Introduction to Molecular Thermodynamics
Prof. Srabani Taraphder
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 22
Ideal Gases (Contd.)

So, let us continue our discussion on the statistical thermodynamics of a monatomic ideal gas where we are looking for the single particle canonical partition function small q as a function of temperature and volume and we have already discussed that the small q is having 3 different contributions on from the translational motion of the atom.

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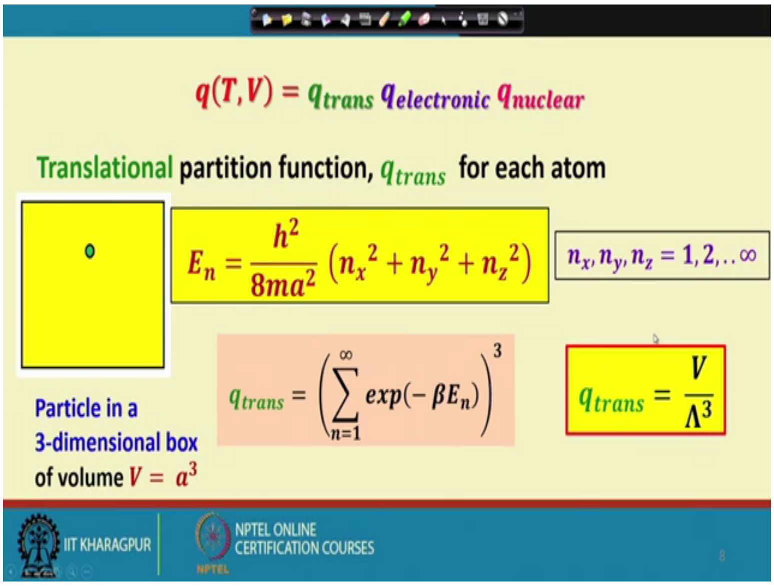

$$q(T,V) = q_{trans}\, q_{electronic}\, q_{nuclear}$$

Translational partition function, q_{trans} for each atom

$$E_n = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$n_x, n_y, n_z = 1, 2, .. \infty$

$$q_{trans} = \left(\sum_{n=1}^{\infty} exp(-\beta E_n)\right)^3$$

$$q_{trans} = \frac{V}{\Lambda^3}$$

Particle in a 3-dimensional box of volume $V = a^3$

In the box then the from the electronic and the nuclear structure associated at the microscopic level of each atom and we have also discussed the determination of the partition function using the solution of Schrodinger equation for the particle in a 3-dimensional box problem and then we have evaluated that q trans is given by v divided by lambda cube, well lambda is the thermal de Broglie wavelength.

Let us next go over and talk about how to get the electronic part of the single particle partition function.

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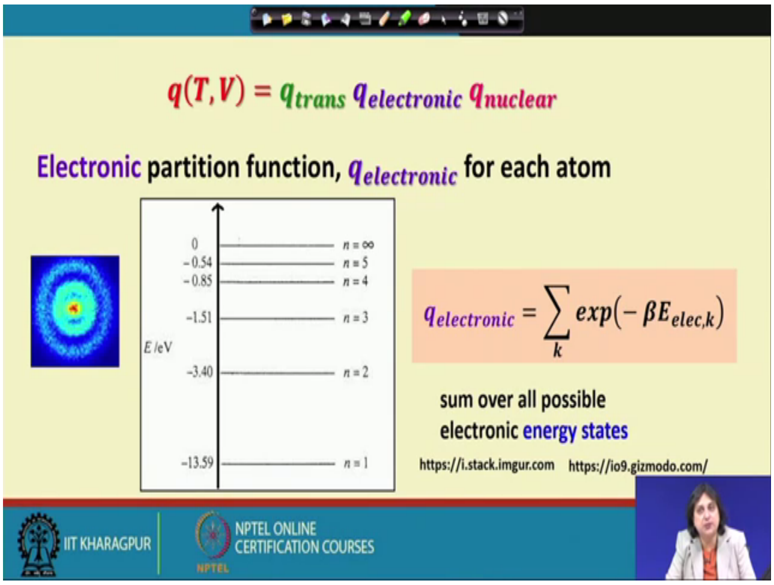

$q(T,V) = q_{trans}\, q_{electronic}\, q_{nuclear}$

Electronic partition function, $q_{electronic}$ for each atom

$$q_{electronic} = \sum_k exp(-\beta E_{elec,k})$$

sum over all possible electronic energy states

https://i.stack.imgur.com https://io9.gizmodo.com/

So, in order to do this, what I need to understand is, now I am focusing on the microscopic structure of the atom here and not only that you know that for any given atom, even for hydrogen atom, you can write down, you can separate out on on the basis of the difference in time scales for electro movement of electrons and nuclei the the solution of the electronic part of the Schrodinger equation.

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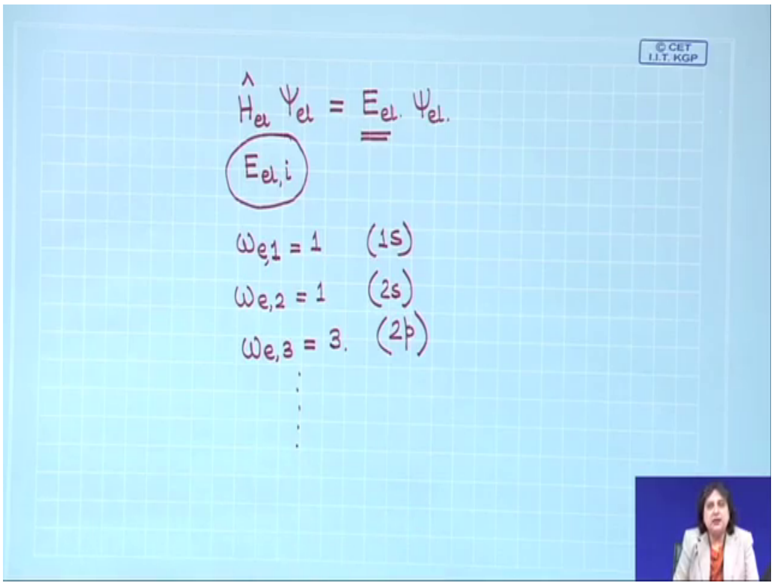

$$\hat{H}_{el}\Psi_{el} = \underline{\underline{E_{el}}}\,\Psi_{el}$$

$\boxed{E_{el,i}}$

$\omega_{e1} = 1$ (1s)

$\omega_{e,2} = 1$ (2s)

$\omega_{e,3} = 3.$ (2p)

⋮

So, if you solve the electronic Schrodinger equation H cap electronic psi electronic you will get e electronic and psi electronic on the right-hand side.

So, what is a electronic? These are the energy eigen values offered by the solution of the Schrodinger equation for the electronic Schrodinger equation. So, there may be many different values, discrete values of these energy and therefore, we are going to represent them as e l and then something like I or j or k. So, this corresponds to the fact that this is the i^{th} solution of the n for the energy eigen value from the electronic Schrodinger equation now if I think about it from the experiment,s this is what we get for the different solutions. As you see that this are the energy levels for or the energy states that are accessible to the hydrogen atom and typically the energy scale is about a few units of electron volt ok.

Now, if I want to find out the electronic partition function therefore, I must write it like this. So, by definition q electronic is summation over all possible electronic energy states, which I represent using this index k and this summation is carried out over this exponential function that has beta into e electronic k, which gives me the k^{th} energy eigen state of this particular electronic energy of this particular atom.

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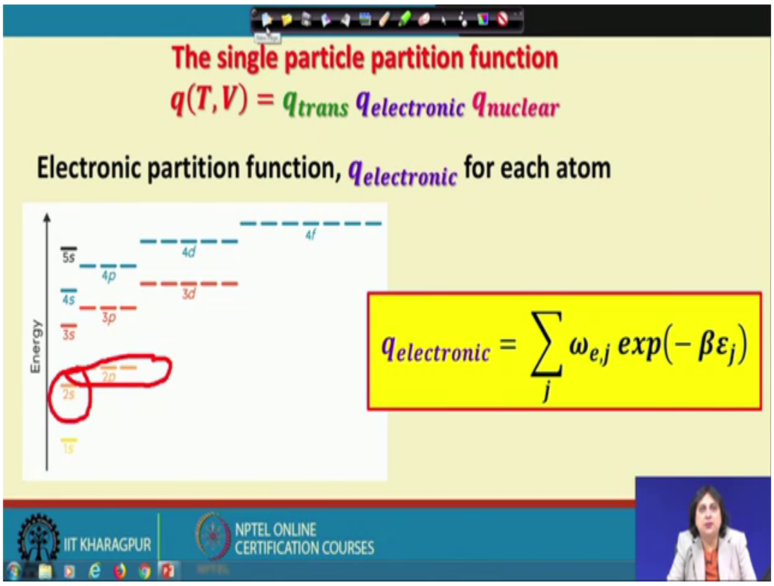

The single particle partition function

$q(T,V) = q_{trans}\, q_{electronic}\, q_{nuclear}$

Electronic partition function, $q_{electronic}$ for each atom

$$q_{electronic} = \sum_j \omega_{e,j} \exp(-\beta\varepsilon_j)$$

In many cases, actually these, it is found convenient to talk in terms of the energy levels because each of the energy states can have many many different states with the same energy ok.

So, here is an example, where the same energy solution can have for a given value of energy, the system can have many different solutions and therefore, instead of summing over the different energy states, one tries to sum over different energy levels. So here, for example, the one estate is singly degenerate and therefore, for this electronic state, the omega e that is the degeneracy of the state for the first electronic state is equal to one; this is the second electronic state for this atom. So, this is omega e 2. So, can you tell me what omega e 2 is? Omega e 2 is once again one because, the s orbital that you see here as a solution is a singly degenerate function.

Now, but here, slightly above this, there is one energy level that is triply degenerate. So, for this particular picture, I must be saying that well, I have omega e 1 that is equal to one because it is an one s orbital. Omega e 2 that is equal to one corresponding to a 2s orbital, then omega e 3 that is equal to I have that 2p orbitals here and there are 3 2p orbitals corresponding to the same energy value. So, omega e 3 is equal to 3 and so on and so forth.

So, this is the very restricted picture of what actually the micro microscopic state of this atom is, but in general, what I am trying to say here is that, for many systems multi electron systems, it is found useful to sum over all the levels rather than over all the microscopic states and then all you have to be careful about is you are summing over all possible energy levels and there can be many energy states having the same energy level and therefore, you must bring into account here the degeneracy of that particular level.

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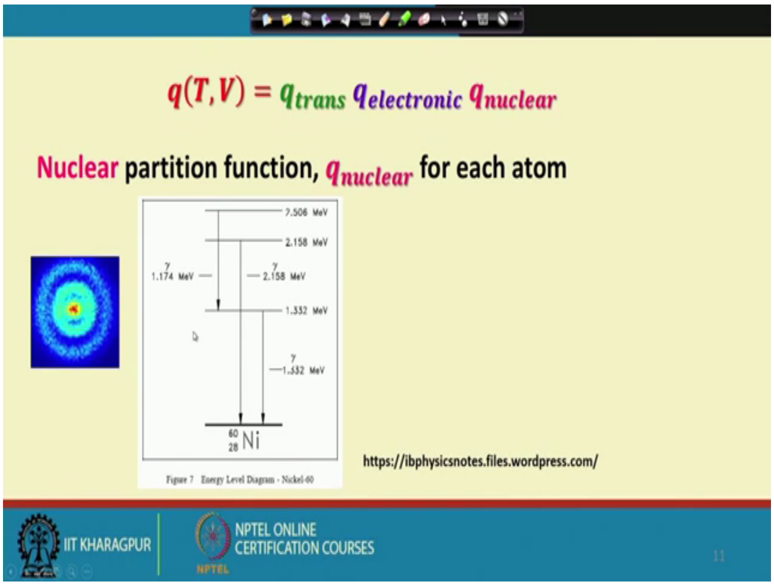

$q(T,V) = q_{trans}\, q_{electronic}\, q_{nuclear}$

Nuclear partition function, $q_{nuclear}$ for each atom

Figure 7 Energy Level Diagram - Nickel-60

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Now, so far, we have talked about q trans; we have talked about q electronics and now we are going to talk about q nuclear. So, how to find out the nuclear partition function for each atom? So, once again we are looking at the microscopic structure associated within the atom and we know that the nucleus is present at the center and one can indeed probe the kind of energy difference between the different nuclear energy states by looking at; let us say, some kind of radioactive process and what is the typical energies of the radiations, which come out in the form of alpha or beta particles or gamma rays.

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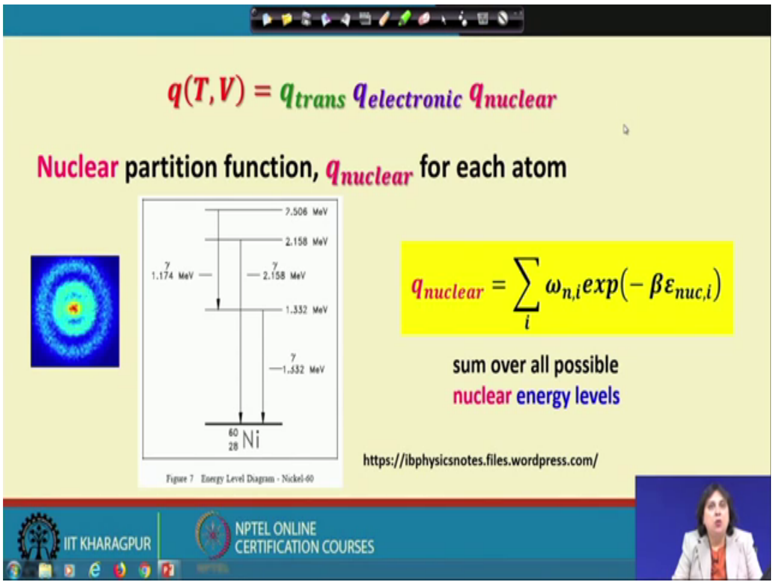

$q(T,V) = q_{trans}\, q_{electronic}\, q_{nuclear}$

Nuclear partition function, $q_{nuclear}$ for each atom

$$q_{nuclear} = \sum_i \omega_{n,i} exp(-\beta\varepsilon_{nuc,i})$$

sum over all possible
nuclear energy levels

https://ibphysicsnotes.files.wordpress.com/

Figure 7 Energy Level Diagram - Nickel-60

So now, let us talk about the nuclear partition function and how to get it for each atom. It is possible to talk about the energy level diagram of a nucleus and here you see that the gap between these energy levels is of the order of M E V and this results are obtained usually by breaking the nucleus of an radioactive atom and looking at the energies of the emissions emitted particles like the alpha or beta or the even the gamma rays. From there, it is possible to say that well these difference between 2 successive energy levels in a nucleus is about 10 to the power of 6 electron volt.

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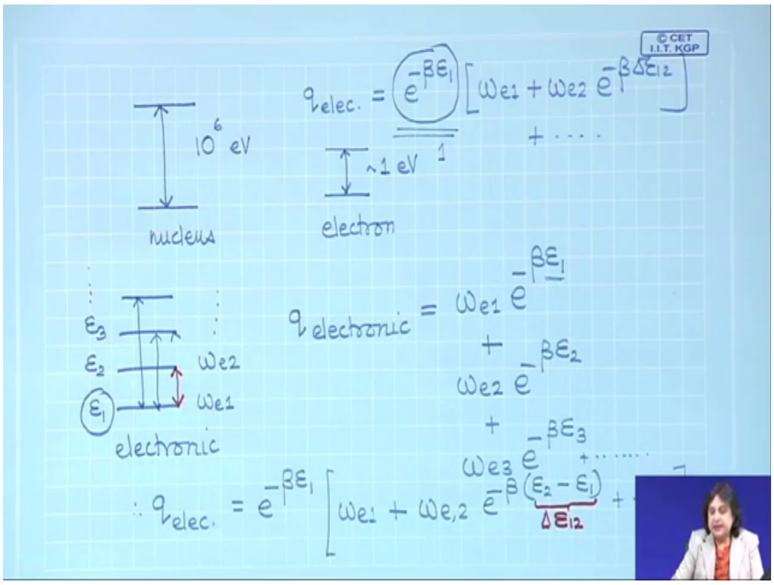

$$q_{elec.} = \underline{\underline{\boxed{e^{-\beta\varepsilon_1}}}}_{1} \left[\omega_{e1} + \omega_{e2}\, e^{-\beta\Delta\varepsilon_{12}} + \ldots\right]$$

$$q_{electronic} = \omega_{e1} e^{-\beta\varepsilon_1} + \omega_{e2} e^{-\beta\varepsilon_2} + \omega_{e3} e^{-\beta\varepsilon_3} + \ldots\ldots$$

$$\therefore q_{elec.} = e^{-\beta\varepsilon_1}\left[\omega_{e1} + \omega_{e,2}\, e^{-\beta\underbrace{(\varepsilon_2-\varepsilon_1)}_{\Delta\varepsilon_{12}}} + \ldots\right]$$

Now, if I look at the difference between 2 successive electronic energy levels, in that case, do you remember what the energy value was? It was of the order of one electron volt. Now this has very, very important consequence when we talk about the a computation of the entire single particle partition function, but before I go into this, this following the prescription of the electronic partition function, here also for the nuclear partition function, we can write down q nuclear is summation over all possible energy levels nuclear energy levels I then, in the sum and I have the degeneracy of the each of the nuclear energy levels and I have this exponential term by definition.

So, at this point, therefore, we are having this ability to evaluate the small one single particle partition functions small q.

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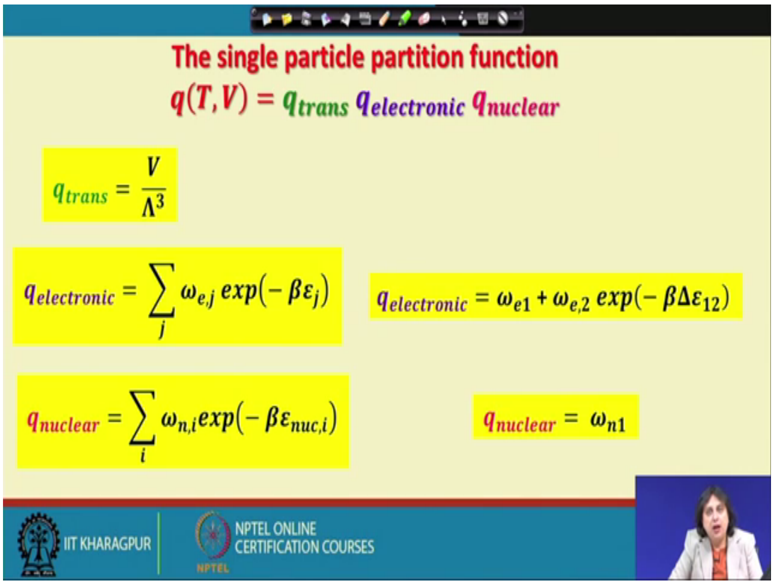

The single particle partition function

$q(T,V) = q_{trans}\, q_{electronic}\, q_{nuclear}$

$q_{trans} = \frac{V}{\Lambda^3}$

$q_{electronic} = \sum_j \omega_{e,j}\, exp(-\beta\varepsilon_j)$

$q_{electronic} = \omega_{e1} + \omega_{e,2}\, exp(-\beta\Delta\varepsilon_{12})$

$q_{nuclear} = \sum_i \omega_{n,i} exp(-\beta\varepsilon_{nuc,i})$

$q_{nuclear} = \omega_{n1}$

So, this is what information we have gathered so far, but at normal temperatures, at normal room temperature, you know the values of k t in electron volt. We have already seen that then you will see that, given the fact that, these energy values the difference in energy values is in the in few electron volts for the case of an electronic energy states at finite temperatures only the may be the first 2 terms will be important and give you the value of q electronics. So, how do I get it? Let us say, that a system, has these electronic energy levels, epsilon one epsilon 2 epsilon 3 and so on. And so, forth these are all electronic energy levels and this is omega e 1 is the degeneracy of the energy level epsilon one this is epsilon 2 like this. So, what is small q electronic? Now small q electronic will be given by omega e 1 into the power of minus beta epsilon 1 plus omega e 2 e to the power of minus beta epsilon 2 plus omega e 3 into e to the power of minus beta epsilon 3 and so on and so forth.

Now, what I do is, I take this epsilon one out. Then, my q electronic will be return as e to the power of minus beta epsilon one then omega e 1 plus omega e 2 into e to the power of minus beta epsilon 2 minus epsilon 1 plus the other terms. Now, let me indicate, this term by epsilon one 2 that is this energy difference, if that is so, then I can very easily write that my q electronic can be written as e to the power of minus beta epsilon one into omega e 1 plus omega e 2 into e to the power of minus beta delta epsilon 1 2 ok.

I am using a delta sign over here; indicating that this is the energy difference between the levels 1 and 2 in the electronic energy. So, once you will and the higher order terms are neglected simply because this; these are unimportant when multiplied with beta the delta epsi e 1 3 like this, this is higher than this, this is even higher than this. So, all the higher energy levels will not contribute much to the to the overall electronic partition function because, beta into that delta epsilon term is very, very small.

Now, very, very large and therefore, their contributions are going to be very, very small. Now if I now set this epsilon one the value of absolute value of epsilon one to be the 0 of my energy scale, then, this term becomes equal to one and that is exactly what we have written here. Now what use is this? The use is that where do we get information about these energy values we get them from spectroscopy? And in spectroscopy you see that the peaks appear at certain energy values which correspond to the energy difference between the starting state from where the transition occurred to the state up to where the transition took place.

As a result, the information regarding delta epsilon one 2 is available from experiments and if I know the corresponding degeneracy of the electronic energy states then I should be able to find out small q electronic. Similarly you can talk about the q nuclear and once again, since the epsilon nuclear for different values these are very, very high in magnitude therefore, beta epsilon nuclear is also going to be very high in magnitude and therefore, this this basically tells you that the nucleus at normal room temperatures will always be located in it is ground nuclear energy level. As a result I can very easily write that q nuclear is a very simple constant like this which is equal to the degeneracy of it is ground nuclear energy level.

Now, we are in a position to calculate the single particle partition function.

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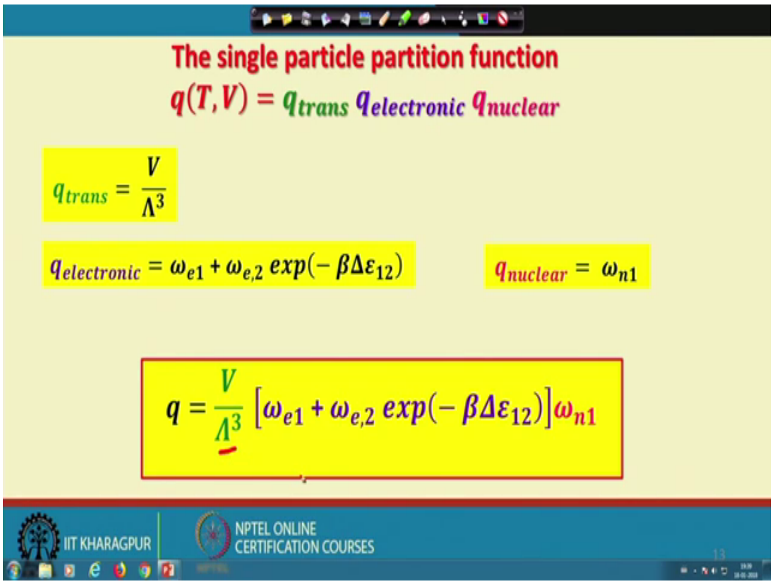

The single particle partition function

$q(T,V) = q_{trans}\, q_{electronic}\, q_{nuclear}$

$q_{trans} = \frac{V}{\Lambda^3}$

$q_{electronic} = \omega_{e1} + \omega_{e,2}\, exp(-\beta\Delta\varepsilon_{12})$

$q_{nuclear} = \omega_{n1}$

$$\boxed{q = \frac{V}{\Lambda^3}\left[\omega_{e1} + \omega_{e,2}\, exp(-\beta\Delta\varepsilon_{12})\right]\omega_{n1}}$$

I have 3 quantities which are now known. I can find out each of these quantities under the experimental conditions in which I have placed the system and then the small q by defination is a product of q trans q electronic and q nuclear and this is given by this kind of an expression. So, the green part that gives the contribution from the translational degrees of freedom. So, this is the part that gives you the translational degree of freedom corresponds to the translation.

This part corresponds to the microscopic structure of the atom in terms of it is electronics structure and this term corresponds to the microscopic structure of the atoms in terms of the discrete energy levels of its nucleus as given by the solution of the Schrodinger equation now with this expression now let us ask this question. We are asking this question that q this is for a single particle and is this a function of temperature? Solet us go back and look at where we could have the contribution of temperature? Yes, lambda is a function of temperature because by defination lambda square is equal to h square divided by 2 pi m k T.

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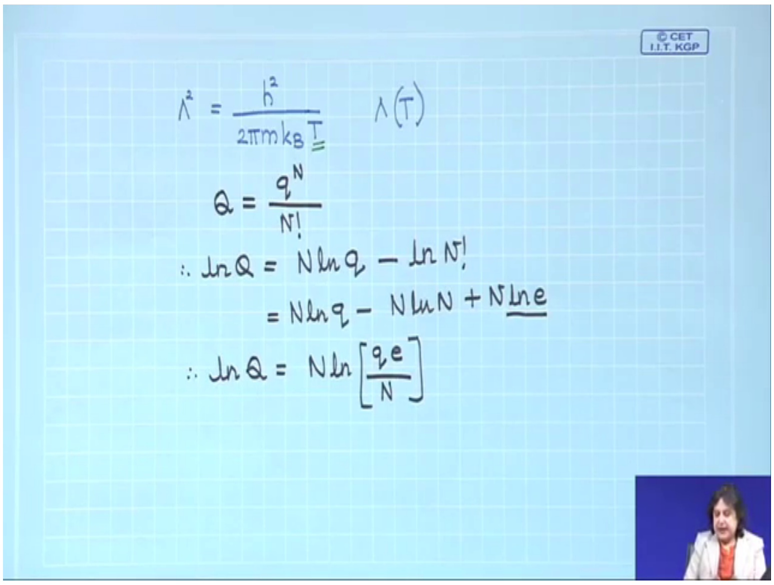

$$\Lambda^2 = \frac{h^2}{2\pi m k_B \underline{\underline{T}}} \qquad \Lambda(T)$$

$$Q = \frac{q^N}{N!}$$

$$\therefore \ln Q = N \ln q - \ln N!$$

$$= N \ln q - N \ln N + N \underline{\ln e}$$

$$\therefore \ln Q = N \ln \left[\frac{qe}{N}\right]$$

So, temperature is present here. So, lambda essentially is function of temperature. So, that is a first round therefore, has contribution from temperature here, then, I have beta over here that is also dependent on temperature. So, q is indeed a function of temperature as given by this expression that we have derived starting from the Hamiltonian of the system.

Now, let us have a look at ask this question that does q depend on the volume V? The answer is yes. As you see, that the volume V explicitly is present here, therefore, q is a function of volume as well and therefore, in general we have been able to show that the single particle partition function is a function of temperature and volume which define the microscopic state of the system now if we go further and have a look at what happens.

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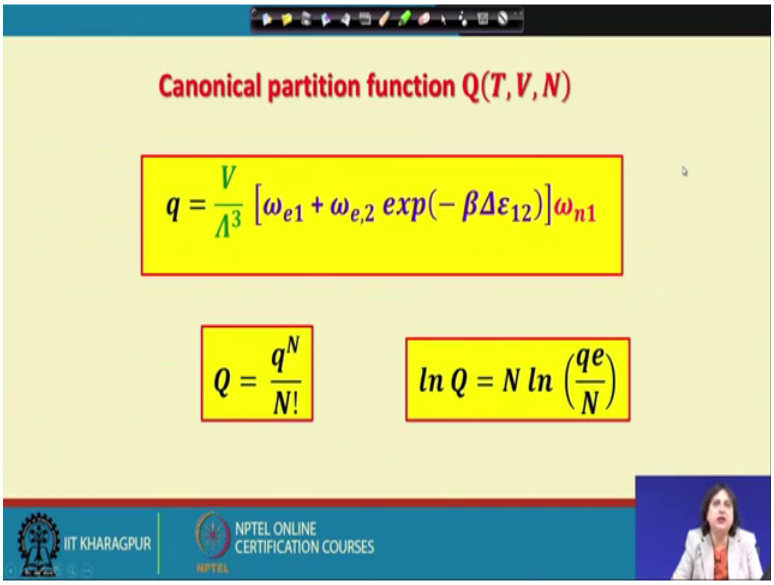

Canonical partition function $Q(T,V,N)$

$$q = \frac{V}{\Lambda^3}\left[\omega_{e1} + \omega_{e,2}\exp(-\beta\Delta\varepsilon_{12})\right]\omega_{n1}$$

$$Q = \frac{q^N}{N!}$$

$$\ln Q = N \ln\left(\frac{qe}{N}\right)$$

If I now try to find out the canonical partition function, then I must realize that, in this case, I must be having that my system is comprised of N independent non-interacting identical particles therefore, by defination Q is related to small q like this and therefore, I would like to find out what l and Q would look like. Now why l and Q? Because, you already know, by the Beijing relationship that f that is a Helmholtz free energy in a canonical ensemble is related to l and Q.

So, let us now try and derive that. So, I have Q is equal to q to the power of n divided by capital n factorial and therefore, I can write down that l n Q is equal to this minus l n of n factorial. Now what is the typical value of N? This is of the order of 10 to the power of 23 which means that, by for all practical purposes, this is a very, very large number. So, we are in a position to use this stirling's approximation here and if I do that then Iam going to write it as minus N ln N plus N ok.

And therefore, what I will do is, actually this N, I am going to replace it by capital N ln e. I mean this is nothing but one. So, that tells me that ln Q can now be simplified and written as small q e divided by N and that is exactly what I have shown you here. Now how do I use this relationships? The way to use this relationships is, I am going to use the partition function to derive the thermodynamic properties of the system.

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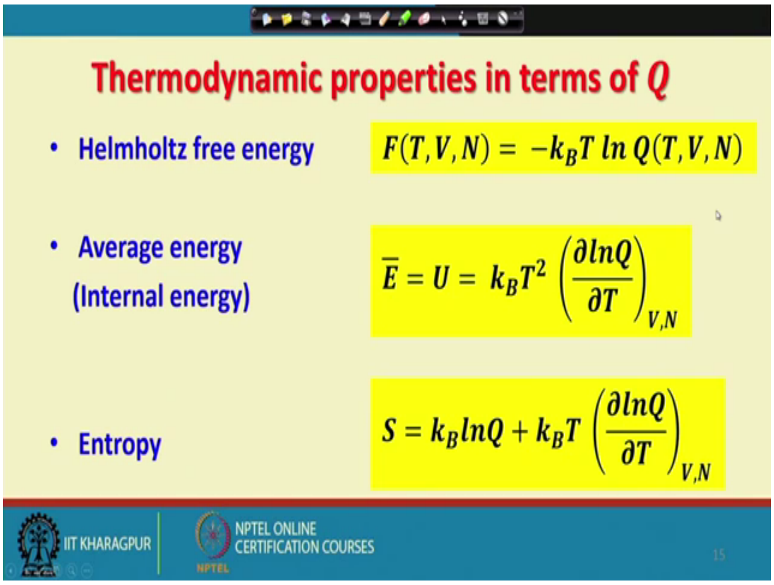

Thermodynamic properties in terms of Q

- Helmholtz free energy $F(T,V,N) = -k_BT \ln Q(T,V,N)$
- Average energy (Internal energy) $\bar{E} = U = k_BT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$
- Entropy $S = k_B \ln Q + k_BT\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$

And these are relationship that we have already figured out that is Helmholtz free energy is minus k BT into log of Q the average energy or the internal energy is related to the del T of ln Q and the entropy again can be written down in terms of ln Q.

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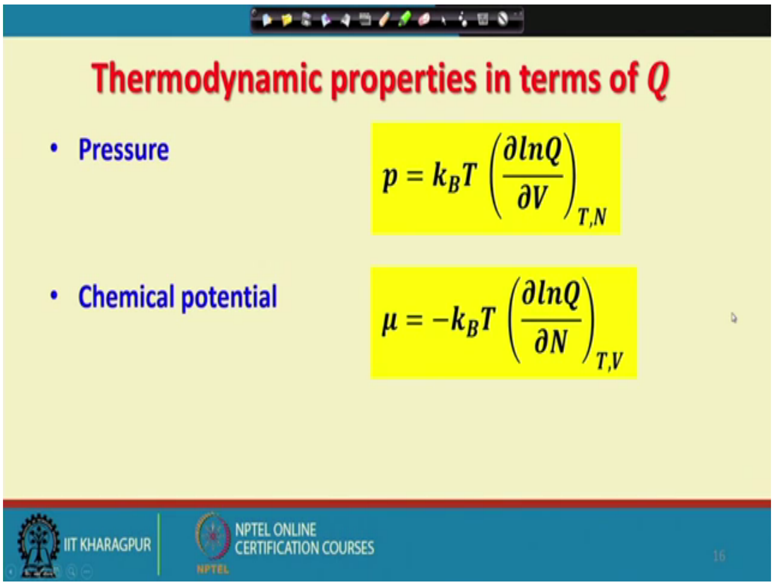

Thermodynamic properties in terms of Q

- Pressure $p = k_BT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$
- Chemical potential $\mu = -k_BT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}$

Finally, the pressure is also dependent can be derived by taking a derivative of ln Q and also we can find out the chemical potential as well if since we have written down the Q explicitly, in terms of N. So, let us now go back and try and find out the simplest possible things and for this purpose what I will be requiring is the expression for Q ok.

So, if I look at what happens to capital q as a function of volume.

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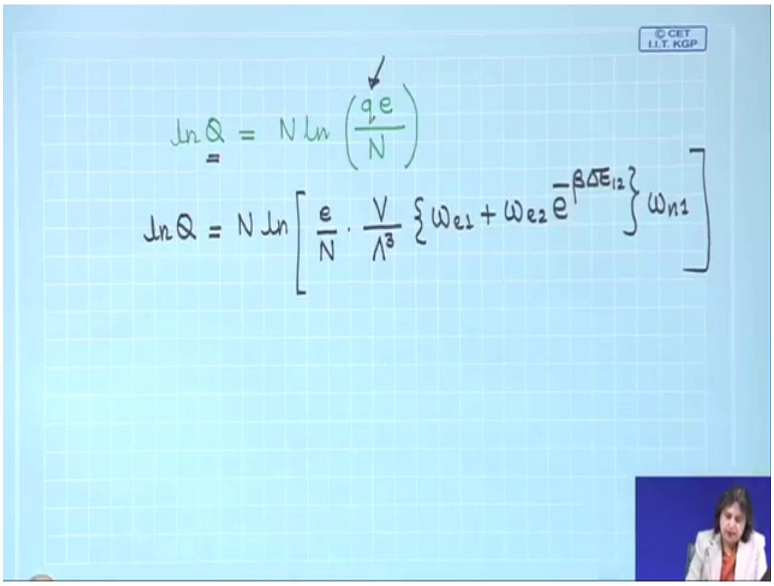

$$\ln Q = N \ln \left(\frac{\overset{\downarrow}{q}\, e}{N}\right)$$

$$\ln Q = N \ln \left[\frac{e}{N} \cdot \frac{V}{\Lambda^3} \left\{\omega_{e1} + \omega_{e2} e^{-\beta \Delta \varepsilon_{12}}\right\} \omega_{n1}\right]$$

I see that ln Q that is equal to N ln q e divided by N. So, where does the dependence on volume in Q come here? That comes through the dependence of q one volume. So, if I write down explicitly what ln Q is, then this is given by, N ln e divided by N into V by lambdaQ into this omega e 1 plus omega e 2 e to the power of minus beta delta epsilon one 2 into omega N 1 right that.

So now we are in a position to calculate the thermodynamic properties of this monatomic ideal gas, that is because, I know the partition function and I know how to calculate thermodynamic properties, by knowing the partition function of the system. So, let us now once again try and find out.

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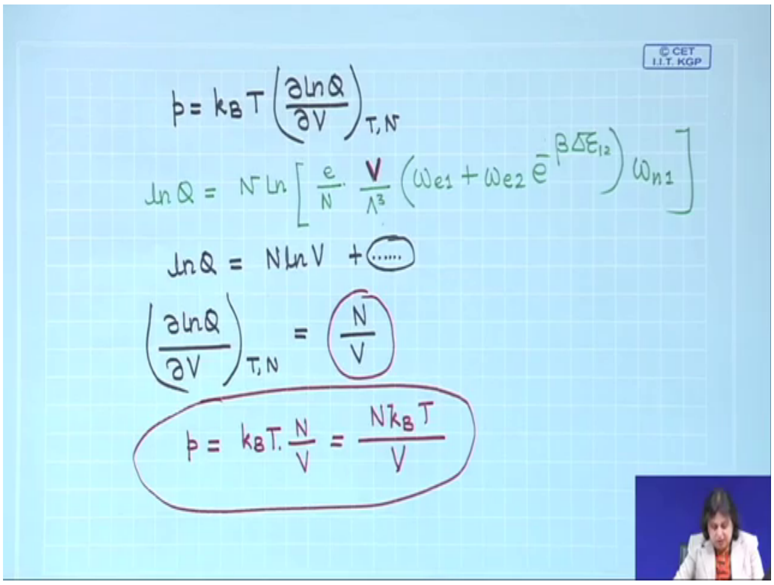

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

$$\ln Q = N \ln \left[\frac{e}{N} \cdot \frac{V}{\Lambda^3} \left(\omega_{e1} + \omega_{e2}\, e^{-\beta \Delta \varepsilon_{12}}\right) \omega_{n1} \right]$$

$$\ln Q = N \ln V + \boxed{\ldots\ldots}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} = \boxed{\frac{N}{V}}$$

$$\boxed{p = k_B T . \frac{N}{V} = \frac{N k_B T}{V}}$$

What the pressure of the system is using the formalism of statistical thermodynamics. So, this is pressure right.

Now, at this point we have found what ln Q is. Now ln Q that is equal to N ln then, e by N into V by lambda cube into these terms that omega e 1 plus omega e 2 e to the power of minus beta delta epsilon one 2 into omega N 1. We have already shown that if that is so, then if I want to take a derivative of ln Q with respect to V,I must understand what are the dependents terms here on V; here this is the only term within this logarithm natural logarithm that depends on V.

Therefore, I can very easily write thatln Q is actually N ln V plus some term which are functions of which a constants as far as the condition constant temperature and constant number of particles is concerned. So, this does not depend on V therefore, if I take this derivative del ln Q del V keeping temperature and number of particles constant what I will be getting is capital n divided by V. So, my formulation from the Hamiltonian up to here gives me that the pressure of this system, that is equal to k BT into this term and that is N by V.

So, that is N k BT by V does it look familiar of course, this is nothing but the ideal gas equation. So, what we have achieved is actually pretty enormous. We have started with a microscopic model where I have N non-interacting in distinguishable atoms each of this atoms are moving about in the 3-dimensional space provided by the box and which the gas is confined and I know that I have some idea about the different degrees of freedom that this system this microscopic particle enjoys. It is executing our translational motion inside the box that is quantized and therefore, you can think about the the written down the q trans for that particular system.

And then you introduce the microscopic structure of the atom in terms of it is electronic energy levels and nuclear energy levels. So now, you have the microscopic picture complete and then you just say that well, I can write down the single particle partition function for a monatomic ideal gas ,in terms of the volume of the system the thermal de Brogliewavelength which depends on the mass of the mass of each gas atom as well as the temperature at which the gas is present also there are contributions from the excitation energy from the ground electronic state to the first excited electronic state and the respective degeneracies of the electronic energy states.

And finally, I have some constant term coming from the degeneracy of the ground nuclear energy level. I combine all of these. I understand that ln Q is given by this expression where Q is this and when I combine this and I wrote down that pressure by the formulation is given by a derivative of ln Q with respect to V under isothermal and constant particle condition then by using the functional expression for ln Q,I find that p indeed conforms to the ideal gas law. So, this is where we say that the usefulness of statistical thermodynamics comes into the picture.

Of course, you can go ahead and try to calculate other quantities. So, what are the other quantities that you can try to calculate? Obviously, average energy entropy or the chemical potential. So, following the prescription that are given here.

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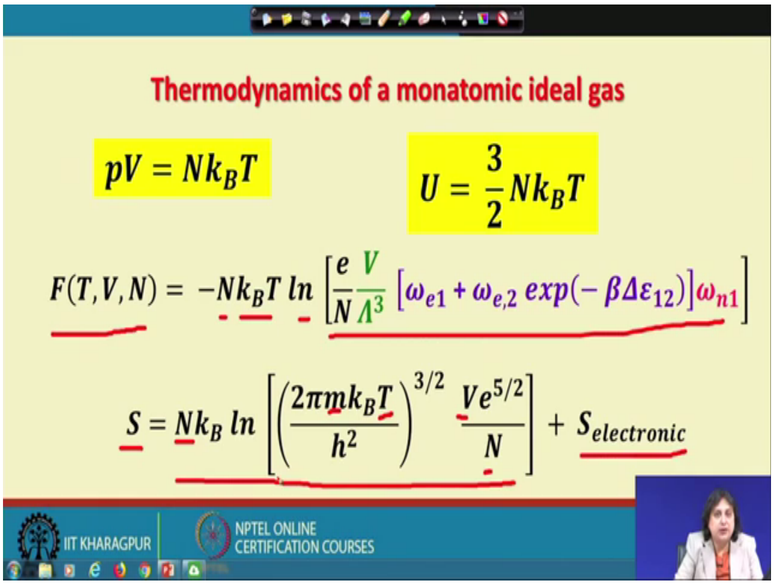

Thermodynamics of a monatomic ideal gas

$pV = Nk_BT$

$U = \frac{3}{2}Nk_BT$

$$F(T,V,N) = -Nk_BT\ ln\left[\frac{e}{N}\frac{V}{\Lambda^3}\left[\omega_{e1} + \omega_{e,2}\ exp(-\beta\Delta\varepsilon_{12})\right]\omega_{n1}\right]$$

$$S = Nk_B\ ln\left[\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\frac{Ve^{5/2}}{N}\right] + S_{electronic}$$

You can very easily show that the internal energy is 3 by 2 N k T the easiest way probably would be to write down ln Q.

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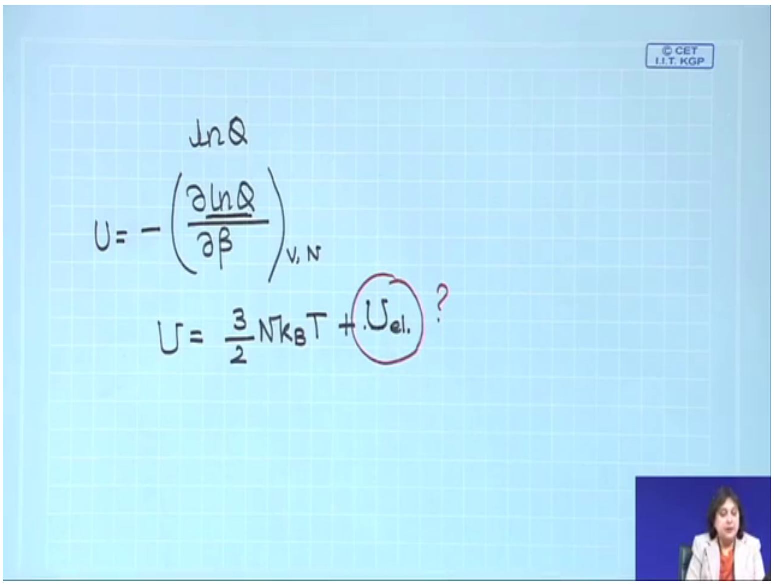

$\ln Q$

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N}$$

$$U = \frac{3}{2}Nk_BT + U_{el.}\ ?$$

And then take del ln Q del beta keeping the volume and the number of particles constant, take a negative sign of this and this is nothing but U.

Since you know ln Q the functional form of ln Q in terms of beta you can carry out this differentiation. This is a simple numerical task and if you do that, you will be able to show that U is equal to 3 by 2 N k T there will be some correction terms. And these correction terms will come from where they will come from the electronic structure of the system. So, I will leave it as an exercise for you to find out that in the case of a monatomic ideal gas, I have already shown here the result that, this is the predominant term, but there will be some correction term coming in terms of U electronic. I will leave it as an exercise for you to find out what this U electronic is.

Similarly, you can very easily write down straight away what the Helmholtz free energy is. That is nothing but minus N k T into ln of this is Q. So, once I know u and and F. I can very easily find out the entropy of the system as U minus F divided by T clear. So, if I do that then, it is possible for us to show that the entropy of the system which is absolute value of entropy can be written in terms of these quantities plus a term which depends on the electronic structure of the atom.

Now, let us have a look at the different contributions. So, what is m? M is the mass of each gas atom, T is the temperature at which the system is present V is the volume of the gas and once again N is the number of particles number of atoms present in the system this equation is known as the sackur tetrode equation. In our next lecture, we will see the utility of these expressions in trying to understand further the properties of monatomic ideal gases and how to generalize these results to atoms to gas ideal gases which are not comprised of simple atoms, but molecules like a die atom or a poly atom. Till then,I will ask you to go back and try to do this algebra at least once, to get the feeling of how these mathematical expressions came into the picture.

Thank you.