,m}$ is equal to Avogadro constant into temperature derivative of mean energy at constant volume that also we know. So that means why don't we first get an expression for the mean energy? Mean energy is minus 1 by q into Δq by Δ β at constant volume. Let us do that. We know that we are going to now derive an expression for mean vibrational energy which will be minus 1 by q vibrational into Δq vibrational Δ β at constant volume. This is what we are going to do.

We also know that q vibrational is equal to 1 over 1 minus exponential minus β E. Therefore, your mean vibrational energy is going to be minus 1 by q that means minus 1 minus exponential minus β E. This is minus 1 by q into derivative of 1 by exponential minus β E. This is going to be minus 1 over 1 minus exponential minus β E square into minus exponential minus β E into minus E. This is all going to be the expression for Ev that is minus 1 by q this is minus 1 by q into derivative of this is minus 1 by 1 over 1 minus exponential minus β E square derivative of this which is minus exponential minus β E then derivative of minus β E is minus E.

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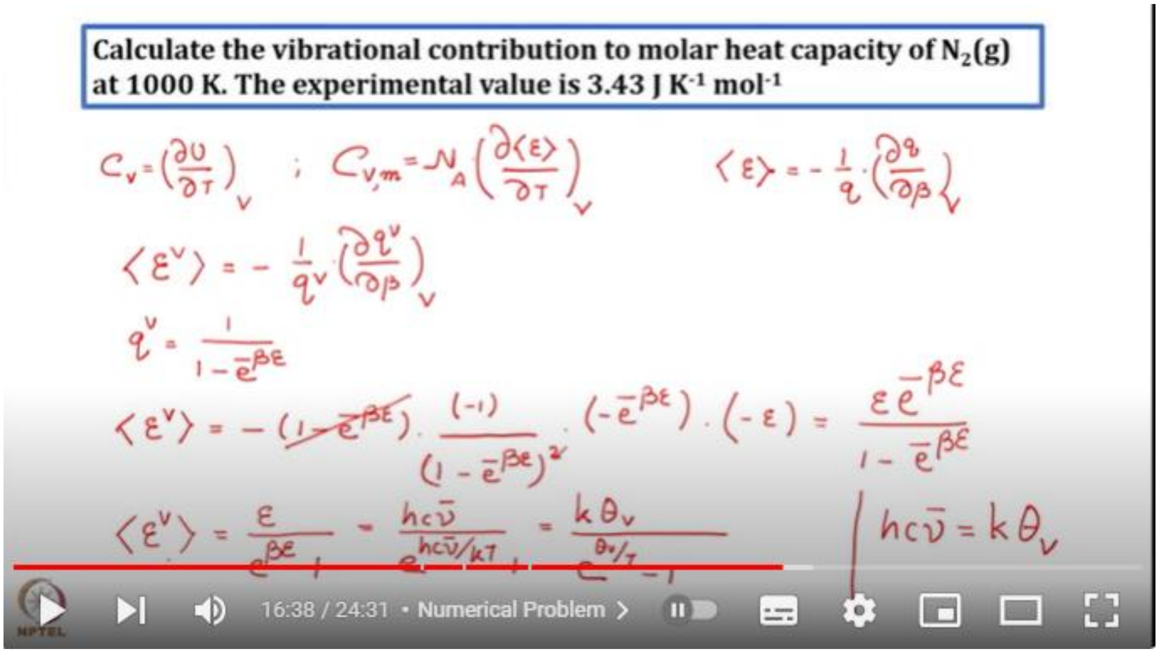

Calculate the vibrational contribution to molar heat capacity of $N_2(g)$ at 1000 K. The experimental value is 3.43 J K^{-1} mol^{-1}

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \quad ; \quad C_{v,m} = N_A\left(\frac{\partial \langle \varepsilon \rangle}{\partial T}\right)_V \qquad \langle \varepsilon \rangle = -\frac{1}{q}\cdot\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$\langle \varepsilon^v \rangle = -\frac{1}{q^v}\left(\frac{\partial q^v}{\partial \beta}\right)_V$$

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

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

$$\langle \varepsilon^v \rangle = \frac{\varepsilon}{e^{\beta\varepsilon}-1} = \frac{hc\bar{\nu}}{e^{hc\bar{\nu}/kT}-1} = \frac{k\theta_v}{e^{\theta_v/T}-1} \quad \Bigg| \; hc\bar{\nu} = k\theta_v$$

So what it comes to now? This is cancelling with this and we have E exponential minus β E over 1 minus exponential minus β E. I can write this again as E over exponential β E minus 1 which is equal to h c ν bar over exponential h c ν bar by k T minus 1. But remember h c ν bar is equal to k times θ_v. So, I can write this k times θ_v divided by exponential h c ν bar by k is equal to θ_v so θ_v by T minus 1. So therefore, my mean vibrational energy is k times θ_v over exponential θ_v by T minus 1.

So what I have now? Mean vibrational energy is k times θ_v over exponential θ_v by T minus 1. This is what I have let us double check k times θ_v over exponential θ_v by T minus 1. Now we are interested in $C_{v,m}$ which is equal to N_A times derivative of ΔE by with respect to T at constant volume. And since there is no volume term appearing in this I will as well may not write at constant volume but it is ok. So this is N_A times I need to take derivative of this which is k θ_v is a constant number into minus 1 over exponential θ_v by T minus 1 square into derivative of θ_v by T this will be minus θ_v by T square.

What I have now? I have k times N_A into there are two θ_v's θ_v square by T square minus minus cancel into 1 over exponential θ_v by T minus 1 square k times N_A this is r. Now you see I have this derived this equation $C_{v,m}$ is equal to R times θ_v by T whole square into yes there has to be another term over here there has to be exponential θ_v by T yes exponential

θ_v by T yes we put there. So exponential θ_v by T over exponential θ_v by T minus 1 whole square. That means now if I have the numbers for θ_v and temperature, I can easily get the value. θ_v can be calculated from h c ν bar is equal to k θ_v from the knowledge of planks constant speed of light wave number is already given 2 3 4 4 cm^{-1} k Boltzmann constant you can get θ_v.

That means your θ_v is going to be h c ν bar by k substitute the numbers and you get a value of θ_v which is 3374.3 374 K. Now θ_v by T T is 1000. So, θ_v by T is 3374 by 1000 which is 3.374 you have the value of θ_v you have the value of θ_v by T substitute what you get is constant volume molar heat capacity equal to 3.48 joules per K per mole.

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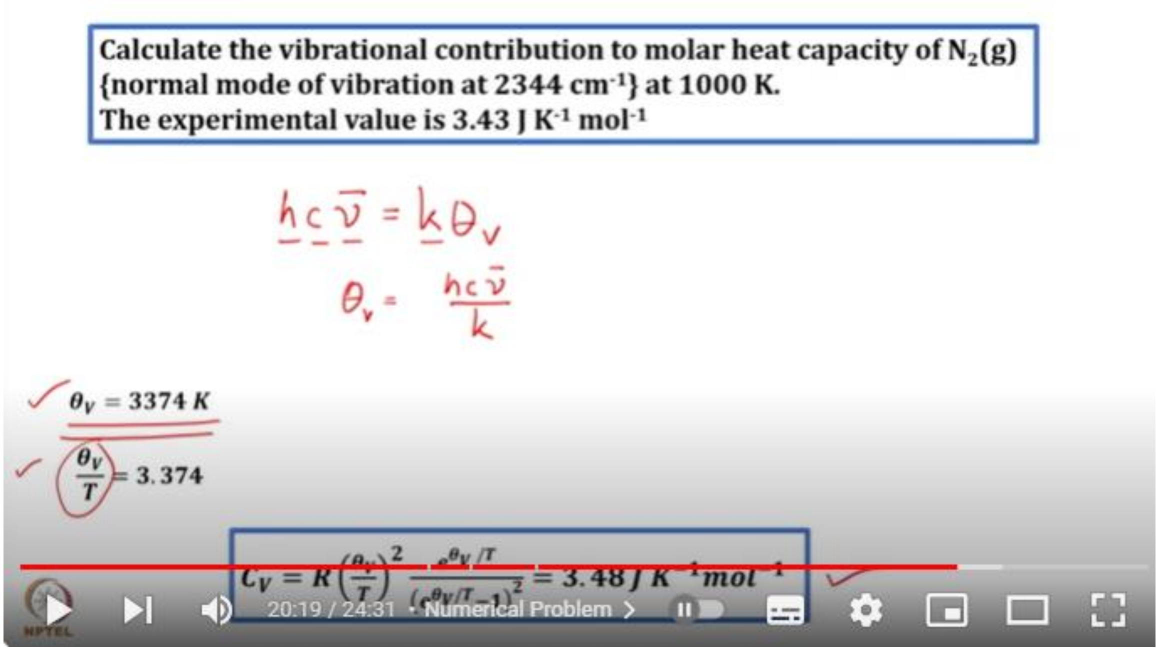

Calculate the vibrational contribution to molar heat capacity of $N_2(g)$ {normal mode of vibration at 2344 cm^{-1}} at 1000 K.
The experimental value is 3.43 J K^{-1} mol^{-1}

$$\underline{h}\,\underline{c}\,\underline{\bar{\nu}} = \underline{k}\theta_v$$

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

$$\theta_V = 3374\ K$$

$$\frac{\theta_V}{T} = 3.374$$

$$C_V = R\left(\frac{\theta_V}{T}\right)^2 \frac{e^{\theta_V/T}}{\left(e^{\theta_V/T}-1\right)^2} = 3.48\ J\ K^{-1} mol^{-1}$$

Continuing this further it also says calculate the fraction of molecule in v^th vibrational state fraction population P_i is equal to N_i upon N is equal to exponential minus β E_i upon q that we know. Therefore, if I replace p i by fraction in the v^th vibrational state this will be equal to exponential minus β vibrational energy level divided by k q q vibrational and what are these vibrational energy levels v h c ν bar because we know it is v plus half h c ν bar half h c ν bar we ignore remember the discussion in the vibrational partition function and we also know that q v is equal to 1 over 1 minus exponential minus β h c ν bar once you have that substitute this you end up with this expression once you have this expression then it is a matter of just putting the numbers. The fraction is given by this to calculate f 0 use v is equal to 0 to calculate f $_0$ use f 1 use v is equal to 1 that is all you are already given the wave number v value can be variable β is 1 over k t h is planks constant. So, use those numbers substitute over here you will find out that the fractional population of the ground state is nearly 1 and the first excited state the fractional population is 1.31 into 10 raise to the power minus 5 it is.

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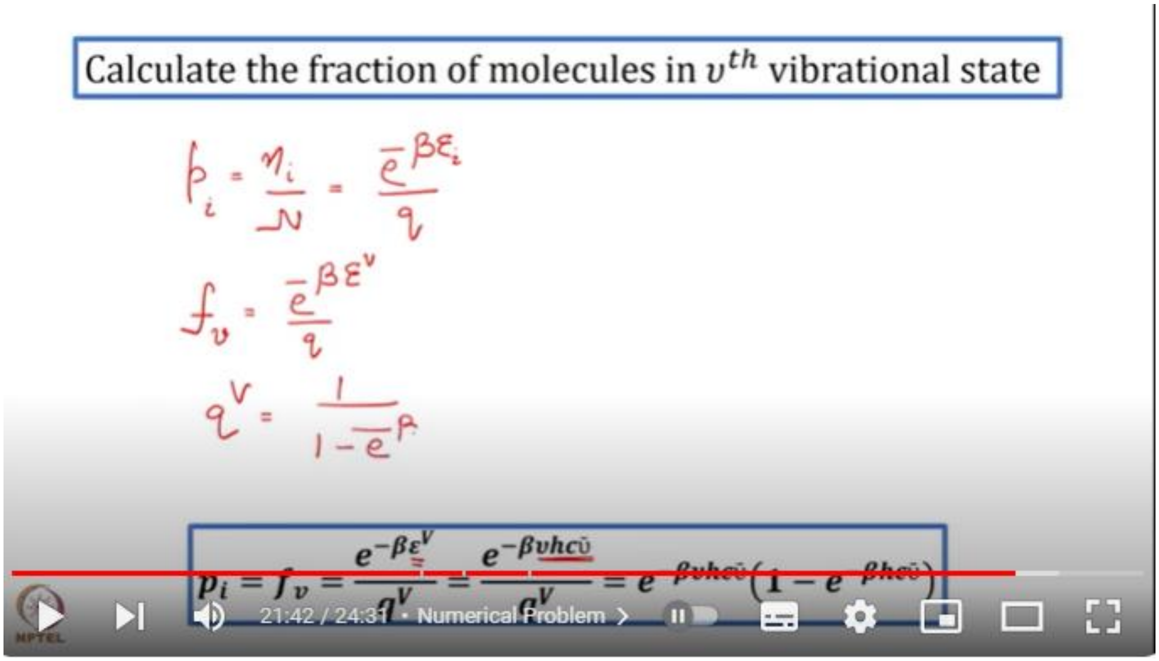

Calculate the fraction of molecules in υ^{th} vibrational state

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{q}$$

$$f_\upsilon = \frac{e^{-\beta\varepsilon^v}}{q}$$

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

$$p_i = f_\upsilon = \frac{e^{-\beta\varepsilon^V}}{q^V} = \frac{e^{-\beta\underline{\upsilon hc\tilde{\upsilon}}}}{q^V} = e^{-\beta\upsilon hc\tilde{\upsilon}}\left(1 - e^{-\beta hc\tilde{\upsilon}}\right)$$

So, less this comparison suggests that even at the temperature which is given temperature given to us is 1000 K even there you see the fractional population in the first excited state is only 1.31 into 10 raise to the power minus 5. That means, most of the molecules are in the ground state only. So, therefore, with the knowledge of the partition functions corresponding to particular mode of motion and the fractional population we can calculate the fractions corresponding of the molecules in the ground state fraction of the molecule in the first excited state provided we know we remember the formulae or we are able to derive the formulae appropriately. In the lectures ahead we are going to take up more examples and do some calculations.

So, that the applications of the derived equations become easier to understand. Thank you very much.

Thank you.