Basic Statistical Mechanics
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Lecture – 27
Ideal Gas of Polyatomic Molecules

Welcome back and we are continuing our study of statistical mechanics of ideal gases. Till now we have done monatomic and diatomic and not only that we have done the statistical mechanics, we derived these statistical mechanical expressions of free energy, entropy and specific heat. For monatomic, we did the translation that part remains invariant in the diatomic but diatomic brings the 2 new ingredients one is the rotation and other is vibration.

And we have used the harmonic oscillator model of quantum mechanics to derive expression for those quantities for harmonic oscillators and we showed that this is one of the most respected, used and time-honored models applied to many systems of physics, chemistry and biology and then we did the rotation using the rigid rotator. We worked out again the statistical mechanics.

Now many of the systems that we are interested in like water, ammonia, alcohols, they are all polyatomic molecules and polyatomic molecules have characteristics which are quite different from that of diatomic.

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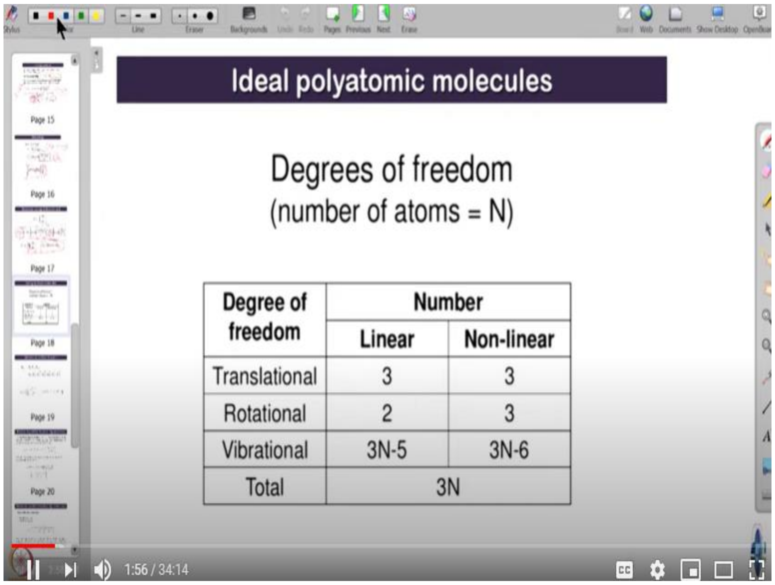

Ideal polyatomic molecules

Degrees of freedom
(number of atoms = N)

Degree of freedom	Number	
	Linear	Non-linear
Translational	3	3
Rotational	2	3
Vibrational	3N-5	3N-6
Total	3N	

The reason is that the polyatomic will have now in addition to translational degrees of freedom and rotational degrees of freedom, it has vibration which is many more now. As we all know that the number of vibrational degrees of freedom is more in case of linear because their rotation is only 2. But for nonlinear molecules where you have 3 rotation, you have (3N-6) vibrational degrees of freedom.

And this is what actually gives rise to when the large molecules like polymers form or when they are sitting together in in a crystalline forming a solid amorphous then we lose the translational degrees of freedom that they have been that get transferred to vibrational degrees of freedom and that shows up as normal modes which play important role in this specific heat and thermodynamic properties of low-temperature solids (not just crystal but also amorphous materials).

And these are at low temperature liquids, they are very important quantities. So, but however the polyatomic molecules are many other peculiarities of their own that we are going to discuss today, and they want to do is how to do statistical mechanics of polyatomic molecules so that the students know how to start talking of entropy, free energy and specific heat; the molecular component of the polyatomic molecule and that statistical mechanics gives you.

You already have it but so will have a slightly more generalized form of what you did in diatomic and so it will be not too demanding a session we did do in a small way the polyatomic earlier. But we are going to do a little bit better now and in certain sense also it is a review of many of the things that we are going to do okay.

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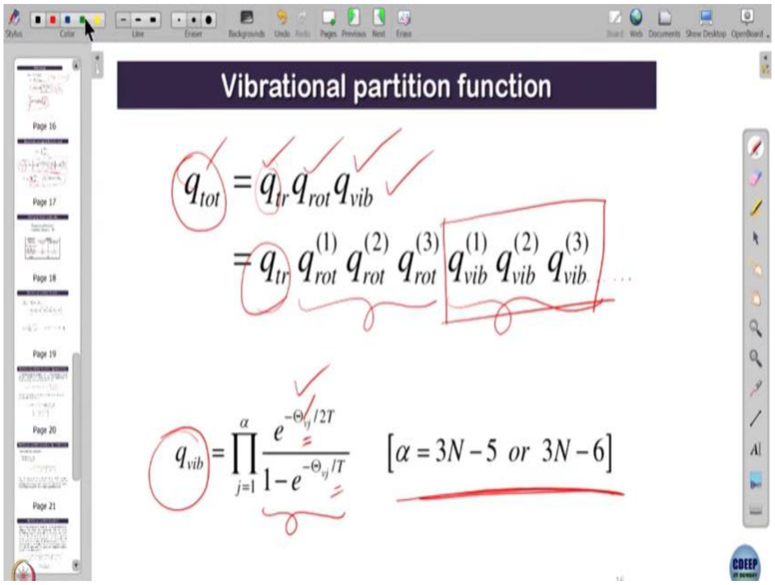

Vibrational partition function

$$q_{tot} = q_{tr} q_{rot} q_{vib}$$
$$= q_{tr}\, \underbrace{q_{rot}^{(1)} q_{rot}^{(2)} q_{rot}^{(3)}}\, \boxed{q_{vib}^{(1)} q_{vib}^{(2)} q_{vib}^{(3)}} \ldots$$

$$q_{vib} = \prod_{j=1}^{\alpha} \frac{e^{-\Theta_{vj}/2T}}{1-e^{-\Theta_{vj}/T}} \qquad [\alpha = 3N-5 \ or \ 3N-6]$$

And we wrote down before, we are neglecting the electronic degrees of freedom because electronic energy level gap is much larger (typical electronic energy levels are of the order of say 10,000 cm^{-1} - 7,000 cm^{-1} which are huge). So, they do not enter at the room temperature, at the ambient conditions electronic degrees of freedom does not show up in the thermodynamics.

It does show up in the spectroscopy when you are giving external source of energy and resonance condition and exciting but in the thermodynamic properties it is a ground state of electron degrees of freedom that is all that you need to worry about and we can take that energy as 0 so that just it does not change your temperature, does not change the pressure or volume, we do not need to talk about it.

So, then I can write the partition function as a product of 3 as we already discussed that it is translational, vibrational and rotational; it is a molecular partition function. So, this is a molecular partition function and these are molecular degrees of freedom. The molecular partition function of a single molecule is denoted by q and my rotation for the partition function of N particle system is Q. So, then,

$$\begin{aligned} q_{tot} &= q_{tr} q_{rot} q_{vib} \\ &= q_{tr}\, q_{rot}^{(1)}\, q_{rot}^{(2)}\, q_{rot}^{(3)}\, q_{vib}^{(1)}\, q_{vib}^{(2)}\, q_{vib}^{(3)} \end{aligned}$$

Now translation is the center of mass, so we do that. Then if I have a nonlinear molecule, 3 rotational degrees of freedom I call it $q_{rot}^{(1)}, q_{rot}^{(2)}$ *and* $q_{rot}^{(3)}$ and then I have the all the other degrees of freedom that is given here and that is of course not just 3, there are 3 vibrational degrees of freedom then it is 3. But otherwise, that can be many more degrees of freedom that would be showing here.

Since these vibrations are independent of each other, the normal modes, then q_{vib} is a product of all the vibrational degrees of freedom which is written here,

$$q_{vib} = \prod_{j=1}^{\alpha} \frac{e^{-\Theta_{vj}/2T}}{1-e^{-\Theta_{vj}/T}}$$

That I have a new stand for vibration in the notation and J is the different normal modes. So then my total vibrational partition function is product of $\frac{e^{-\Theta_{vj}/2T}}{1-e^{-\Theta_{vj}/T}}$ and this is the alpha is given here and Θ_{vj} is the vibrational temperature and this one is the one that comes from 0 point energy, I remind you.

And this is the one that comes from details some of these power series $1+x+x^2+.........=\frac{1}{1-x}$ for $x < 1$. So, this is the one we derived in the last or the one before last class. So, now the if we know this so then we can set up the partition function now so vibrational part is fairly simple because we have this thing and you give me the frequencies and that gives me the vibrational temperature and I can I can give you the partition function. So now we will concentrate on the rotational part.

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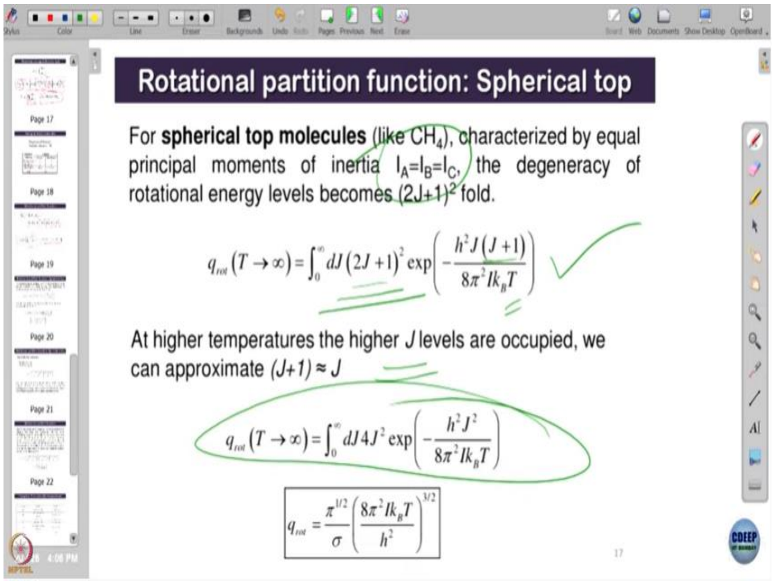

Rotational partition function: Spherical top

For **spherical top molecules** (like CH_4), characterized by equal principal moments of inertia $I_A=I_B=I_C$, the degeneracy of rotational energy levels becomes $(2J+1)^2$ fold.

$$q_{rot}(T\to\infty)=\int_0^\infty dJ\,(2J+1)^2\exp\left(-\frac{h^2J(J+1)}{8\pi^2 I k_B T}\right)$$

At higher temperatures the higher *J* levels are occupied, we can approximate *(J+1) ≈ J*

$$q_{rot}(T\to\infty)=\int_0^\infty dJ\,4J^2\exp\left(-\frac{h^2J^2}{8\pi^2 I k_B T}\right)$$

$$\boxed{q_{rot}=\frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I k_B T}{h^2}\right)^{3/2}}$$

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Rotational partition function is very important in polyatomic molecules and because there is, you know, this kind of, can be jittery and all the kind of motions that many times you face as basically some kind of restricted rotation. Now rotation has very different cases we need to consider. One case is where all the moment of inertia is the same. Because there are 3 direction in a non-linear molecule and you can have 3 principal axis and you have 3 moment of inertia.

Now if this is completely spherical, we call spherical top molecule like methane then we have no problem, we have all the moment of inertia are the same which is like $I_A = I_B = I_C$, this spherical top. The degeneracy of rotational energy levels becomes $(2J+1)^2$ fold, if equal principal moment of inertia then all these and we can then write these $(2J+1)^2$ the degeneracy of the rotational energy levels.

The equal principal moments of inertia is then you instruct this product will have $(2J+1)^2$ and then we get this expression for the rotational partition function and then we take the following limit at high temperature when temperature becomes very high then and moment of inertia also not too small then the ones that will be involved at very large J large quantum number should be involved.

$$q_{rot}(T\to\infty)=\int_0^\infty dJ\,(2J+1)^2\exp\left(-\frac{h^2J(J+1)}{8\pi^2 I k_B T}\right)$$

And large quantum numbers then I can approximate $(J+1) \approx J$ that is a very neat approximation and then my rotational partition function becomes these become 4J square then it becomes like this this beautiful thing. So, in the high temperature limit I can do this integration now. It is no longer that the difficulty I had but remember even in the diatomic case we could evaluate the large high temperature limit. Here also in the polyatomic case the high temperature limit can be worked out and again we get a very neat expression of the rotational partition function.

$$q_{rot}(T \to \infty) = \int_0^\infty dJ\, 4J^2 \exp\left(-\frac{h^2 J^2}{8\pi^2 I k_B T}\right)$$

This integral can be performed without any difficulty. For three rotational degrees of freedom, the partition function becomes,

$$\boxed{q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I k_B T}{h^2}\right)^{3/2}}$$

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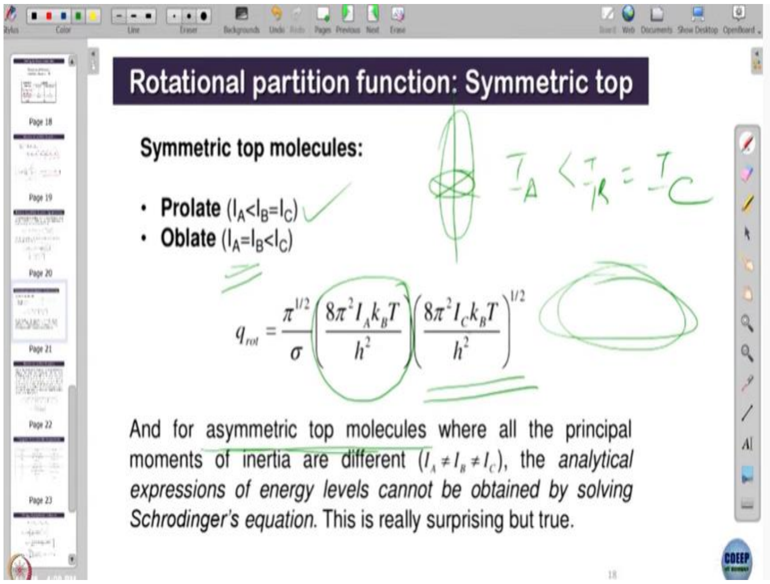

Rotational partition function: Symmetric top

Symmetric top molecules:

- **Prolate** ($I_A<I_B=I_C$)
- **Oblate** ($I_A=I_B<I_C$)

$I_A < I_B = I_C$

$$q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A k_B T}{h^2}\right)\left(\frac{8\pi^2 I_C k_B T}{h^2}\right)^{1/2}$$

And for asymmetric top molecules where all the principal moments of inertia are different ($I_A \neq I_B \neq I_C$), the *analytical expressions of energy levels cannot be obtained by solving Schrodinger's equation.* This is really surprising but true.

So, continuing we now do symmetric molecules. Now symmetric top molecules are the ones who which are like symmetric top which are 2 moment of inertia are the same and third one is different. It can be prolate ($I_A < I_B = I_C$) or oblate ($I_A = I_B < I_C$).

So this direction C is different from in the spherical direction which is A and B. So Prolate and oblate are 2 different things and indeed in that case we can calculate the partition function by using the method similar to this one that remember that if you go to rotational case in the diatomic case the partition function is,

$$q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A k_B T}{h^2}\right)\left(\frac{8\pi^2 I_C k_B T}{h^2}\right)^{1/2}$$

So, the quantity is that 2 of them comes with $\left(\frac{8\pi^2 I_A k_B T}{h^2}\right)^{1/2}$. So, when A = B then this half and half becomes just 1 and then you have this C half okay. So, whatever I do either prolate or oblate depending on A and B like for example in the case of prolate it would be A here and then okay B here and A here in the case of oblate it is the other way around A here and C here.

Just the same thing, of course values can be very different. So, but then one comes the most general case with the asymmetric top molecules. In asymmetric top molecule all the principal moments of inertia are different and this is the general case that in case of water molecules case they are all asymmetric top molecules where all the moment have been different and these analytical expression materials cannot be obtained by solving Schrodinger equation that is the real unfortunate part.

So, in the previous case part, this case these things come from solving the Schrodinger equation. The degeneracy factor of a spherical top molecules that it is $(2J+1)^2$, the polyatomic molecule this comes from Schrodinger equation. However, in the case of completely asymmetric molecule we cannot do we cannot solve this Schrodinger equation and as a result we cannot get those energy levels.

So Schrodinger equation can be cannot be solve analytically. So, for the diatomic we get analytically, for symmetric top the spherical top we get in analytically with the different degeneracy. Now for the prolate and oblate we again get, prolate and oblate they are when they decomposed separately, and we can get the energy levels again and we can solve for the at least high temperature limit partition function.

But in the case of fully asymmetric molecule by moment of inertia A,B,C are different it cannot be we do not have any closed form analytical expression for the energy levels and that poses the problem. So, in that case this Schrodinger equation has to be solved numerically to obtain the energy levels this is very difficult, and this is a laborious process.

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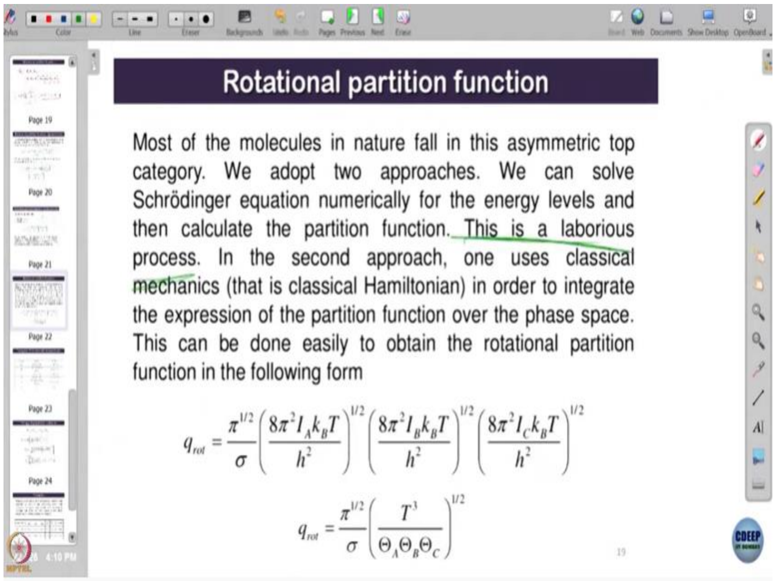

Rotational partition function

Most of the molecules in nature fall in this asymmetric top category. We adopt two approaches. We can solve Schrödinger equation numerically for the energy levels and then calculate the partition function. This is a laborious process. In the second approach, one uses classical mechanics (that is classical Hamiltonian) in order to integrate the expression of the partition function over the phase space. This can be done easily to obtain the rotational partition function in the following form

$$q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_B k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_C k_B T}{h^2}\right)^{1/2}$$

$$q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2}$$

But we can we can obtain to these the classical limit, the high temperature limit that the high temperature as I said the quantum goes over to classical partition function in the high temperature that means I can start partition function from classical Hamiltonian, I can do from quantum Hamiltonian then I can show that high temperature the quantum goes over to classical it is very nice and has to be because there is nothing no surprise there at all.

But in this case where you cannot do anything for the quantum case because energy levels are not known we can do anything other than numerically that is actually done many cases numerically one solves and gets. But we can make progress with the classical Hamiltonian which can be done, and classical Hamiltonian of course can be just integrated I write down the moment of inertia, I have ABC and write down, there is no potential energy still it is just the rotating and it has the rotational kinetic energy.

And rotational kinetic energy I know how to do the rotational kinetic energy rotational angular momentum divided by *2I* and then I can integrate that and that will I we know that that gives this kind of form.

$$q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_B k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_C k_B T}{h^2}\right)^{1/2}$$

So now I have one for A one for B and one for C. So, I have 3 rotational partition function is product of these 3 which is just that we got in classical statistical. Mechanics or the high temperature limit of the quantum diatomic case with one moment of inertia but here also when they are written in terms of moment of inertia they are already decomposed.

And then we can get that and then we can write the rotational partition function I can combine these things and define Θ_A, Θ_B and Θ_C in terms by using all these quantities because that quantity then becomes 1 over theta B oh sorry 1 over theta A and that becomes 1 over theta B and these becomes 1 over theta C. Then my partition function becomes this quantity $q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2}$. It is very neat very nice and neat and very elegant expression and remember the half is preserved now because each comes with a half and that half shown here.

So, this is the rotational partition function that compete rotational partition function of a polyatomic molecule. So now we do you have these, so we go back and we have the we go back and we have these total partition function and now we want to do certain thermodynamics with these expressions. And what are my kind of values that you get okay.

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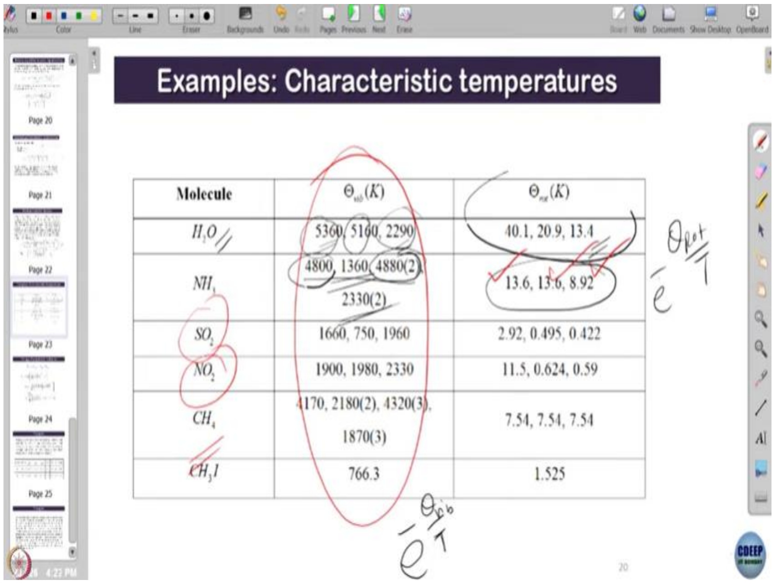

Examples: Characteristic temperatures

Molecule	$\Theta_{vib}(K)$	$\Theta_{rot}(K)$
H_2O	5360, 5160, 2290	40.1, 20.9, 13.4
NH_3	4800, 1360, 4880(2), 2330(2)	13.6, 13.6, 8.92
SO_2	1660, 750, 1960	2.92, 0.495, 0.422
NO_2	1900, 1980, 2330	11.5, 0.624, 0.59
CH_4	4170, 2180(2), 4320(3), 1870(3)	7.54, 7.54, 7.54
CH_3I	766.3	1.525

$e^{-\theta_{rot}/T}$

$e^{-\theta_{vib}/T}$

So, let us now consider some specific cases. Now the temperature, the rotational temperature and vibrational temperature gives you a measure is a very important thing they give you a measure of the quantumness of the system and the importance of that particular mode in my thermodynamic properties. For example, in case of water I have 3 vibrations, what are the 3 vibrations. One is symmetric stretching; one is asymmetric stretching, other is bending the 3 vibrations for water.

Now look at them. We already know one is 3650 centimeter inverse symmetry stretching a little bit higher is asymmetric stretching that is 3,700 centimeter inverse, bending is half of nearly half of that, that is 1885 centimeter inverse very nicely placed those 3 and that plays a very important role in vibrational relaxation. There is some of the outstanding discoveries that made in these recent times okay now if we do that then look at these in case of water.

So, this is asymmetric stretching, this is symmetric stretching, this is the bending all right. Now if it is so then I can easily see that in thermodynamic properties by if temperature it will be relevant at 5000 Kelvin, no so at room temperature, I do not need to worry at all for water. But look at wrote a rotation, rotational temperatures are really very low the 3 moment of inertia of asymmetric water molecules the 3 axis of rotation they come so these temperatures that means they are that almost classical and I they do influence the thermodynamics.

So, I need to take into rotational degrees of freedom in understanding thermodynamics and this has a very interesting story. So, for some time why sometime people are trying to calculate the entropy of water this is actually began now of last some 15-20 years what is the entropy of water. Because the entropy of water as I said plays a very important role in many chemical reactions and when I give you an example when a drug goes into DNA then of course the drug loses the entropy.

But the system gains entropy, the way system gains entropy the water molecules which are inside where in binding inside the residing inside the major or minor groves, they are displaced. So, when they are in minor groves that did not have not any entropy there is extra enthalpy but they are no entropy. So, when they go out they gain lot of entropy so we kind of take into account way that 10 molecules that are made in this space that 10 molecules going from minor group of DNA to water.

So, what is the entropy per water molecule if I know then 10 times that is the entropic gain in the process and then I can use Sackur-Tetrode equation or something to get the entropy. But some great equations still linear the liquid water is not a great approximation but it is that they get you started very interesting. Now when all these calculations were done in initially people are not getting very good agreement of the entropy of water.

The entropy of water can be obtained also experimentally in a laborious process by starting from all the way from 0 Kelvin ice then going in to make it melt, going to liquid then you know you can calculate at take the latent heat of fusion into and we know the entropy of water experimentally, that was not working that well. Then we realized that we did not take into account the vibration and rotational entropy contribution. But as I show you vibration is not important, but rotation important, translation is of course important.

So, it turns out the rotational contribution to entropy of water is about 30% is a huge contribution that comes from rotation. It is something like that one in the entropic unit rotational contribution is about 5 or 5.2 and the translation contribution is 17. So, if total entropy is 22 you already added table saying 17 the translation comes and then these this another 5 comes from rotation and you know to calculate that entropy. I have to calculate I have to use this expression this expression are used to calculate the rotational partition function I get the Free energy, $A = -k_B T \ln Q(N,V,T)$ and I take the derivative of that and get the entropy.

That entropy now is and is extremely important contribution. For water rotational entropy contribution at room temperature is 30% of the translational contribution. This is a really very important that we missed you know is very recently that we missed this thing this is just about I think 10 years old. Now another system interest is ammonia. Ammonia has again 4 vibrations systematic stretching. anti-systematic stretching and bending mode.

Now those are vibrational temperature the theta phi that we define in terms of the frequency and that is pretty large. So, one is 4,800 that is very large a vibration these another vibration these 2 are some kind of bending modes I do not remember fully the modes, but they are certainly not one stretching modes. But even then, these are pretty high temperature the room temperature remember it will be e to the power minus the contribution comes as $e^{\left(-\frac{\Theta_{vib}}{T}\right)}$.

And since set of vibration is so large temperature at 300 Kelvin even this guy is e to the power minus 4 and if you are yeah 4 point something these are of course much larger. So, these this contribution is minimum however the same $e^{\left(-\frac{\Theta_{rot}}{T}\right)}$, all in Kelvin, look at that, they are small. So, all these things play very important role, so all these 3 modes play very important role in the entropy or the thermodynamic properties of ammonia.

Similar things you find in Sulphur dioxide, nitrous oxide, methane everywhere you see the vibrational temperature is very high. So, when it comes in $e^{\left(-\frac{\Theta_{vib}}{T}\right)}$ the vibrational degrees of freedom do not contribute significantly at ambient conditions to the thermodynamic properties. So molecular partition function and molecular thermodynamics the vibration is a silent thing we do not see it we find huge contribution of translation but then a significant 20 to 30, 35% contribution comes from rotation.

So rotational degrees of freedom cannot be ignored when we are doing and this is a very important thing because so most of the books and most of the studies that we hear everywhere that people are doing they as if the world a begins and ends with monatomic molecules maybe a little bit of diatomic like take the phase transition theories and all the thing that we will be doing something.

We start with spherical molecules, you know and we end with spherical molecules like it was studies of last transition theory, theory of liquids that we do they are all models, Lennard-Jones models and others but they are all spheres but this is something so when we did statistical mechanics in 1970s and 80s we learnt towards the end of 70s and 80s when I was doing PHD and Post Doc., we really never bothered about it, you know, the popular textbooks of statistical mechanics they do not have much of polyatomic molecules.

So, our emphasis and the book that I have written this statistical mechanics books for chemistry and material science that is why we have a very big discussion of polyatomic molecules and a lot of emphasis is given on polyatomic molecules because these days we are interested in these kinds of systems okay.

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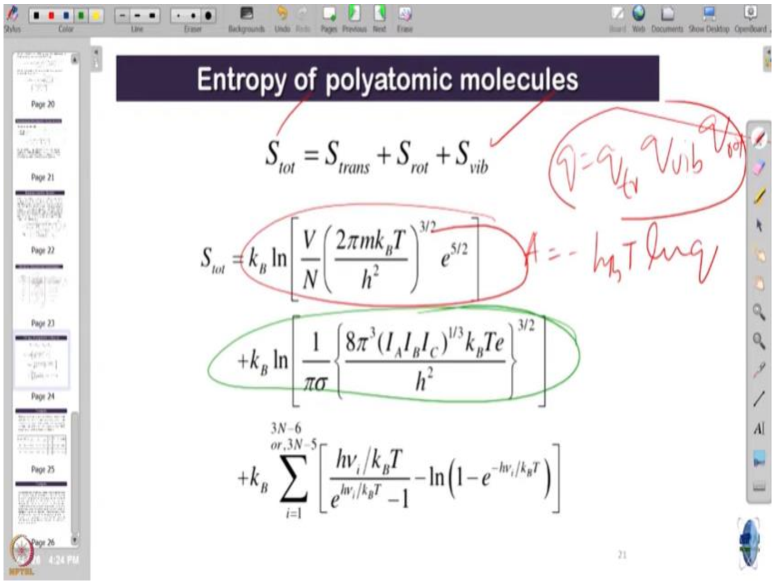

Entropy of polyatomic molecules

$$S_{tot} = S_{trans} + S_{rot} + S_{vib}$$

$$q = q_{tr}\, q_{vib}\, q_{rot}$$

$$S_{tot} = k_B \ln\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{5/2}\right]$$

$$A = -k_B T \ln q$$

$$+ k_B \ln\left[\frac{1}{\pi\sigma}\left\{\frac{8\pi^3 (I_A I_B I_C)^{1/3} k_B T e}{h^2}\right\}^{3/2}\right]$$

$$+ k_B \sum_{i=1}^{3N-6 \text{ or}, 3N-5}\left[\frac{h\nu_i/k_B T}{e^{h\nu_i/k_B T} - 1} - \ln\left(1 - e^{-h\nu_i/k_B T}\right)\right]$$

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So let us continue then entropy of a polyatomic molecule is just a wonderful thing as I just discussed to you So this is the thing the translational part so entropy since put a partition function is $q_{tot} = q_{tr} q_{rot} q_{vib}$ and then free energy is, $A = -k_B T \ln Q(N,V,T)$ so if composed free energy becomes some of the free energy and entropy becomes sum of the entropy, this is trivial.

$$S_{tot} = S_{trans} + S_{rot} + S_{vib}$$

$$\begin{aligned} S_{tot} = k_B \ln&\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{5/2}\right] \\ &+ k_B \ln\left[\frac{1}{\pi\sigma}\left\{\frac{8\pi^3 (I_A I_B I_C)^{1/3} k_B T e}{h^2}\right\}^{3/2}\right] \\ &+ k_B \sum_{i=1}^{\substack{3N-6 \\ or,3N-5}} \left[\frac{h\nu_i / k_B T}{e^{h\nu_i/k_B T} - 1} - \ln\left(1 - e^{-h\nu_i/k_B T}\right)\right] \end{aligned}$$

But sometimes it is good to spell out the trivial thing because to help the thinking that is then this is Sackur-Tetrode equation and then this is the rotational. Now I have arranged it such that most important thing in translation which water and ammonia has about 65 to 70% of the total entropy then the rotation which is classical limit, but classical limit works out really well as I showed you in these things fortunately for us Θ_{vib} is small.

So, we are okay because the room temperature is much larger than these so we can rely doing classical mechanics, this is a lucky break. In quantum no ways, this is too quantum, but this is nearly classical this is very interesting how lucky one can get some time. So, like for translation you get away by classical Mechanics for rotation for translation you get away rotation you also get away by doing as I showed you for many of the molecule’s vibration, we are not that lucky but vibration with a harmonic is a good approximation. So this is translation these rotation and these vibrational contribution to the total entropy and as I say this is actually negative. So, these two does the job perfectly for us good.

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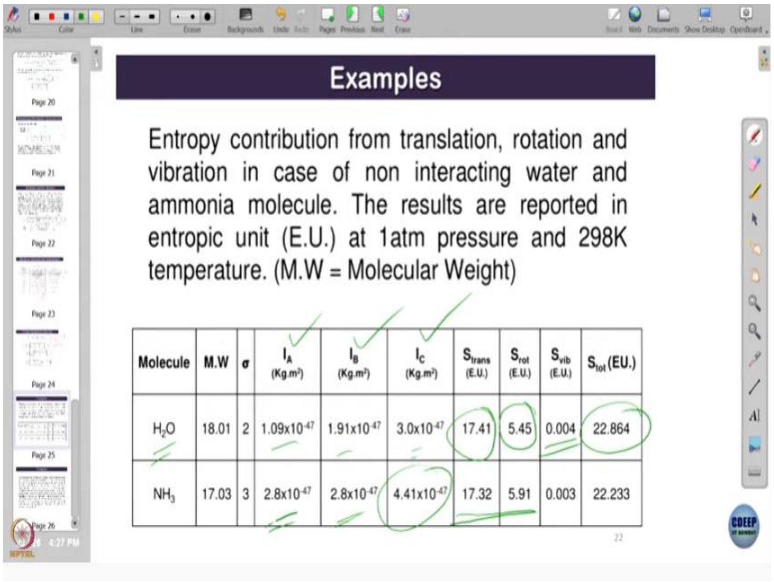

Examples

Entropy contribution from translation, rotation and vibration in case of non interacting water and ammonia molecule. The results are reported in entropic unit (E.U.) at 1atm pressure and 298K temperature. (M.W = Molecular Weight)

Molecule	M.W	σ	I_A (Kg.m²)	I_B (Kg.m²)	I_C (Kg.m²)	S_{trans} (E.U.)	S_{rot} (E.U.)	S_{vib} (E.U.)	S_{tot} (EU.)
H_2O	18.01	2	1.09×10^{-47}	1.91×10^{-47}	3.0×10^{-47}	17.41	5.45	0.004	22.864
NH_3	17.03	3	2.8×10^{-47}	2.8×10^{-47}	4.41×10^{-47}	17.32	5.91	0.003	22.233

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So now where I have given you a table actually this, I pre-empted a little bit I told you I already showed the table 17 and 5 which is I was talking from memory but there it is that water, molecular weight and every detail is given and these are the 3 moment of inertia I have given water these are the things you do not get in the physics textbooks or even earlier versions of step back. But now these are so important in the present in such and present-day calculations that polyatomic study of statistical mechanics or polyatomic molecule is the important thing.

That is what I am discussing it, do I discuss this a little bit before, I am discussing it again more detail. And as I tell there is no damage is done by doing it these beautiful things more than once. Okay so look at that in water has this nice thing is the two of the moment of inertia are very close to each other and these are these two A and B 1.09, 1.91 and this is quite different now this is what are saying 17.41 is the translational part in the entropy unit in the k_B.

And this is the one that rotation 5.45 but look at vibration contribution is negligible when you add up all these things you get this is the entropy of water beautiful very nice. Now the other thing I have ammonia how many are there of these things that two things that nearly degenerate and then this one is larger moment of inertia. Now a very similar story unfolds for ammonia, translation and rotation, now rotational contribution little bit larger that you put guess because go back you could guess that it will larger because look at the rotational temperature.

Rotational temperature of ammonia is lower than that of water. So as soon as rotational temperature become lower its contribution becomes more to the partition function and to free energy and to entropy and right that is the one that happens. So, 5.45 this is slightly less than 5.91 but then at the end of the day we have these values of the entropy and as I said a very important thing in thermo dynamic properties to get the ideal entropy.

There are many expressions of entropy and for example connection between diffusion entropy there is a property called a Rosenfeld scaling which needs the ideal entropy ideal gas entropy and what uses this value of ideal gas entropy of water molecules to predict the diffusion constant in liquid which is done in other examples involving but this plays a very important role in in the properties of liquid okay.

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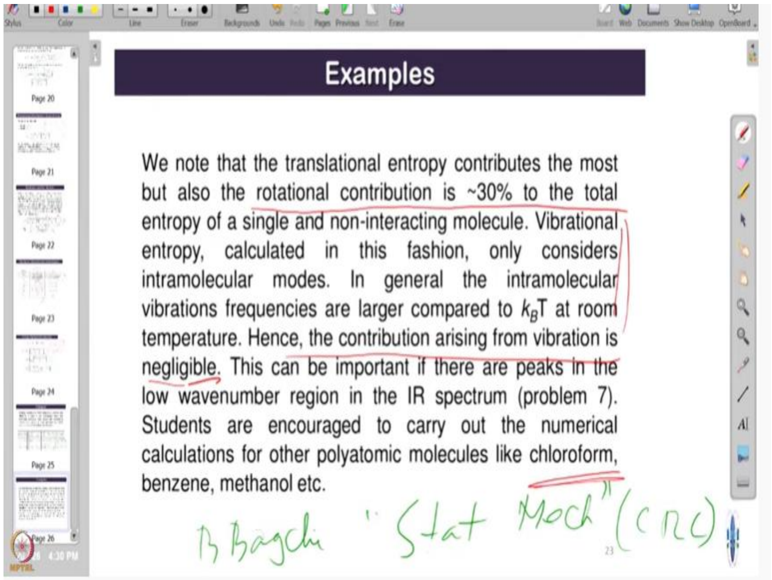

Examples

We note that the translational entropy contributes the most but also the rotational contribution is ~30% to the total entropy of a single and non-interacting molecule. Vibrational entropy, calculated in this fashion, only considers intramolecular modes. In general the intramolecular vibrations frequencies are larger compared to k_BT at room temperature. Hence, the contribution arising from vibration is negligible. This can be important if there are peaks in the low wavenumber region in the IR spectrum (problem 7). Students are encouraged to carry out the numerical calculations for other polyatomic molecules like chloroform, benzene, methanol etc.

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So, this area summarize here that the this is straight from the book, statistical mechanics book by CRC press from that it is taken that a translator interview continues in the most, but also rotational contribution is this is my favorite I did not know myself about 6 years ago. The original contribution is 30% because we also grew up like doing as if the everything is Lennard-Jones as if there is everything can be modelled as spheres.

But then you miss out all these things. Molecular vibration entropy is only considers intermolecular models are not very important. So, pipe the contribution lies from vibration is negligible. So, this is very encouraged to carry out numerical calculations for polyatomic molecules like chloroform this is a this is a homework that we will set up to make you do something like methanol and you can calculate them by doing the homework things.

So here ends the statistical mechanics of ideal gases. I just summarize what we did in 1 minute that we have done now in great detail monatomic gas which is spheres non-interacting spheres then we did diatomic like nitrogen, oxygen they are rotating, and they have a vibrational degrees of freedom. Vibrational degrees of freedom have beautifully come with this harmonic oscillator and this Schrodinger solution.

And however, in thermodynamics those vibrational degrees of freedom do not play role but the translation rotation place then we did polyatomic molecules and we did statistical mechanics of polyatomic molecules; very important case of water very important in case of ammonia or other Sulphur dioxide and all other important molecules that we need to do in everyday life and in a real problems like you know and that then at the end of this part so stop here we take a break and we will go over to the next class.