Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

Indian Institute of Technology, Bombay

Lecture – 32

Rotational Partition Function

In this lecture, we will discuss further on Rotational Partition Function. By now, we have had a thorough discussion on rotational partition function for a linear rotor and a non-linear rotor. Now, let us apply those learned concepts in solving some numerical problems. We have discussed that for a non-linear rotor, we need to have the knowledge of A, B and C. And for a linear rotor, we need to have a knowledge about B, rotational constant. And rotational constant basically involves moment of inertia and moment of inertia involves knowledge about the mass and the bond length.

So, with this background, now we will start discussing some numerical problems. Let us revisit that symmetry number is very very important, because symmetry number that comes in the denominator and reduces the value of q^R. Let us now consider this numerical problem. The NOF molecule is an asymmetric rotor.

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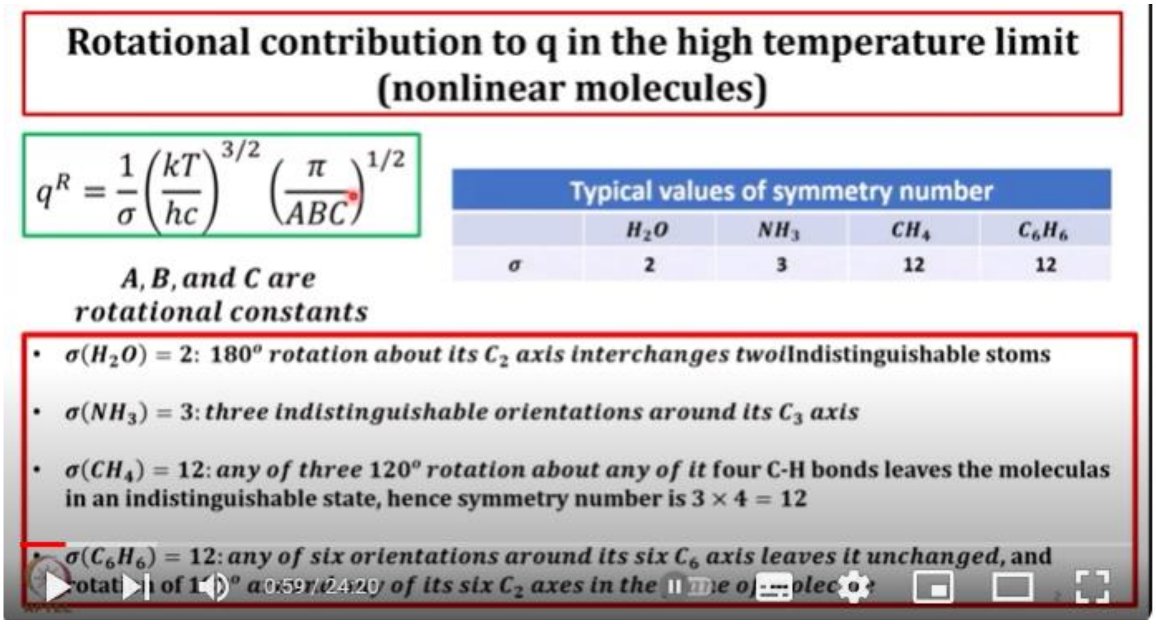

Rotational contribution to q in the high temperature limit (nonlinear molecules)

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2}$$

A, B, and C are rotational constants

Typical values of symmetry number				
	H_2O	NH_3	CH_4	C_6H_6
σ	2	3	12	12

- $\sigma(H_2O) = 2$: 180° *rotation about its* C_2 *axis interchanges two* Indistinguishable stoms
- $\sigma(NH_3) = 3$: *three indistinguishable orientations around its* C_3 *axis*
- $\sigma(CH_4) = 12$: *any of three* 120° *rotation about any of it* four C-H bonds leaves the moleculas in an indistinguishable state, hence symmetry number is $3 \times 4 = 12$
- $\sigma(C_6H_6) = 12$: *any of six orientations around its six* C_6 *axis leaves it unchanged,* and rotat[illegible] of 1[illegible]° a[illegible] *of its six* C_2 *axes in the* [illegible]e o[illegible]olec[illegible]

It is given information asymmetric rotor. You can take a look at the structure of molecular structure of NOF. It is asymmetric. One side is oxygen, other side is flow unit with rotational constants 3.1752 centimeter inverse, 0.

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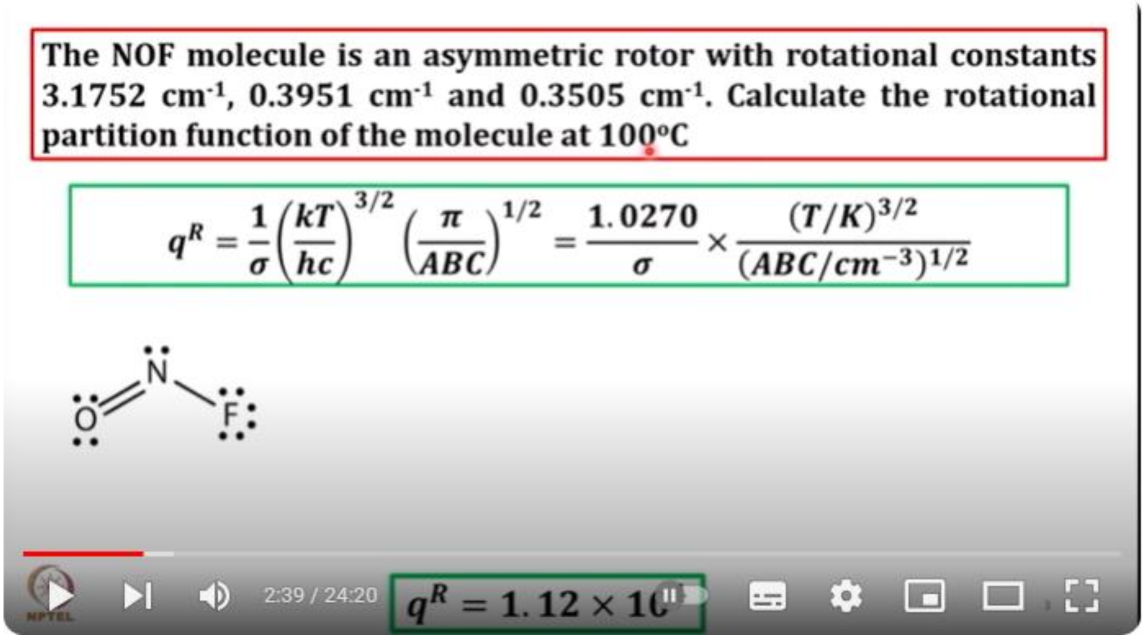

The NOF molecule is an asymmetric rotor with rotational constants 3.1752 cm^{-1}, 0.3951 cm^{-1} and 0.3505 cm^{-1}. Calculate the rotational partition function of the molecule at 100°C

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2} = \frac{1.0270}{\sigma} \times \frac{(T/K)^{3/2}}{(ABC/cm^{-3})^{1/2}}$$

$q^R = 1.12 \times 10$

395 one-centimeter inverse and 0.3505-centimeter inverse. So, basically these are A, B and C. And we have been asked to calculate the rotational partition function of the molecule at 100 °C. Now, once we are asked to calculate the rotational partition function, then we need to make a decision that whether to go by direct summation method or to go by high temperature approximation.

In order to use high temperature approximation, we need to calculate characteristic rotational temperature. And how do we calculate characteristic rotational temperature is $k\theta_r$ is equal to h C B or you can have $k\theta_r$ is equal to h C A, $k\theta_r$ is equal to h C C. So, you will have the rotational temperature. The values of h C B everything is available. So, once we calculate θ_r, if temperature is much much higher than θ_r or characteristic rotational temperature, then we can straight away go ahead and use the high temperature approximation result.

In this case, you please calculate yourself, find out the value of θ_r and you will find out you will observe that 100 °C which is 373 K is much much higher than any of the θ_r's corresponding to A B and C. And once you establish that, then you are free to use this high temperature approximation result. k is Boltzmann constant, T is temperature, h is Planck's constant, C is the speed of light, A B C all these three values are given to you. Another alternate form which is a simplified form comprising of k h C because these all are constant. So, you combine all these k h c also includes π into all these constants multiplied.

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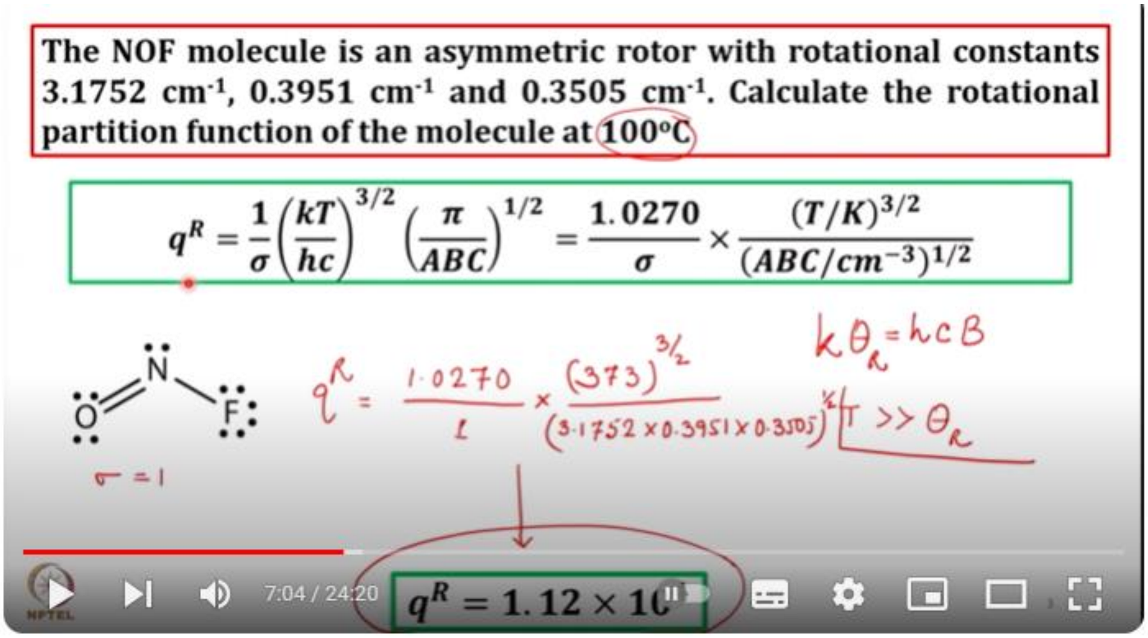

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$$q^R = \frac{1.0270}{1} \times \frac{(373)^{3/2}}{(3.1752 \times 0.3951 \times 0.3505)^{1/2}}$$

$k\theta_R = hcB$

$T >> \theta_R$

$\sigma = 1$

$q^R = 1.12 \times 10$

It transforms into 1.0270 divided by symmetry number into substitute temperature in K raise to the power 3 by 2 and put A B C each one in centimeter inverse. So, it becomes centimeter minus 3, it is a square root. We should know this formula and this formula leads to another formula where you combine k h C π, these are all constants combine them and the value is 1.0270. So therefore, we just need to now substitute the values. So, what we will have now q^R, you can use any of the result. Let us say if I use 1.0270, now σ here if you rotate the molecule by 180 degree centigrade, fluorine will be on the other side, oxygen will be on this side. So therefore, it is distinguishable that means σ is equal to 1 here. So, once I have σ equal to 1 into temperature in K 373 raise to the power 3 by 2 and A B C each one in centimeter inverse, you have 3.1752 into 0.3951 into 0.3505 raise to the power 1 by 2, treat this as separate and once you solve, you should get a value of 1.12 into 10 raise to the power 4.

Please note that this number is very high. So, for a non-linear rotor obviously, the value of rotational contribution to partition function is inversely proportional to A B C and A B C involves moment of inertia h cross by 4 π c I right. So, the higher the value of mass, then the higher will be the value of moment of inertia and since moment of inertia comes in the denominator for A B C. So, higher value of moment of inertia will lower the value of A B or C and if A and B and C are low, the value of q r is going to be high. The previous example in the previous lecture, we talked about oxygen.

The value was something around 79. Here we are talking about NOF molecule and see, but the value the temperature here is 100 degree centigrade. At 100 °C, you have 1.12 into 10 raise to the power 4 thermally accessible rotational states alright. I hope this is clear. When we want to address rotational partition function, we need to identify this I am saying again and again.

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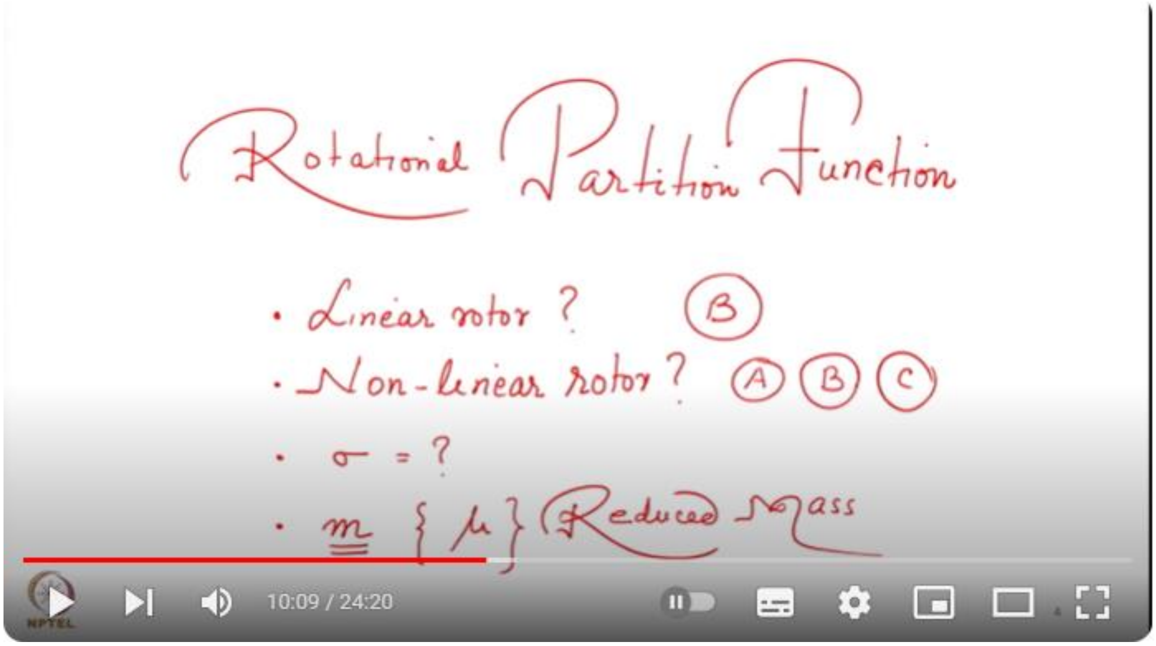

Rotational Partition Function

- Linear rotor ? Ⓑ
- Non-linear rotor ? Ⓐ Ⓑ Ⓒ
- σ = ?
- $\underline{\underline{m}}$ $\{\mu\}$ (Reduced Mass

Is it a linear rotor or is it a non-linear rotor and the third thing we need to know what is the value of symmetry. The other information which you need is in this case, linear rotor means you need the value of rotational constant B non-linear rotor. You need to have the value of A B and C. Everything else is a constant there h planks constant k Boltzmann constant c speed of light everything else is a constant and the fourth thing which you need is mass or more precisely you need the reduced mass.

Once you have this information, it is very easy to obtain the value of rotational partition function alright. Let us move ahead. We will also now discuss some associated numerical problems. We have earlier discussed that pressure is given by k T del log Q by del B. Q is the canonical partition function.

Canonical partition function can be written in terms of molecular partition function that is either Q is equal to Q raise to the power n or Q is equal to Q raise to the power n by n factorial. The problem here which is being discussed says calculate the equation of state associated with the partition function Q which is given by 1 by n factorial 2 π m over β H square raise to the power 3 n by 2 into V minus n B raise to the power n into β A n square by B. This n V B these are the constraints n V β. β is 1 by k T. So, essentially it is n V T that means it is a canonical partition function and if you look at this expression carefully, it involves B and A.

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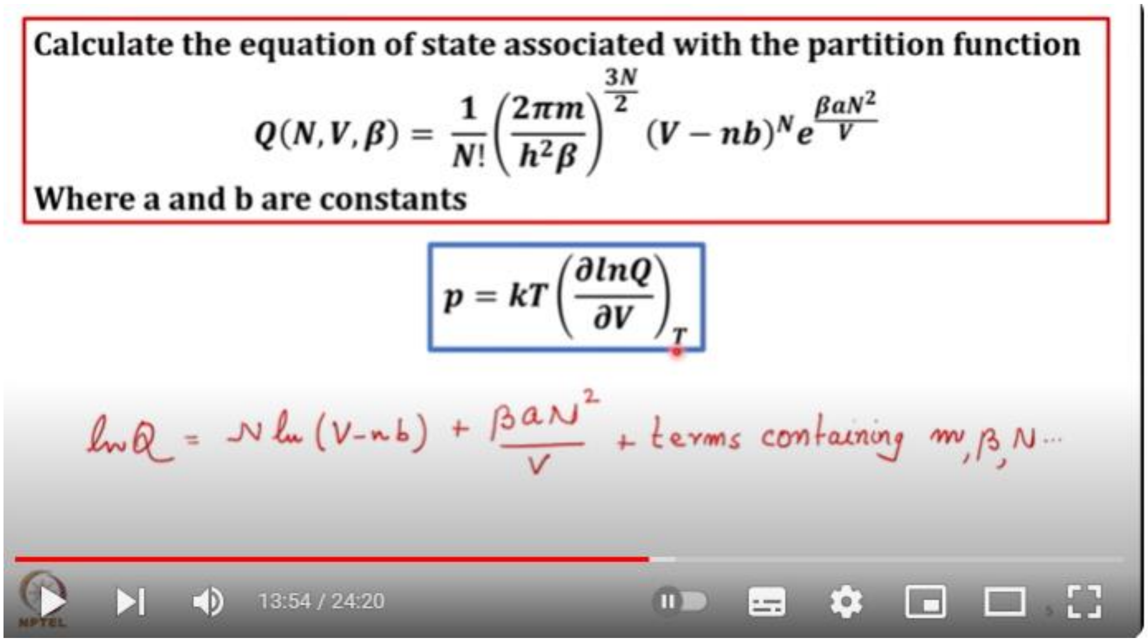

Calculate the equation of state associated with the partition function

$$Q(N,V,\beta) = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3N}{2}} (V-nb)^N e^{\frac{\beta a N^2}{V}}$$

Where a and b are constants

$$\boxed{p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T}$$

$$\ln Q = N\ln(V-nb) + \frac{\beta a N^2}{V} + \text{terms containing } m, \beta, N \cdots$$

So, that reminds you of Van der Waals equation of state where the attraction and repulsion terms are included. The question is to derive or calculate the equation of state. What is an equation of state? An equation of state is an equation which connects P V and T. For ideal gas P V is equal to n R T. For non-ideal gas, we should get an expression from the given expression because the given expression involves B and A which are repulsive and attractive parameters.

So, since we want to derive an expression between P V and T, it is wise to start with the expression for pressure and pressure is equal to k T times del log Q del V at constant temperature. We need partial derivative of Q or log Q with respect to volume at constant temperature. So, let us now write an expression for log Q because we will need to take derivative of log Q. Let us write log Q. Log Q is equal to let me write first V minus n B term that will be n log V minus n B plus β n B.

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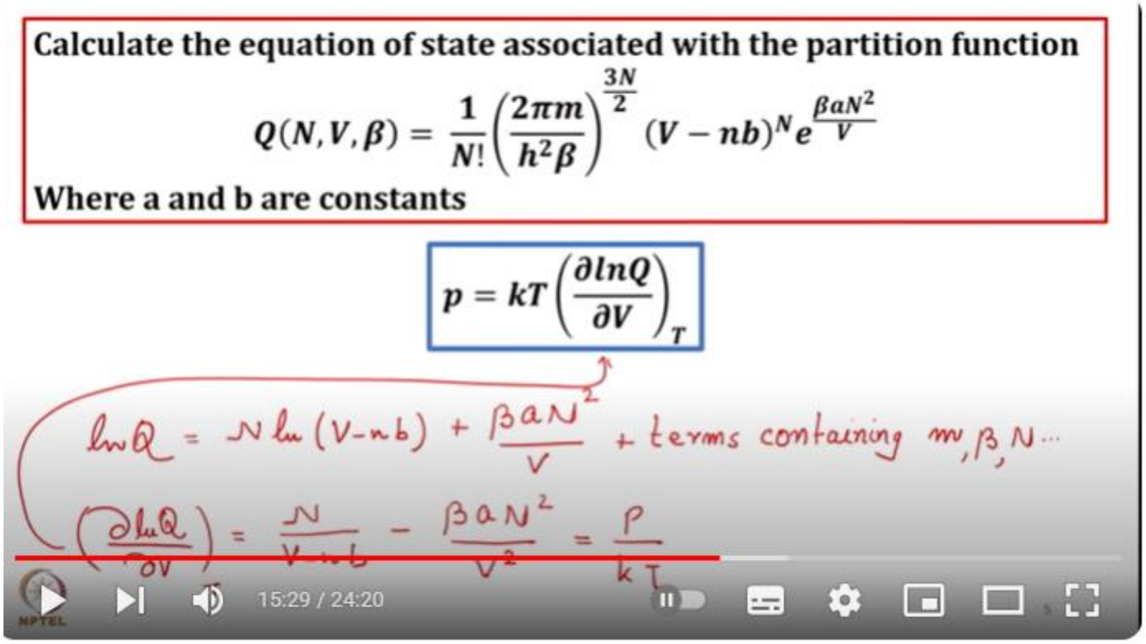

Calculate the equation of state associated with the partition function

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Where a and b are constants

$$\boxed{p = kT\left(\frac{\partial lnQ}{\partial V}\right)_T}$$

$$\ln Q = N\ln(V-nb) + \frac{\beta a N^2}{V} + \text{terms containing } m, \beta, N \ldots$$

$$\left(\frac{\partial \ln Q}{\partial V}\right) = \frac{N}{V-nb} - \frac{\beta a N^2}{V^2} = \frac{P}{kT}$$

So, β A n square by V log E is 1 plus you have terms containing m β n and some other constants. Why I wrote specifically only two terms is that I need to know the value of the partial derivative. So, let us now take derivative of this constant term. So, let us now take partial derivative with respect to volume at constant temperature and this first part of this equation n is constant, π is constant for a given system, m is constant, term with respect to volume is going to be 0. So, let us now take derivative of log Q with respect to volume at constant temperature because this is what I need over here.

So, therefore, let us take the derivative. Del log Q with respect to volume at constant temperature is going to be n log Q plus n B at constant temperature over V minus n B. This is for the first term. For the second term, β A n are constants of 1 over V that means minus β A n square over V square and all other terms the derivative is 0. This is del log Q by del V at constant temperature.

And, this is equal to P over k T from this. If I substitute this over here, then I get this is equal to P over k T. So, let us continue. What we have now is P over k T is equal to n over

V minus n B, n over V minus n B minus β A n square by V square minus β A n square by V square.

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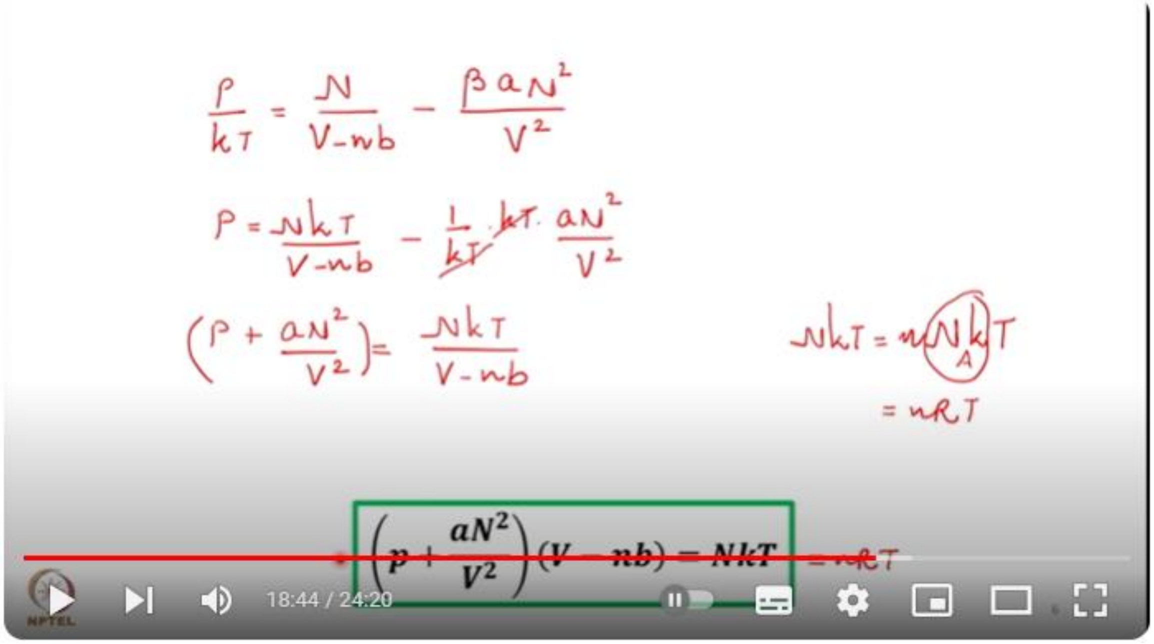

$$\frac{P}{kT} = \frac{N}{V-nb} - \frac{\beta a N^2}{V^2}$$

$$P = \frac{NkT}{V-nb} - \frac{1}{\cancel{kT}} \cancel{kT} \, \frac{aN^2}{V^2}$$

$$\left(P + \frac{aN^2}{V^2}\right) = \frac{NkT}{V-nb}$$

$$NkT = n\boxed{N_A k}T$$

$$= nRT$$

$$\boxed{\left(p + \frac{aN^2}{V^2}\right)(V - nb) = NkT} = nRT$$

This is what it is. So, therefore, P is equal to n k T over k T. So, this is what we have. So, this is what V minus n B minus β is 1 over k T, β is 1 over k T into k T into A n square over V square. This k T and this k T cancel. So, P plus A n square by V square is equal to n k T over V minus n B.

That is what we get. And, when you rearrange this, if you put this in one bracket, so this into V minus n B is equal to n k T. In fact, n k T is equal to n is equal to small n number of moles into Avogadro constant into Boltzmann constant into temperature and that k times n A is equal to R is equal to n R T. I can write this is equal to n R T. And, I am sure that you recognize this expression. This is Van der Waals equation of state.

For ideal gas, P V is equal to n R T because you ignore A and B. For a real gas or a non-ideal gas where attractive and repulsive interactions can be present, the equation is modified to P plus A n square by V square into V minus n B is equal to n R T. This is the Van der Waals equation of state. And, that is what the question was that derive an equation of state for the given canonical partition function. So, by statistical means, we have now arrived at the same equation which you have studied in theory of ideal and non-ideal gases. In other words, we have derived the expression for a non-ideal gas which obeys P plus A n square by V square into V minus n B is equal to n R T that is Van der Waals equation of state. Let us try one more. Numerical problem or theoretical problem. The question is deriving an equation for energy, average energy for a simple system of a bare proton in a magnetic field B_z. So, we need to derive an equation for the energy. So, therefore, the problem that we need to solve is for obtaining an expression for U minus U 0. And, the other information which is important and given to us is they have defined, they have fixed the magnetic field at a constant magnetic field. So, therefore, we can safely put the magnetic field constant. In any case, when we write an expression for any thermodynamic quantity in terms of canonical partition function, we need to have the information about its energy levels.

And, the energy levels or energy for a bare proton is given by E plus minus half is equal to minus plus half cross-γ B_z, where gamma which is magneto-gyric ratio is a product of nuclear factor g_N and nuclear magneton β_N. So, there the energy is given by both the terms with plus sign and with the minus sign representing two different energy levels. Once you have these two different energy levels, then I can write Q is equal to go back to your definition Q is equal to summation j exponential minus βE_j if the degeneracy is not there. So, you expand this and once you expand this, you include the energy corresponding to plus β term is also there and energy corresponding to minus β term is also there. The internal energy is given by U minus U(0) is equal to minus del log Q by del β at constant B_z, which is also equal to minus 1 by Q del Q by del β at constant B_z.

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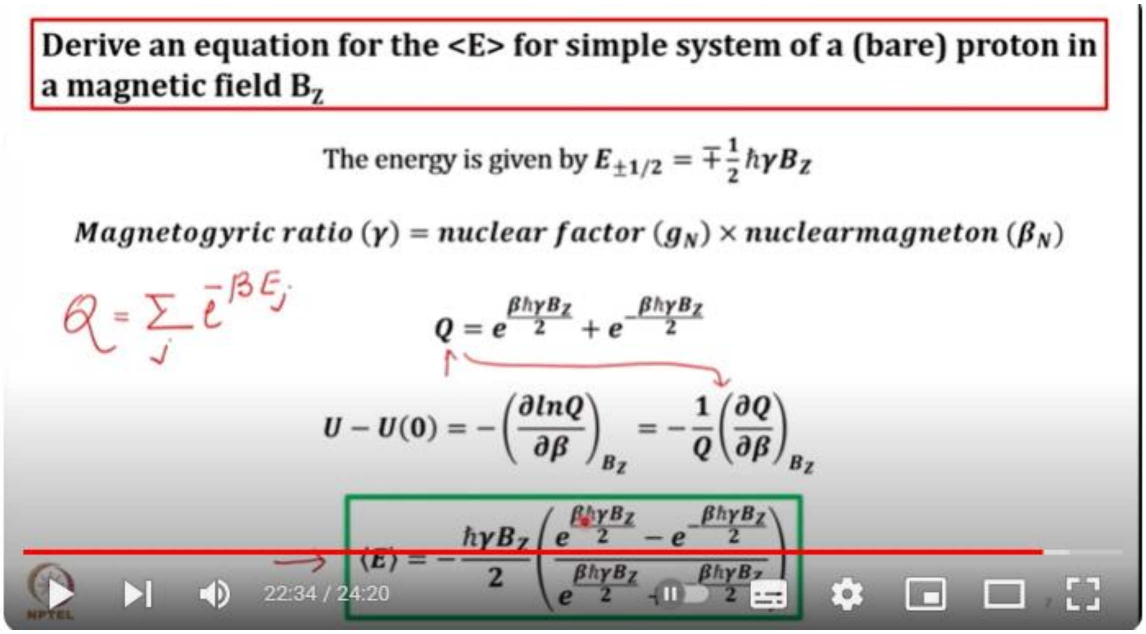

Derive an equation for the <E> for simple system of a (bare) proton in a magnetic field B_Z

The energy is given by $E_{\pm 1/2} = \mp \frac{1}{2}\hbar\gamma B_Z$

Magnetogyric ratio $(\gamma) =$ *nuclear factor* $(g_N) \times$ *nuclearmagneton* (β_N)

$Q = \sum_j e^{-\beta E_j}$

$$Q = e^{\frac{\beta\hbar\gamma B_Z}{2}} + e^{-\frac{\beta\hbar\gamma B_Z}{2}}$$

$$U - U(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{B_Z} = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{B_Z}$$

$$\boxed{\langle E\rangle = -\frac{\hbar\gamma B_Z}{2}\left(\frac{e^{\frac{\beta\hbar\gamma B_Z}{2}} - e^{-\frac{\beta\hbar\gamma B_Z}{2}}}{e^{\frac{\beta\hbar\gamma B_Z}{2}} + e^{-\frac{\beta\hbar\gamma B_Z}{2}}}\right)}$$

We have the expression for Q. Once we have the expression for Q, then this Q can be used over here. Take the partial derivative of Q with respect to β at constant P Z, you work out yourself. Eventually, you are going to get this expression. This is what we were asked for that is to derive an expression for energy for simple system of bare proton in magnetic field B_z and it turns out that this energy expression is given in terms of this expression, where we need information about gamma B_z and temperature. Once we have, then we can calculate the value of energy for a simple system of bare proton, which is in a fixed magnetic field B_z.

So, in this lecture, we have calculated or derived some expressions, which were relevant to rotational contribution to partition function and also in general further applications of canonical partition function. Keep in mind that whenever you convert canonical partition function to molecular partition function, that molecular partition function can be a product of different contribution to the partition function. For example, of translational, rotational, vibrational and electron and when you have to derive expressions for different thermodynamic quantities, for example, in this case for internal energy, we should be able to write in terms of canonical partition function and then take appropriate derivatives to arrive at the desired equation. We will further solve more numerical problems and also discuss the vibrational contribution to partition function, but those things are we will discuss in the next lectures. Thank you very much.