Fundamentals of Statistical Thermodynamics

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Lecture – 52

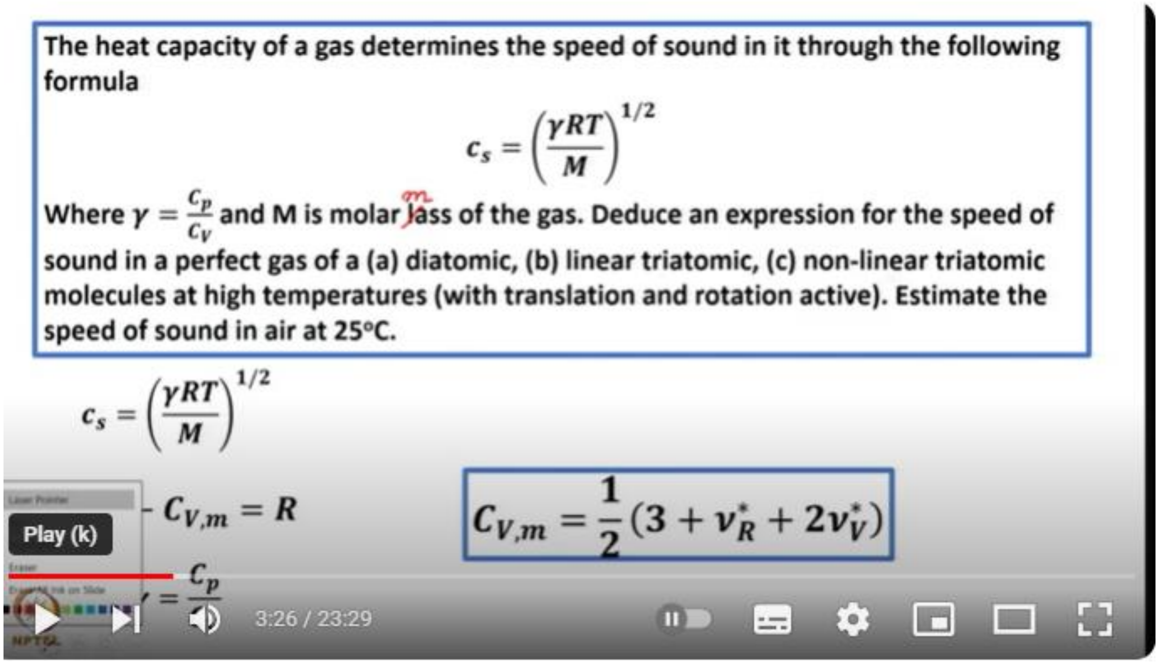
Problem solving

Welcome back. Today also we are going to solve some numerical problems. After having established relationship of almost all thermodynamic quantities with the molecular partition function, now we should be able to apply those developed concepts in solving the problems and addressing the problems. Let us continue with different types of problems and see that how the derived equations, the derived concepts can find their applications. The first question that we would like to solve today is on heat capacity. The question is the heat capacity of a gas determines the speed of sound in it through the following formula.

The formula is c_s is equal to γ R T by m raise to the power 1 by 2. c_s is the speed of sound and the heat capacity determines that means in the given expression there should be something which is connected to heat capacity and that is given to us that γ is the ratio of C_p by C_v, m is the molar mass of the gas, deduce an expression for the speed of sound in a perfect gas of a diatomic, linear triatomic and non-linear triatomic molecules at high temperatures. And it is also given to us that consider only translation and rotation activity. The question is estimate the speed of sound in air at 25 °C.

Let us first of all try to understand the question. According to the given question to us, the speed of sound depends upon the heat capacity of a gas that means you are talking about what is the speed of sound when it travels through a gas. The heat capacity in the given question is represented as ratio of C_p and C_v and we need to deal with diatomic, linear triatomic and non-linear triatomic molecules at high temperatures. Then it says estimate the speed of sound in air at 25 °C. Let us see how to proceed.

See Slide Time: 3:26



The heat capacity of a gas determines the speed of sound in it through the following formula

$$c_s = \left(\frac{\gamma RT}{M}\right)^{1/2}$$

Where $\gamma = \frac{C_p}{C_V}$ and M is molar mass of the gas. Deduce an expression for the speed of sound in a perfect gas of a (a) diatomic, (b) linear triatomic, (c) non-linear triatomic molecules at high temperatures (with translation and rotation active). Estimate the speed of sound in air at 25°C.

$$c_s = \left(\frac{\gamma RT}{M}\right)^{1/2}$$

$$- C_{V,m} = R$$

$$\boxed{C_{V,m} = \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)}$$

$$\gamma = \frac{C_p}{\ }$$

This information that c_s equals γ R T by m square root is given to us. We also know that C_p ,minus C_v or $C_{p,m}$ minus $C_{v,m}$ is equal to R and this is for an ideal gas. Therefore, the disclaimer here is that we are dealing with the ideal gas. The ratio of C_p to C_v is called γ which is also given to you and from here we have to now proceed. Now, let us go back to our discussion when we connected heat capacity with mean energy and then from there, we came up with an approximation.

Why I am saying an approximation is that the equation which is written over here Cv,m is equal to 1 by 2 into 3 by ν R* + 2 ν v*. By using this expression you can estimate the value of C_v. Carefully see what I am saying I said you can estimate the value of Cv. I am not saying that you can calculate exactly calculate because there are approximations involved here. For a gas translational contribution is always there and in three dimensions that is why this 3 by 2 R there is an R over here also.

This 3 by 2 R contribution is always going to be there for a gas at room temperature. Now, then as the temperature increases the rotational contribution also comes in. So, therefore, we have ν R* and ν R* is equal to 2 for linear molecule and 3 for non-linear molecules we have discussed it earlier. Then we have 2 ν v* and this ν v* is equal to either 1 or 0. If the vibrational modes are not active, we are taking the value as 0.

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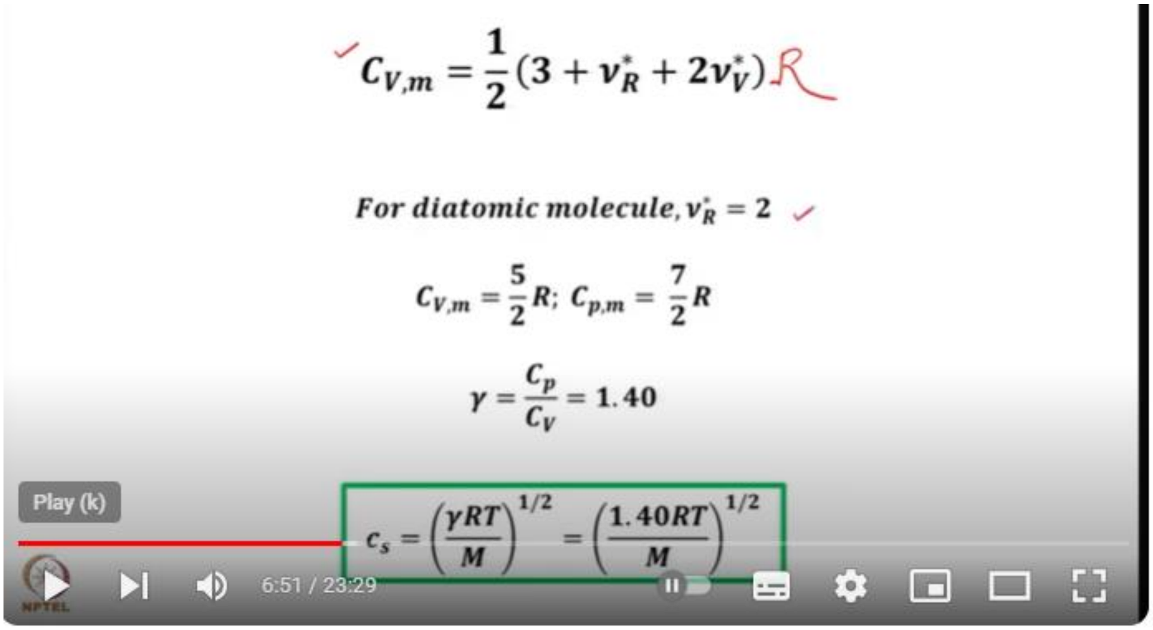


✓ $$C_{V,m} = \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R$$

For diatomic molecule, $\nu_R^* = 2$ ✓

$$C_{V,m} = \frac{5}{2}R;\ C_{p,m} = \frac{7}{2}R$$

$$\gamma = \frac{C_p}{C_V} = 1.40$$

$$\boxed{c_s = \left(\frac{\gamma RT}{M}\right)^{1/2} = \left(\frac{1.40RT}{M}\right)^{1/2}}$$

If the vibrational modes are fully active then we are taking the value of 1. We are not taking any in between value over here that is why I said you can estimate heat capacity by using such a formula. So, for vibrational modes remember that this is for one normal mode of vibration. If there is only one normal mode of vibration ν v* is 1. If there are 2, 3, 4 you have to substitute that number.

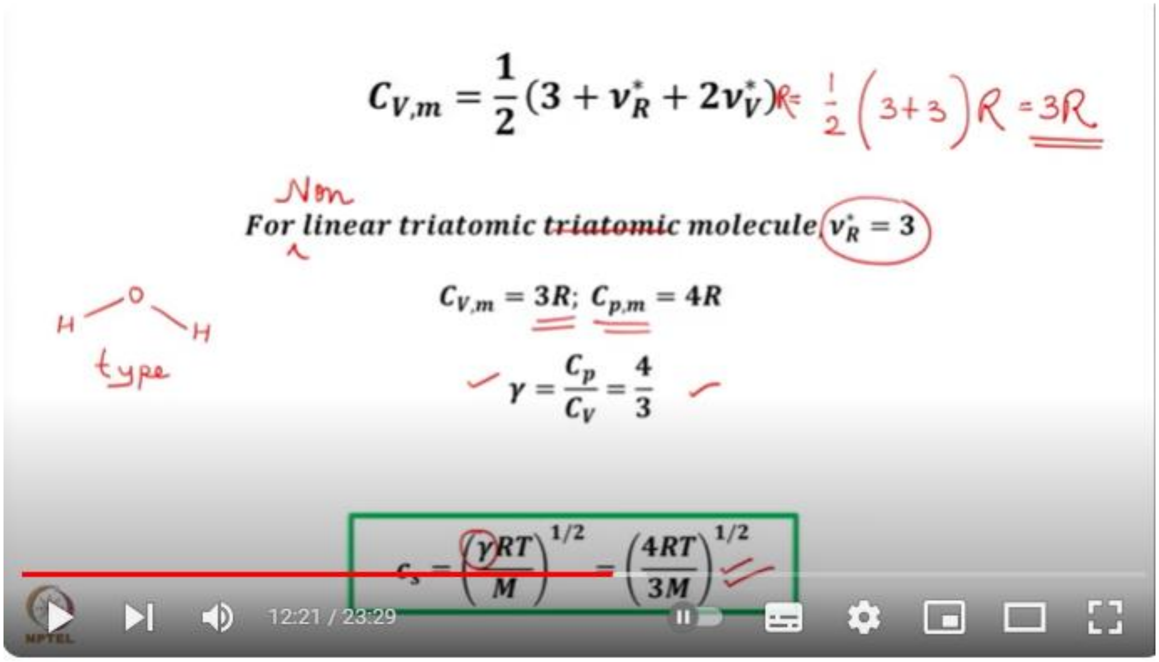
Now, let us proceed. So, we have discussed that the constant molar volume heat capacity can be given by 1 by 2 into 3 + ν_R^* + ν 2 ν v* into gas constant. And we just discussed that for diatomic molecule ν_R^* is equal to 2 because diatomic molecule is linear right. For example, A B and given to us let us look at the statement. What it is given to us? Only translation and rotation active that means the temperature is not that significantly high enough for the vibrations to become active.

Fine with this knowledge translation is active we will keep 3 here. Ration is active. So, ν R since we are dealing with diatomic molecule linear molecule then ν_R^* is equal to 2. So, then 3, 3 + 2 is 5, 5 by 2 R ν v* is 0 because vibrational modes are not active. So, 3 + 2 5, 5 by 2 R.

So, $C_{v,m}$ is 5 by 2 R and as we just discussed that $C_{p,m}$ minus $C_{v,m}$ is equal to R right. I am not writing N over here because we are talking about differences in the molar heat capacities. So, using this equation $C_{p,m}$ is equal to Cv,m + R. So, if $C_{v,m}$ is 5 by 2 R then

$C_{p,m}$ is going to be 7 by 2 γ which is the ratio of Cp and Cv then becomes 7 by 5, 7 by 5 right 7 by 2 divided by 5 by 2 which is 7 by 5 which is 1.

See Slide Time: 12:21



$$C_{V,m} = \frac{1}{2}(3 + \nu_R^* + 2\nu_V^*)R = \frac{1}{2}(3+3)R = \underline{\underline{3R}}$$

Non

For linear triatomic ~~triatomic~~ molecule $\boxed{\nu_R^* = 3}$

H O H

type

$$\underline{\underline{C_{V,m} = 3R}};\ \underline{\underline{C_{p,m}}} = 4R$$

$$\gamma = \frac{C_p}{C_V} = \frac{4}{3}$$

$$\boxed{c_s = \left(\frac{\gamma RT}{M}\right)^{1/2} = \left(\frac{4RT}{3M}\right)^{1/2}}$$

40. Therefore, substituting in this equation the value of γ you get c_s is equal to 1.40 R T by M square root. Now, you can evaluate this at any temperature and you can estimate the speed of sound alright I hope it is clear. Now the second part of the question was for a linear triatomic molecule, linear triatomic molecule something like this A B C carbon dioxide. As long as the system is linear the molecule is linear ν R* is to be used 2.

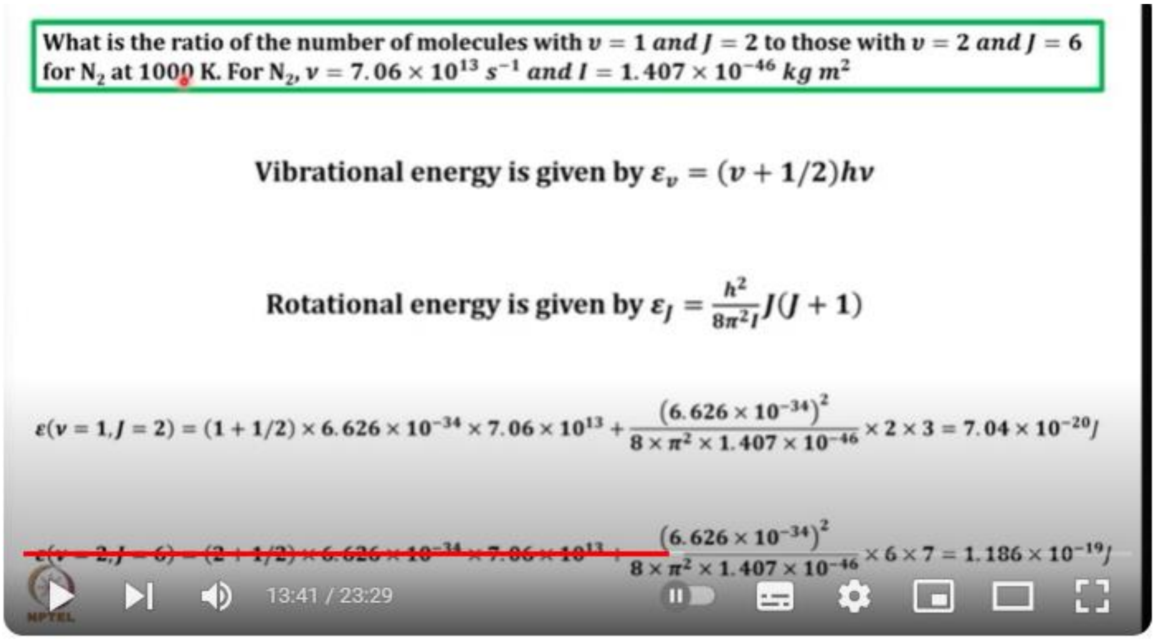
That means $C_{v,m}$ remains same 5 by 2 R how 5 by 2 R 3 + 2 $C_{p,m}$ also remains 7 by 2 γ remains 1.4 and the expression for the speed of sound also remains the same. Only what is differing here is compared to the previous one your molar mass is going to be different. When you talk about diatomic molecule versus triatomic molecule the molar mass is going to be different and by these expressions you can now estimate the value of speed of sound ok. Now, let us talk about linear triatomic molecule linear triatomic we have already we have already done I will modify it for non-linear triatomic molecule non-linear.

Non-linear one of the example is H O H type. When non-linear you are talking about ν R* is equal to 3. That means this is going to be 1 by 2 into 3 + 3 ν V* is 0. So, therefore, you can put R this is equal to 3 R. $C_{v,m}$ is 3 R obviously, then Cp,m means add another R to 3 R it becomes 4 R and γ which is the ratio of C_p and C_v that becomes 4 R divided by 3 R which is equal to 4 by 3.

Substitute γ is equal to 4 by 3 over here. So, you have 4 R T by 3 M square root. Now, you can substitute the numbers and estimate the value of speed of sound in this medium the medium here is gas. So, to solve these kind of problems what is important is to remember this expression which can be used to estimate the value of C_V. This value will depend upon the temperature.

If temperature is high enough for all the rotational modes to be active you substitute the value of ν R* and if the temperature is not high enough for the vibrational modes to be active then ν V* is 0, but if they are active then you put the number depending upon how many normal modes of vibrations are fully active. So, I hope that with this example it is clear that how to obtain or obtain an estimate of heat capacity at constant volume. Now, let us take another example a different type of example. The question here is what is the ratio of the number of molecules with V equal to 1 and J is equal to 2 to those with V equal to 2 and J is equal to 6 for nitrogen at 1000 K. For nitrogen the frequency is given 7.06 into 10 to the power 13 per second and the moment of inertia is given.

See Slide Time: 13:41



What is the ratio of the number of molecules with $v = 1$ and $J = 2$ to those with $v = 2$ and $J = 6$ for N_2 at 1000 K. For N_2, $\nu = 7.06 \times 10^{13}\ s^{-1}$ and $I = 1.407 \times 10^{-46}\ kg\ m^2$

Vibrational energy is given by $\varepsilon_v = (v + 1/2)h\nu$

Rotational energy is given by $\varepsilon_J = \frac{h^2}{8\pi^2 I} J(J+1)$

$$\varepsilon(v = 1, J = 2) = (1 + 1/2) \times 6.626 \times 10^{-34} \times 7.06 \times 10^{13} + \frac{(6.626 \times 10^{-34})^2}{8 \times \pi^2 \times 1.407 \times 10^{-46}} \times 2 \times 3 = 7.04 \times 10^{-20} J$$

$$\varepsilon(v = 2, J = 6) = (2 + 1/2) \times 6.626 \times 10^{-34} \times 7.06 \times 10^{13} + \frac{(6.626 \times 10^{-34})^2}{8 \times \pi^2 \times 1.407 \times 10^{-46}} \times 6 \times 7 = 1.186 \times 10^{-19} J$$

The question is to calculate the ratio of the number of molecules with a different set of vibrational or rotational quantum numbers. If it were only belonging to one set of quantum numbers things would have been very very easy, but here you have to deal with the molecules in which the vibrational quantum number V is equal to 1 and rotational quantum number J is equal to 2 and for the other state the vibrational quantum number V is equal to 2 and rotational quantum number J is equal to 6. How to now address this kind of problems? When we talk about how to evaluate the number of molecules, we have an expression Ni upon N is equal to exponential minus β E_i over Nq. Now, remember that if there are more than one energy states, if there are more than one energy states corresponding to a particular level, then that particular level is twofold, threefold or in general g fold degenerate.

In that case g_i will come here, but to address this kind of problem first of all we need to know energy levels and we need to know degeneracies. These two things are required to solve this problem. One is energy levels and second is the degeneracy. The question given to us talks about vibrational and rotational levels. Therefore, we will be dealing with the vibrational energy and rotational energy.

Vibrational energy is given by E_V is equal to V + ½ h ν or you can also write V + half h c ν bar where V can take value from 0, 1, 2 etcetera ok. And the rotational energy is given by h cross by 8 π square I into j into j + 1. When we discussed the rotational partition function, we talked in terms of rotational constant B, A B C where B is h cross by 4 π ci and the total energy then we calculated in terms of B, but in terms of moment of inertia this is the expression. You can get from that by substituting B is equal to h cross by 4 ci ok. Now the first step is for this set of quantum numbers V is equal to 1 and j is equal to 2, we will add this and this.

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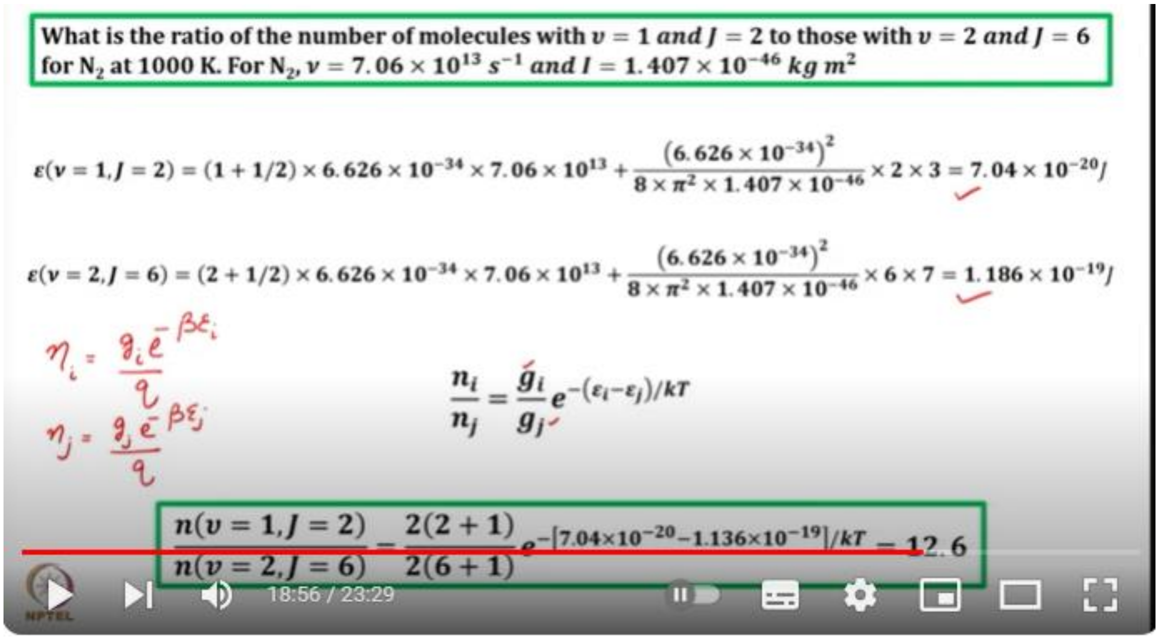

What is the ratio of the number of molecules with $v = 1$ *and* $J = 2$ to those with $v = 2$ *and* $J = 6$ for N_2 at 1000 K. For N_2, $\nu = 7.06 \times 10^{13}\ s^{-1}$ *and* $I = 1.407 \times 10^{-46}\ kg\ m^2$

$$\varepsilon(v = 1, J = 2) = (1 + 1/2) \times 6.626 \times 10^{-34} \times 7.06 \times 10^{13} + \frac{(6.626 \times 10^{-34})^2}{8 \times \pi^2 \times 1.407 \times 10^{-46}} \times 2 \times 3 = 7.04 \times 10^{-20} J$$

$$\varepsilon(v = 2, J = 6) = (2 + 1/2) \times 6.626 \times 10^{-34} \times 7.06 \times 10^{13} + \frac{(6.626 \times 10^{-34})^2}{8 \times \pi^2 \times 1.407 \times 10^{-46}} \times 6 \times 7 = 1.186 \times 10^{-19} J$$

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

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

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

$$\boxed{\frac{n(v = 1, J = 2)}{n(v = 2, J = 6)} = \frac{2(2+1)}{2(6+1)} e^{-[7.04 \times 10^{-20} - 1.136 \times 10^{-19}]/kT} = 12.6}$$

We will add for E_V and we add for E_j. For first set V is equal to 1. So, therefore, 1 1 + 1 by 2 into h ν we are given information in terms of the frequency + h square by 8 π square I. So, h square by 8 π square i j into j + 1, j is 2. So, 2 into 3 when you solve everything you get 7.04 into 10 raise to the power minus 20 joules this is the energy. Similarly, you repeat this exercise for V equal to 2 and j equal to 6. So, you put V equal to 2 and j equal to 6. Do the calculations and you will get then now the calculate the energy is little higher this is 1.186 into 10 raise to the power minus 19 joule.

We have the energies now for the set of quantum numbers given to us then after having solved this and this I just said that N_i is equal to g_i exponential minus β E_i over q. And similarly, I can write N_j is equal to g_j exponential minus βE_j over q. When you take the ratio N_i upon N_j then you get N_i upon N_j is equal to g_i upon g_j into exponential minus E_i minus E_j by k T. We have to calculate N_i upon N_j that means we need to have information on g_i we need to have information on g_j. This difference E_i minus E_j that is the difference between these numbers 7.04 into 10 raise to the power minus 20 and 1.186 into 10 raise to the power minus 19. Now the degeneracy for rotational levels for rotors g_j is equal to 2 j + 1. So, in the first case v is equal to 1 j is equal to 2. So, 2 j + 1 is 2 into 2 + 1 for the second one v is equal to 2 and j is equal to 6.So, 2 j + 1 what we have here is 5 this is 2 + 1 is 3 into 2 6 6 divided by 6 + 1 is 7 into 2 is 4 14. So, 6 by 14 into exponential minus ΔE , ΔE is difference between these two numbers and it turns out to be 12.6. What was the question given to us? What is the ratio of the number of molecules with v equal to 1 and j is equal to 2 to those with v equal to 2 and j is equal to 6 for nitrogen at 1000 K. Since these quantum numbers belong to different states of motion or modes of motion therefore, the problem becomes little complex.

You need to involve degeneracy and you need to include the differences in their energy states. First you have to calculate the energies which they are occupying for v equal to 1 and j is equal to 2 it was easy to compute it was easy to calculate that it is 7.04 into 10 raise to the power minus 20. Similarly, for the second it came to 1.186 into 10 raise to the power minus 19. The degeneracies were also possible to evaluate because we know that for rotational levels the degeneracy is 2 j + 1. Therefore, by writing such a number what we have is we have this ratio of number of molecules with v equal to 1 and j is equal to 2 to those with v equal to 2 and j equal to 6 the answer is 12.6. So, you might have noted in today's discussion that when you are dealing with such type of questions you need to know the rotational constants in simple terms. For example, b is equal to h cross by 4 π c_i and if I use i is equal to μ r square then even μ I can express in terms of masses.

So, therefore, do not get confused if these expressions are written in terms of the moment of inertia or in terms of the masses molar masses. So, I hope that solution of these kind of problems has brought little more clarity on how to use the derived equations on molecular partition function in solving the numerical problems of this type. We are going to solve some more numerical problems, but those we will do in the next lecture. Thank you very much.