Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

Indian Institute of Technology, Bombay

Lecture: 30

The Rotational Contribution to Molecular Partition Function (Nonlinear Rotor)

Welcome back to the discussion on Rotational Contribution to Molecular Partition Function. In the previous lecture, we started with discussion on rotational contribution to molecular partition function for a linear rotor. We will continue the discussion and if time permits, we will also discuss in this lecture the rotational contribution to molecular partition function for a non-linear rotor. But prior to that, let us continue our discussion for a linear rotor. For an asymmetric linear rotor, we derived that the rotational partition function is given by 1 by β h c B, where we know that β is equal to 1 by k T. So, I can even write k T over h c B, but this is for a rotor linear rotor of type AB.

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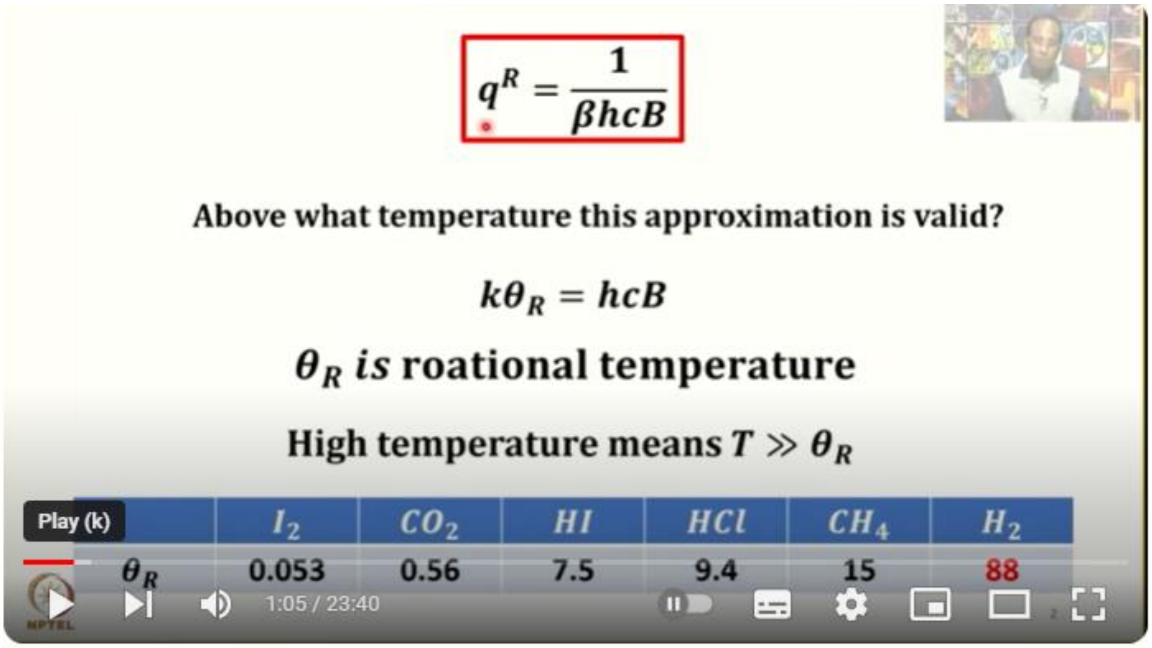

$$\boxed{q^R = \frac{1}{\beta hcB}}$$

Above what temperature this approximation is valid?

$$k\theta_R = hcB$$

θ_R is roational temperature

High temperature means $T \gg \theta_R$

	I_2	CO_2	HI	HCl	CH_4	H_2
θ_R	0.053	0.56	7.5	9.4	15	88

And then we were discussing about that this derivation required an approximation, where we converted that summation into integration and above what temperature this approximation is valid. We discussed that that temperature is described by rotational temperature or you call it characteristic rotational temperature, which is given the symbol theta r and theta r can be calculated from hcB by k. And when do we say high temperature? So, this expression we say that we can use in the high-temperature limit. And what is that high temperature? That is given by when T the experimental temperature is much higher than the rotational temperature.

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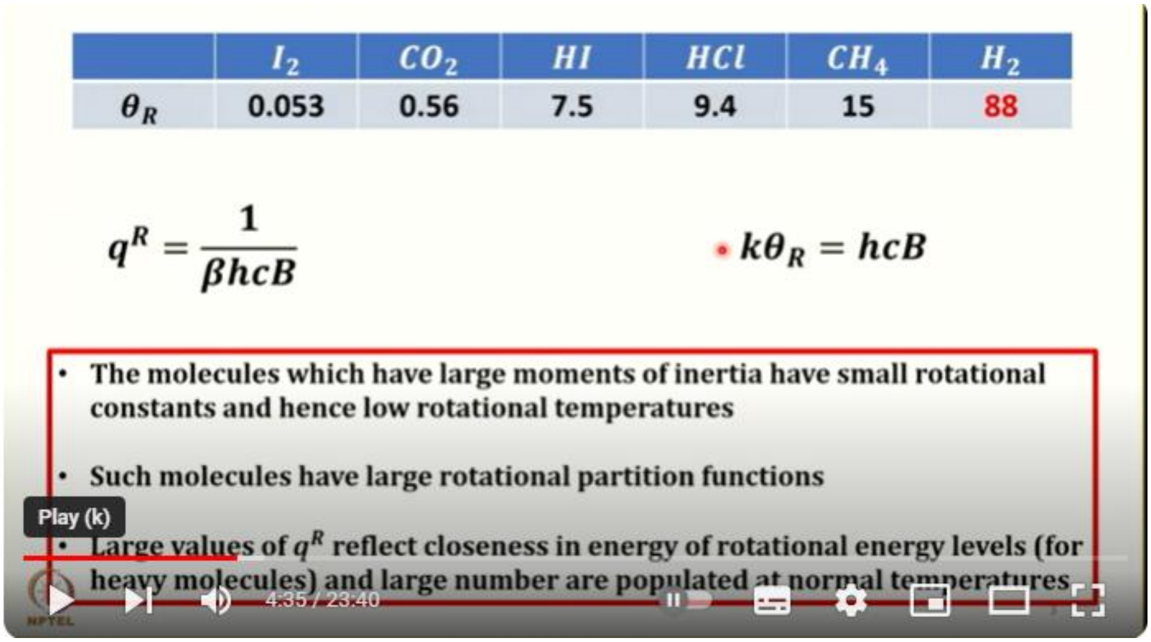

	I_2	CO_2	HI	HCl	CH_4	H_2
θ_R	0.053	0.56	7.5	9.4	15	88

$$q^R = \frac{1}{\beta hcB}$$

$$k\theta_R = hcB$$

- The molecules which have large moments of inertia have small rotational constants and hence low rotational temperatures
- Such molecules have large rotational partition functions
- Large values of q^R reflect closeness in energy of rotational energy levels (for heavy molecules) and large number are populated at normal temperatures

The rotational temperatures calculated by this expression for some of the molecules are given in this table. For example, for iodine 0.053, for carbon dioxide 0.56, for hydrogen iodide 7.5, for hydrogen chloride 9.4, methane 15, hydrogen 88. If you see a trend in this, iodine is a heavy molecule, then carbon dioxide is relatively lighter molecule, then you have hydrogen iodide, hydrogen chloride, methane, hydrogen. Hydrogen has relatively higher value of rotational temperature. These all are given in terms of Kelvin. So therefore, if we talk about normal temperature, let us say 298 Kelvin. 298 Kelvin is much higher than 0.053, is much much higher than 0.56, is much much higher than 7.4, but when we reach at 88, we need to be little careful. In any case, when we say high temperature, high temperature means that the experimental value of temperature that is temperature at which you want to calculate rotational partition function should be much much higher than the rotational temperature.

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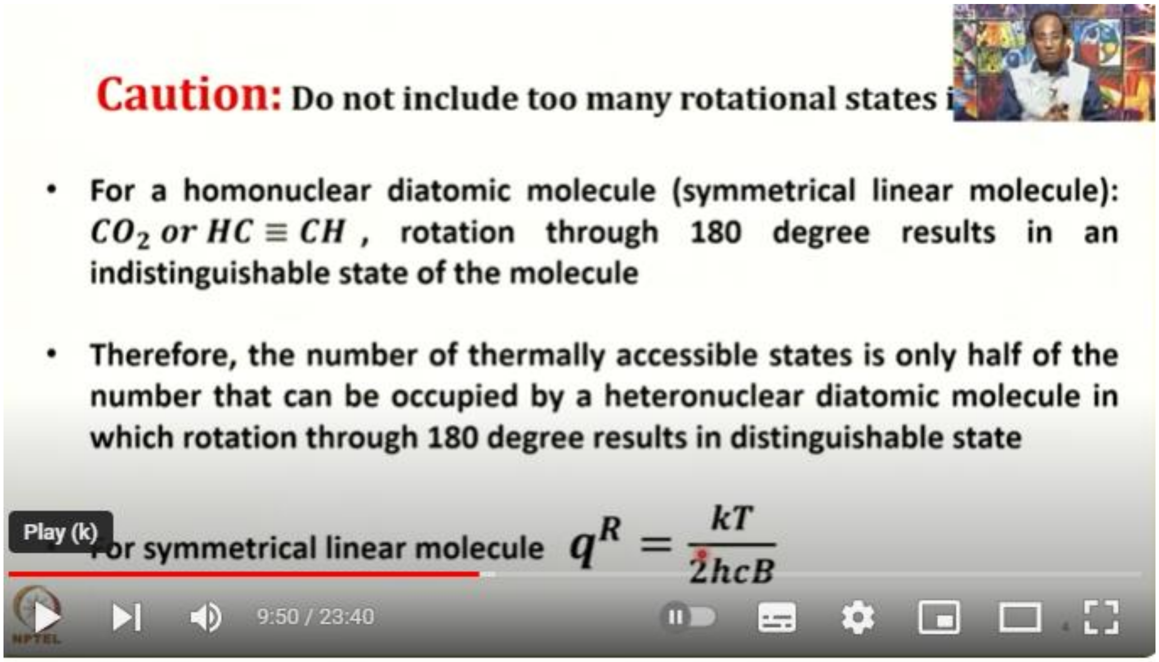

Caution: Do not include too many rotational states i

- For a homonuclear diatomic molecule (symmetrical linear molecule): CO_2 or $HC \equiv CH$, rotation through 180 degree results in an indistinguishable state of the molecule
- Therefore, the number of thermally accessible states is only half of the number that can be occupied by a heteronuclear diatomic molecule in which rotation through 180 degree results in distinguishable state

or symmetrical linear molecule $q^R = \frac{kT}{2hcB}$

Only then you can use this approximation, otherwise you will have to go by direct summation method, numerical evaluation of rotational contribution. So now let us look at the trend which you see in this table. This is how you define rotational contribution to partition function and we already discussed that theta r can be calculated from this relation, but now let us look at the comments which are made over here. The molecules which have large moment of inertia have small rotational constants and hence low rotational temperatures. If the rotational constant is small, then the rotational temperature will also be small and then we know that B is given by h cross by 4 π c I. That is what is being mentioned over here that if the moment of inertia is large, if I is large, B will be small and if B is small, your theta r is going to be small. That is what you see for iodine. So that means such molecules will have large rotational partition function.

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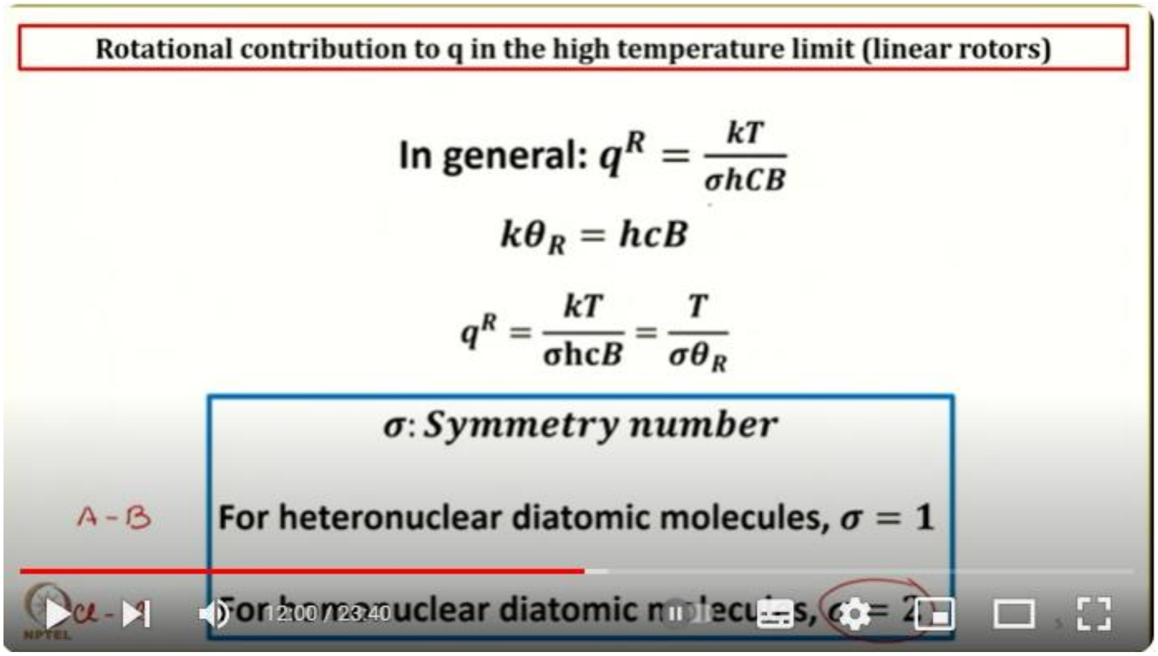

Rotational contribution to q in the high temperature limit (linear rotors)

In general: $q^R = \frac{kT}{\sigma hcB}$

$$k\theta_R = hcB$$

$$q^R = \frac{kT}{\sigma hcB} = \frac{T}{\sigma\theta_R}$$

σ: Symmetry number

A - B

For heteronuclear diatomic molecules, $\sigma = 1$

For homonuclear diatomic molecules, $\sigma = 2$

If B is small, then q r is going to be large. So the conclusion is that the molecules which have large moment of inertia, they will have small rotational constant and they will also have large values of rotational partition functions and what does that mean? You know if the value of q^R is very large, then what does that mean? We go back to our discussion of what is the physical meaning, literal physical meaning of partition function. Partition function is a measure of how many thermally accessible states the molecule can exhibit. So large values of q r reflect closeness in energy levels of rotation for heavy molecules and large number are populated at normal temperatures. Higher the value of q, the more is the fractional population of the upper states. That means the energy levels are very close to each other. Therefore even at normal temperature such as room temperature, many rotational energy levels will be populated. Alright, now let us talk about caution. The formula that we derived does that require some modification. We have been discussing from time to time that we should not include too many states when we carry out the sum. That is what is commented over here. Do not include too many rotational states in the sum and when such situation can arise.

Let us take the example of a homonuclear diatomic molecule. That means now from non symmetrical linear rotor, we are going to discuss about symmetrical linear rotor and one such example is C H triple bond C H, acetylene or carbon dioxide. These are linear symmetrical linear rotor. Why because when you have this homonuclear diatomic molecule or symmetrical linear molecule, then the rotation through 180 degree results in an indistinguishable state of the molecule. For example, if I consider this is one atom, this is another atom and then when I rotate it by 180 degree, you cannot distinguish this atom from this atom.

That means 180 degree rotation results in an indistinguishable state of the molecule. So therefore, by this way you may be counting the rotational states twice just because 180

degree rotation results into indistinguishable state of the molecule. So therefore, the number of thermally accessible states is going to be only half of the number that can be occupied by heteronuclear diatomic molecules. For example, if I take for example, this pen and consider this as one atom and this tip as the other atom and I rotate by 180 degree, I can distinguish. I can distinguish this from this.
That is why this comment that the number of thermally accessible states is only half of the number that can be occupied by a heteronuclear diatomic molecule in which rotation through 180 degree results in distinguishable state. So therefore, that factor of half needs to be applied. Therefore, when you want to modify that expression for symmetrical linear rotor, it will be q r is equal to k T by 2 h c B. This additional factor 2 is introduced in the denominator because if you do not include this factor of 2, then you may be counting too many rotational states. That means you may be counting double the rotational states.

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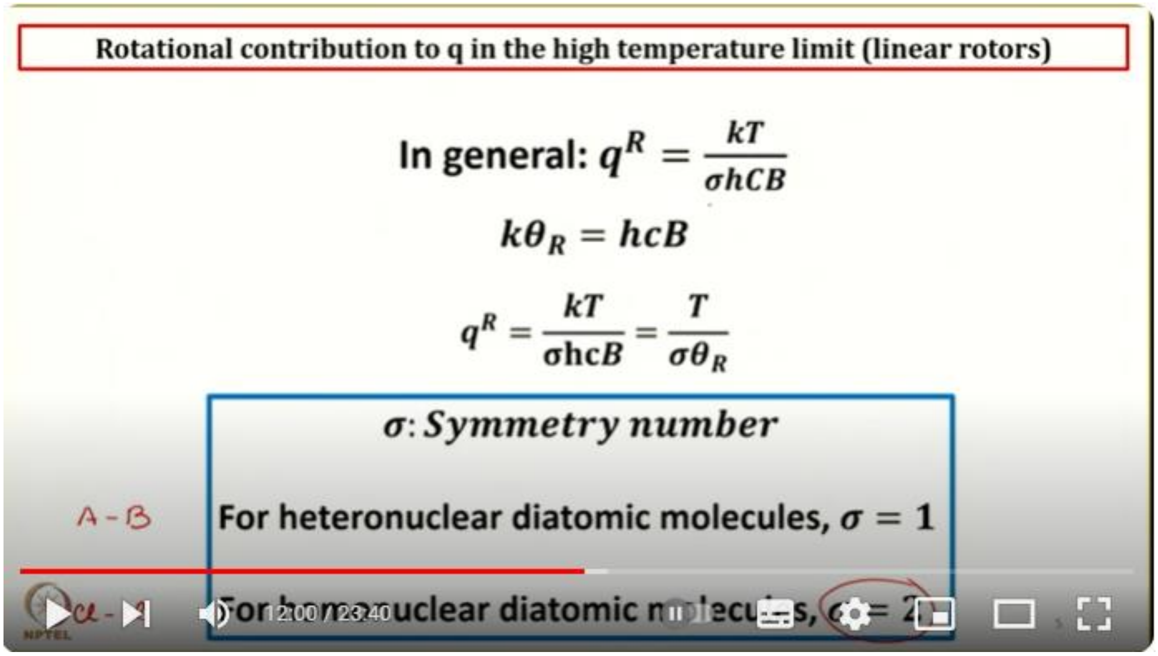

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For homonuclear diatomic molecules, $\sigma = 2$

So that is why this caution is given that do not include too many rotational states in the sum. Can we include some factor and make it a general formula? Yes, that can be done. That means in general, let us include that factor in the denominator sigma which is called symmetry number. Here you will require the knowledge of symmetry. So what is q^R is k T by sigma h c B and h c B by k is equal to θ_R. So include that over here. That means you can express the rotational partition function for a linear rotor as k T by sigma h c B or T by sigma theta r. So do not get confused when you come across different versions of the rotational partition function. Different books may give only in terms of b or may also include in terms of theta r. So therefore there should not be any confusion.

Sigma as we just discussed is the symmetry number for heteronuclear diatomic molecules. What are those? Heteronuclear diatomic molecules that is for the molecule type a b because here when you rotate by 180 degrees you can distinguish between a and b. So therefore sigma is equal to 1. You do not require then this correction over there. For homonuclear diatomic molecules for example Cl Cl here when you rotate by 180 degree what you see is the atoms are indistinguishable. So in that case you require a factor of 2 correction factor of 2 that symmetry number becomes 2. But this is for simple diatomic molecules. What about if there are more complex molecules? We will discuss about that a bit later. Let us first now discuss how to evaluate rotational partition function for a given molecule. Look at the problem given to us. Evaluate the rotational partition function of HCl at 25 degrees centigrade and what is given is the rotational constant. HCl it is a heteronuclear diatomic molecule. So straight away when you rotate by 180-degree centigrade you can distinct when you rotate by 180 degree you can distinguish between H and C l. But that you know we need to worry about if we can use the high-temperature approximation result. Let us first establish whether the high temperature approximation result can be used in this case or not.

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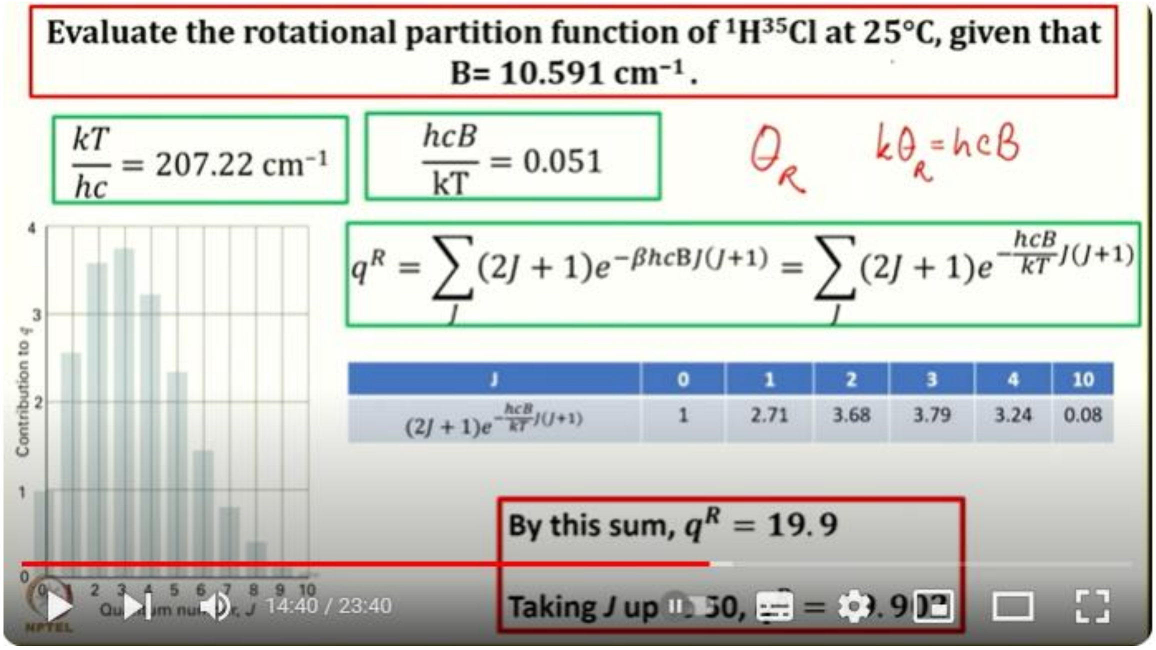

Evaluate the rotational partition function of $^{1}H^{35}Cl$ at 25°C, given that B= 10.591 cm^{-1}.

$$\frac{kT}{hc} = 207.22\ \text{cm}^{-1}$$

$$\frac{hcB}{kT} = 0.051$$

θ_R $k\theta_R = hcB$

$$q^R = \sum_J (2J+1)e^{-\beta hcBJ(J+1)} = \sum_J (2J+1)e^{-\frac{hcB}{kT}J(J+1)}$$

J	0	1	2	3	4	10
$(2J+1)e^{-\frac{hcB}{kT}J(J+1)}$	1	2.71	3.68	3.79	3.24	0.08

By this sum, $q^R = 19.9$

Taking J up [illegible] 50, [illegible] = [illegible].9[illegible]

So what we have is the values of K T by H C which is 207.22 and h c B by K T is 0.051. Why do we need this? Because q r rotational contribution to partition function for a linear rotor is 2 J plus 1 into exponential minus β h c B J into J plus 1 β can be written as 1 by K T. So therefore, your expression becomes hcB by K T J into J plus 1. Here we need to decide whether we should go by this explicit summation method or can we use the high temperature approximation result that is q r is equal to 1 over sigma hc β B can we use that.

But for that we need to first calculate the value of rotational temperature. How do you get that? $K\,\theta_R$ is equal to h c B and when you actually calculate this value of theta r you will see that you cannot ignore that compared to 25 degree centigrade. So therefore, only if 25 degree centigrade is much much higher than the value of Θ_R then you can use the high temperature approximation result. In this case when you calculate you will see that you cannot ignore. Therefore let us go by direct summation method. How do you go by direct summation method? You start with the values of J as 0 1 2 3 4 and let us say we go up to 10. The value of 2 J plus 1 into exponential term that is this one for different J values are listed over here when J is equal to 0 obviously this value is going to be 1 J is equal to 0 the 1 exponential 0 is 1. So, you have 1 when J is equal to 1 value is 2.

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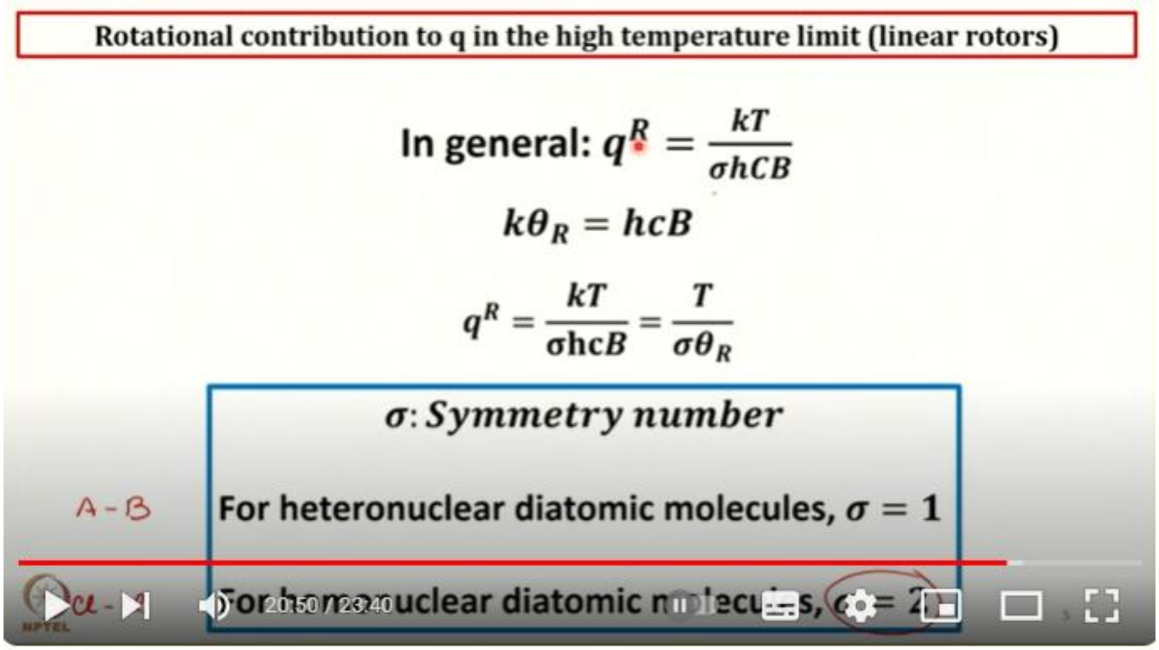

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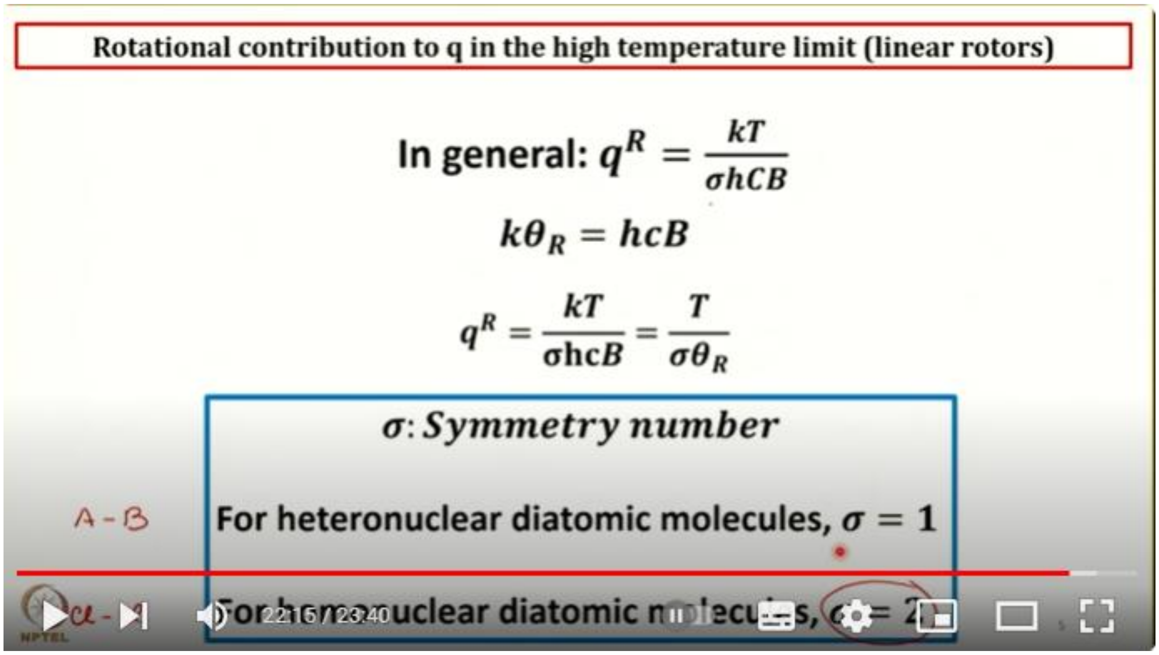
71 when J is equal to 2 3.68 J is equal to 3 3.79 J is equal to 4 3.24 you can continue and when you see that when J is equal to 10 the value is decreasing to value of 0.08. Look at the trend 1 2.71 increase 3.68 increase 3.79 increase increase decrease which is following this trend you see there is increase and then decrease. If you include the result from J equal to 0 to J equal to 10 you sum up all these when you sum these all up you get value of 19.9. 19.9 reflects that many rotational states are and then suppose if you keep on calculating and you calculate up to J equal to 50. Let us say you include all the terms for J equal up to J equal to 50 then the sum becomes instead of 19.9 it becomes 19.9 0 2. So that means eventually the if you keep on increasing the value of J the additional contribution becomes less and less.



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Alright. So, in this numerical problem what we did we first checked whether can we ignore the temperature constraint and directly jump to high temperature result for that first calculate θ_R compare that with the experimental temperature. We decided here let us go by explicit summation method where you vary the value of J from 0 onwards we saw that even for variation of J from 0 to 10 and then sum up all these term gives rotational partition function to be 19.9 and then even if you include the other contributions up to J equal to 50 19.9 only changes to 19.9 0 2. Now let us look at some of the comments made over here. The graph shown over here plot shown over here represents contribution to rotational partition function for HCl this is on y axis that means this y axis is the value of 2 J plus 1 into exponential minus β H c B J into J plus 1 this term for different values of J for J is equal to 0 when you put J equal to 0 this is 1 this factor is 1. So, this should be 1 and you can see here 1 when J is equal to 1 this becomes 3 and then the value rises to this value eventually if you see this passes through a maxima obviously why this passes through a maxima because when you increase the value of J this degeneracy actor gives it gives it a push up that is increases the value, but this exponential term decreases the value. So, therefore when you consider both then your result passes through a maxima. Successive terms which are proportional to the populations of the levels pass through a maximum because the population of individual states decreases exponentially, but the degeneracy of the levels increases with J. Once again when J is equal to 0 this value is 1 this is equal to 1 you have 1 as J increases you see the value increases as it passes through a maxima and then decreases the reason for this is that you have 2 terms 1 which corresponds to the degeneracy of the system and other which includes the exponential term, but with a negative sign 1 increases the other decreases the compromise of the both is equal to that it passes through a maxima. So, what we have discussed in this case is the result exclusively based upon direct summation and not using the high-temperature limit. The high temperature result high-temperature limit result is given by this expression where in general we write rotational partition function to be equal to k T by sigma hcB but in order to use this result I am once again reiterating that you will have to calculate the rotational temperature which can be calculated from the value of b b is an experimental result because b is equal to h cross by 4 π c I. So, moment of inertia is needed once you have the value of b you can get the value of rotational partition function provided you know the symmetry number and in order to have this symmetry number you will require some knowledge of symmetry some knowledge of how many indistinguishable forms of the molecules will appear when it is rotated through some number. So, today in this lecture we have completed only the discussion for a linear rotor whether it is a symmetric or asymmetric. When it is symmetric that is homo nuclear diatomic molecule like species for example, Cl Cl you require sigma equal to 2 and for non-symmetric a b type then you do not require the value of sigma to be different than 1 it is equal to 1. So, by now we have completed the translational contribution and the rotational contribution, but only for a linear molecule to the overall molecular partition function. In the next lecture we will continue our discussion for non-linear molecules when the molecule is linear spherical rotor we need to consider only one moment of inertia when it is non-linear then we will need to bring other moments of inertia and we will be talking in terms of 2 or 3 rotational constants a b or even including C, but that we will discuss in more details in the next lecture.

Thank you.