Introduction to Molecular Thermodynamics
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Lecture - 28
Statistical Thermodynamics of Ideal Gases (Contd.)

Welcome we are discussing the statistical thermodynamics of an ideal gas, where we have derived several very important results regarding how to start with the Hamiltonian of the system and then try to understand how to use the different exactly solvable results of Schrodinger equation under certain approximations for the ideal gas and then derive the thermodynamic properties from it.

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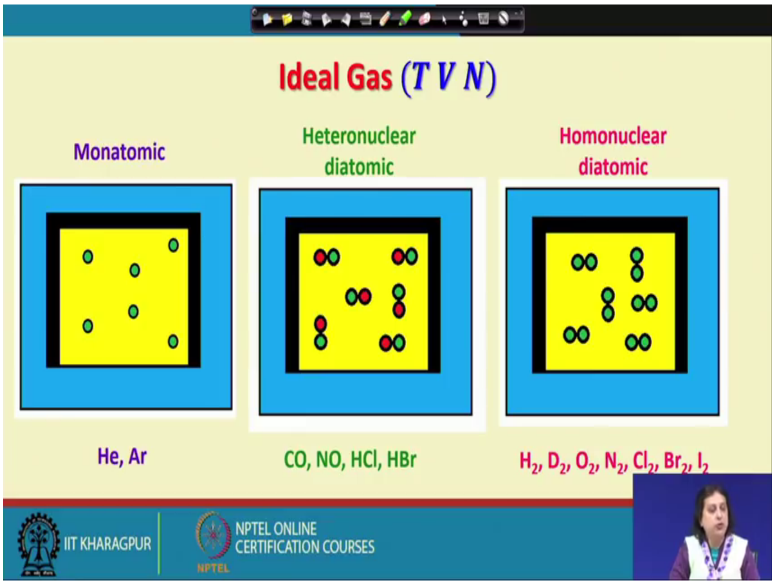

Ideal Gas (T V N)

Monatomic

Heteronuclear diatomic

Homonuclear diatomic

He, Ar

CO, NO, HCl, HBr

H_2, D_2, O_2, N_2, Cl_2, Br_2, I_2

The first thing that we have learnt is the information that is present for an ideal gas maintained at a thermodynamic state of constant temperature volume and number of particles. We can visualize at the microscopic level this gas has being comprised of atoms or heteronuclear diatomic molecule or homonuclear diatomic molecule.

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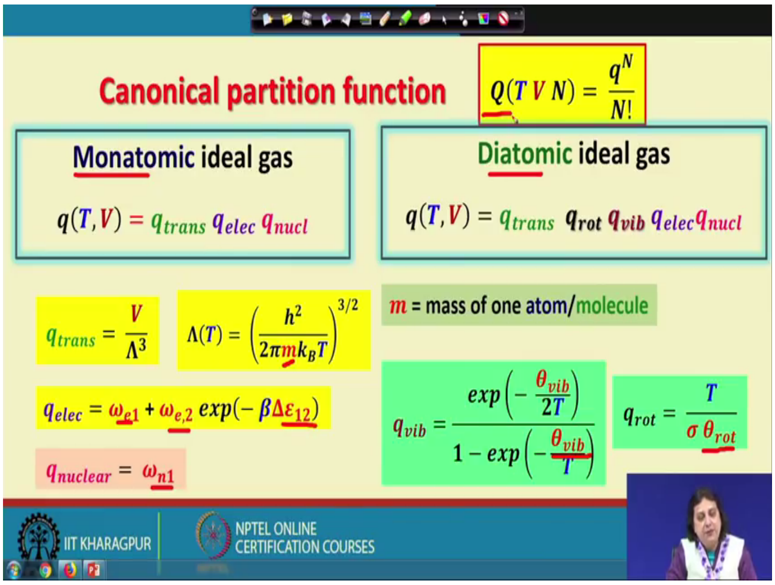

Canonical partition function

$Q(T\,V\,N) = \frac{q^N}{N!}$

Monatomic ideal gas

$q(T,V) = q_{trans}\, q_{elec}\, q_{nucl}$

Diatomic ideal gas

$q(T,V) = q_{trans}\, q_{rot}\, q_{vib}\, q_{elec} q_{nucl}$

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

$\Lambda(T) = \left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}$

m = mass of one atom/molecule

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

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

$q_{vib} = \frac{exp\left(-\frac{\theta_{vib}}{2T}\right)}{1 - exp\left(-\frac{\theta_{vib}}{T}\right)}$

$q_{rot} = \frac{T}{\sigma\,\theta_{rot}}$

And we have already seen how to talk about putting the information regarding the microstates of the system in terms of the canonical partition function. And the canonical partition function is defined like this for the total N number of particles which are present in the system, which are identical to which each other and which are not interacting with each other.

Under this given condition then we have also seen that for a monoatomic ideal gas we have this following expression for the single particle canonical partition function that is small q. Now, since I already said that it is for the single particle, so N equal to 1 that is a particular case and small q depends both on temperature and the volume at which the entire system is present. In the case of monatomic ideal gas we have been able to show that we have the small q for an ideal gas it derives contributions from 3 distinct factors, one is the translational partition function for the single particle, the electronic partition function for this single particle as well as the nuclear partition function for this single particle. So, this first term corresponds to the movement of the molecule as a whole or the atom as a whole in the confining volume and these two terms correspond to the underlying microscopic structure as given by the solution of the Schrodinger equation at 0 Kelvin temperature.

Now, if we compare what has happened in the case of the diatomic ideal gas where each particle in the gas is a molecule comprised of two atoms in that case what we find is that we will have the same terms as we have seen in the case of monatomic ideal gas such as q trans, q electronic and q nuclear, but here we have two additional terms coming in because of the presence of an underlying molecular structure in the form of a chemical bond between the 2 nuclei of the system. Therefore we could highlight how the this difference in underlying chemical structure of the two systems will affect the overall small q that is a single particle canonical partition function, and hence affect the capital Q that is the total canonical partition function.

Now, if we go ahead and remember what happens as a consequence of this we know that we are able to calculate the small q's under certain approximations and its possible to show that irrespective of whether you have atoms or molecules constituting the gas, the translational partition function can be written in terms of the volume V in which the gas is present and lambda cube.

Now, we have introduced the lambda cube as the debroglie thermal debroglie wave function which tells us something at finite temperature and it gives us the finite temperature analog of the debroglie wavelength associated with each particle. We will come back to this concept later on, but as we see here that the debroglie thermal debroglie wavelength it depends on two key quantities, the mass of the particle the signal particle and the temperature at which the system is present. So, on the whole q trans is a function of volume and temperature at the level of thermodynamic properties and for each given system this small m decides the what is the mass of the overall moving particle that we are considering.

Therefore, in the case of monatomic ideal gas this small m is a mass of each atom present in the system and in the case of the diatomic ideal gas this corresponds to the mass of each molecule which evidently is the total mass or the mass associated with the center of mass of the molecule. We have discussed all these in the last lectures.

Now, the next important factor which appears in both the cases are the q electronic and the q electronic is given by an expression like this which we have discussed in detail. And we have seen that if you know the electronic absorption spectrum or if using quantum mechanics you are able to find out the energy eigenstates corresponding to the electronic Schrodinger equation then you have information of quantities such as degeneracy of the ground electronic state, degeneracy of the first excited electronic state and the energy difference between the first ground and the first excited electronic state and also beta is nothing but inverse of k T. As a result using experimental data or by using results from theoretical calculations it is possible to determine what q electronic is, irrespective of whether you have monatomic or a diatomic ideal gas, the prescription is the same.

Now, the next thing that we need to worry about that is common in both the I mean diatomic as well as a monatomic case is the q nuclear, and we have seen in our earlier lecture that q nuclear is essentially approximated in terms of the degeneracy of the ground nuclear energy level. So, once we know this then the task of finding the small q that is a single partition function for the atoms constituting the monatomic ideal gas is complete. But as I have already noted here that we need to worry about these two parts q rot and q vib if you are talking about the diatomic ideal gas, and by definition under the rigid rotor simple harmonic approximation we have been able to show that q vib, if I assume the vibrations of the chemical bond connecting the 2 nuclei in my diatomic molecule is associated with an intrinsic angular frequency omega then we can define a temperature which is called theta vib and theta vib is given by h cross omega divided by k B.

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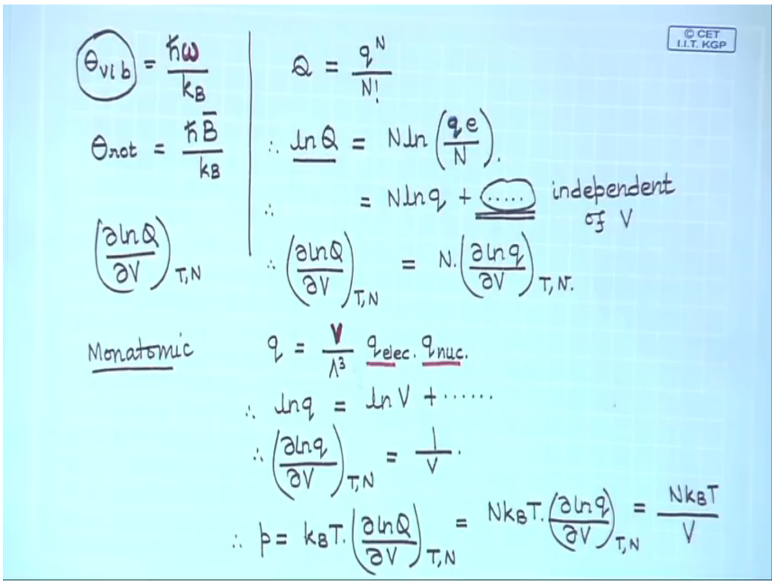

$$\boxed{\theta_{vib}} = \frac{\hbar\omega}{k_B}$$

$$\theta_{rot} = \frac{\hbar\bar{B}}{k_B}$$

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

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

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

$$\therefore \quad = N\ln q + \underline{\underline{\boxed{\cdots\cdots}}} \text{ independent of } V$$

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

Monatomic

$$q = \frac{V}{\Lambda^3}\,\underline{q_{elec}}.\underline{q_{nuc}}.$$

$$\therefore \ln q = \ln V + \cdots\cdots$$

$$\therefore \left(\frac{\partial \ln q}{\partial V}\right)_{T,N} = \frac{1}{V}.$$

$$\therefore p = k_BT.\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} = Nk_BT.\left(\frac{\partial \ln q}{\partial V}\right)_{T,N} = \frac{Nk_BT}{V}$$

So, as you see that omega this is an intrinsic frequency of the bond under consideration. So, this is going to be an typical characteristic property of the system and this is a quantity that I am representing in red; h cross in k B are universal constants therefore, theta vib that vibrational temperature is also a characteristic property of the system that you are looking at of the molecule or atom of the molecule that you looking at. And therefore, q vib it depends on temperature because of the presence of temperature term both in the numerator and in the denominator and theta vib is a characteristic property of the system that you are talking about.

The additional property that we paid a lot of attention to is the rotational single particle partition function. And here theta rot is given by h cross B bar by k B, where B bar is a rotational constant that can be found out from the rotational spectrum of the molecule under consideration. So, this is an once again a characteristic property of the system and there is this term sigma that we have used we have discussed extensively in the last class as a characteristic property which we call a symmetry number and sigma is equal to 1 for heteronuclear diatomic cases and sigma equal to 2 for homonuclear diatomic molecules.

So, now, with all these in picture we can obviously, for a given system if I have information regarding the characteristic properties like theta rot theta vib. And then small m and omega e 1 omega e 2 delta epsilon 12 and omega n 1 depending on whether I have an monatomic case or a diatomic case I am in a position to calculate the small q's and correspondingly I am in a position to calculate capital Q. And this is important because all the microscopic information is now, contained within the N particle canonical partition function capital Q.

So, what do we do next? We have seen within the formulation of statistical mechanics that q is connected to the thermodynamic properties especially in the canonical ensemble the natural law rhythm of q is related to the Helmholtz free energy. So, let us next see or revise what we have learnt regarding this connection.

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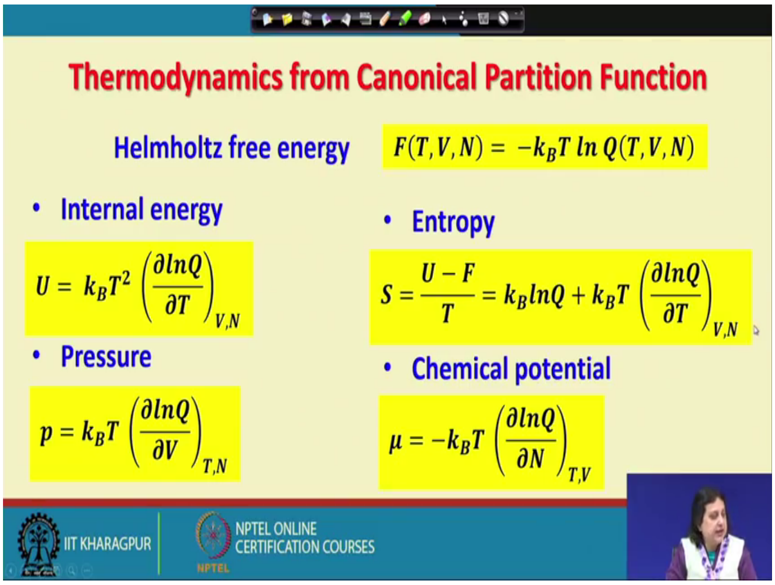

Thermodynamics from Canonical Partition Function

Helmholtz free energy $F(T,V,N) = -k_BT \ln Q(T,V,N)$

- Internal energy

$$U = k_BT^2 \left(\frac{\partial lnQ}{\partial T}\right)_{V,N}$$

- Pressure

$$p = k_BT \left(\frac{\partial lnQ}{\partial V}\right)_{T,N}$$

- Entropy

$$S = \frac{U-F}{T} = k_B lnQ + k_BT \left(\frac{\partial lnQ}{\partial T}\right)_{V,N}$$

- Chemical potential

$$\mu = -k_BT \left(\frac{\partial lnQ}{\partial N}\right)_{T,V}$$

So, we have said that the Helmholtz free energy is nothing, but negative of k T multiplied by natural logarithm of ln natural logarithm of q that is ln Q, T V N. And using this definition we can find out the internal energy, the pressure, the entropy and the chemical potential and we have discussed each of these criteria, each of these equations in our earlier lectures.

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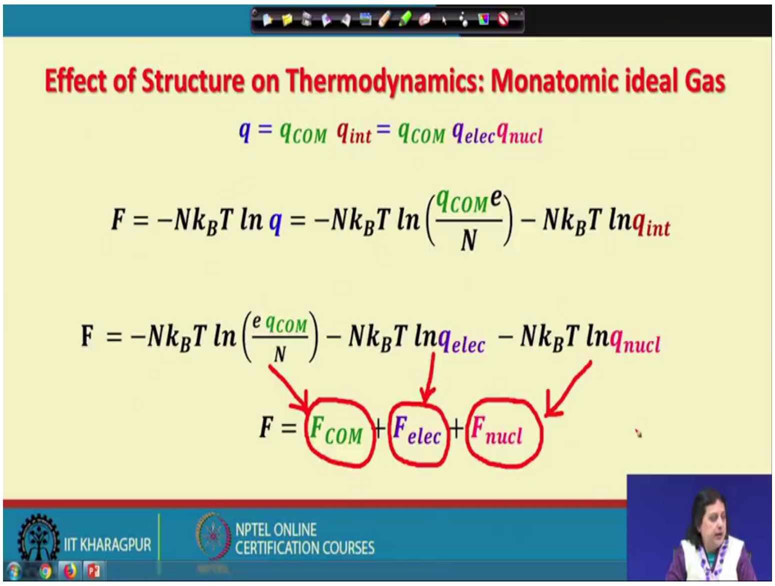

Effect of Structure on Thermodynamics: Monatomic ideal Gas

$$q = q_{COM}\, q_{int} = q_{COM}\, q_{elec} q_{nucl}$$

$$F = -Nk_BT \ln q = -Nk_BT \ln\left(\frac{q_{COM}e}{N}\right) - Nk_BT \ln q_{int}$$

$$F = -Nk_BT \ln\left(\frac{e\, q_{COM}}{N}\right) - Nk_BT \ln q_{elec} - Nk_BT \ln q_{nucl}$$

$$F = F_{COM} + F_{elec} + F_{nucl}$$

And we have also seen that if it is our goal to understand what is going to be the effect of structure on thermodynamics then we found that especially in the case of a monatomic ideal gas that writing small q and partitioning it into two factors corresponding to the contribution of the center of mass and internal structure gives you these two different contributions which further can be factorized into q electronic and q nuclear for the q internal part.

So, what was the consequence of this kind of partitioning? The result of this kind of partitioning was that in F which is related to capital Q which in turn is related to small q can now, be written as contribution of two terms, this is the first term and this is the second term. Now, this first term actually is involving the partition single particle partition function corresponding to the centre of mass and this part is corresponding to the single partition function corresponding to the internal structure of the molecule. So, we can very easily identify that if I write out the contributions to the internal structure therefore, F corresponding to these 3 terms here will have 3 different contributions, one corresponding to q com, one corresponding to q electro electronic and the other corresponding to q nuclear.

Now, in each case I associate one free energy function corresponding to this and in that case what I will be able to do is I should be able to write down a an equation like this so obviously, what I am doing here is I am relating this F the contribution of the center of mass to the overall Helmholtz free energy is nothing, but this factor. Now, there is some contribution of the electronic structure to the overall Helmholtz free energy and that is defined like this. And finally, it may so happen that there will be some contribution to the overall Helmholtz free energy from the underlying nucleus structure which is related to this term.

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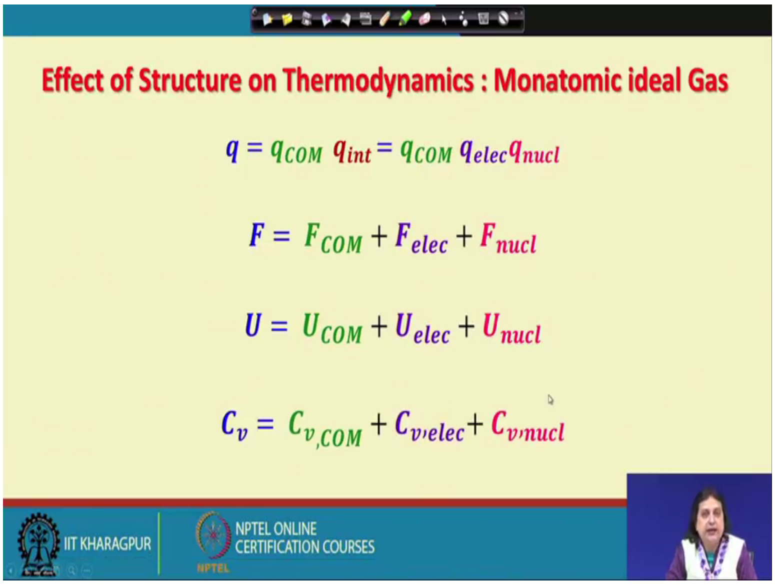

Effect of Structure on Thermodynamics : Monatomic ideal Gas

$$q = q_{COM}\, q_{int} = q_{COM}\, q_{elec} q_{nucl}$$

$$F = F_{COM} + F_{elec} + F_{nucl}$$

$$U = U_{COM} + U_{elec} + U_{nucl}$$

$$C_v = C_{v,COM} + C_{v,elec} + C_{v,nucl}$$

Now, once this happens we understand that this kind of property is not unique to the Helmholtz free energy itself, therefore I can say that using the same type of argument I should be able to partition the total internal energy of the system in terms of 3 different contributions in a monatomic ideal gas. While the first one is the internal energy corresponding to the translational motion of each atom in the system multiplied by capital N the number of atoms. This is the total electronic energy of the N atoms present in the system and this corresponds to the corresponding contribution coming from the nuclear energy states and since U is related to the specific heat and therefore, I should be able to repeat exactly the same kind of partitioning also in studying the property of specific heat and we have already seen that there are 3 different such contributions possible.

And extending this discussion on the effect of structure on thermodynamics we now, consider the diatomic ideal gases and there once again I will remind you that the overall small q, now involves two additional terms q rot and q vib.

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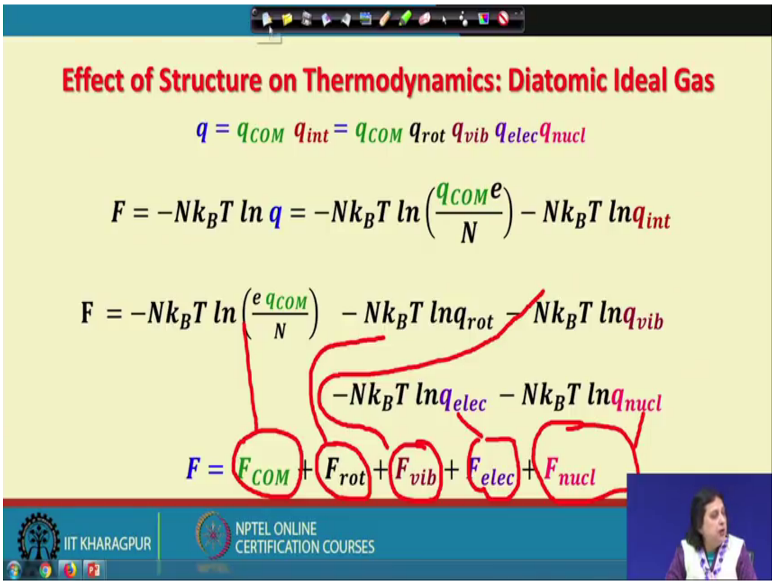

Effect of Structure on Thermodynamics: Diatomic Ideal Gas

$$q = q_{COM}\, q_{int} = q_{COM}\, q_{rot}\, q_{vib}\, q_{elec} q_{nucl}$$

$$F = -Nk_BT \ln q = -Nk_BT \ln\left(\frac{q_{COM}e}{N}\right) - Nk_BT \ln q_{int}$$

$$F = -Nk_BT \ln\left(\frac{e\, q_{COM}}{N}\right) - Nk_BT \ln q_{rot} - Nk_BT \ln q_{vib}$$
$$-Nk_BT \ln q_{elec} - Nk_BT \ln q_{nucl}$$

$$F = F_{COM} + F_{rot} + F_{vib} + F_{elec} + F_{nucl}$$

And these are the two additional terms which will appear in the as some additive terms in the thermodynamic properties like Helmholtz free energy.

So, that is exactly what we see here therefore, what I find is now, the Helmholtz free energy can be written as a sum of one term corresponding to the center translational motion of the center of mass which is this term. That is a term corresponding to the rotational motion of the diatomic molecule which is related to this term. There is one contribution from the vibrational motion which actually corresponds to this term. Now, I have F electronic arising from this term and finally, F nuclear as before arising from this term. So, once again the consequence of having these two additional contributions in the diatomic case is that, now there will be two additional contributions to the overall internal energy and here they are U vib and U electronic.

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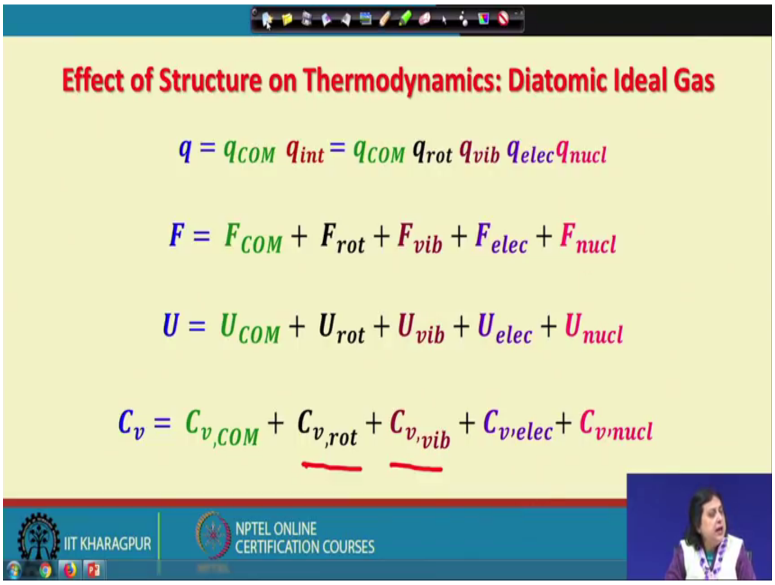

Effect of Structure on Thermodynamics: Diatomic Ideal Gas

$$q = q_{COM}\, q_{int} = q_{COM}\, q_{rot}\, q_{vib}\, q_{elec} q_{nucl}$$

$$F = F_{COM} + F_{rot} + F_{vib} + F_{elec} + F_{nucl}$$

$$U = U_{COM} + U_{rot} + U_{vib} + U_{elec} + U_{nucl}$$

$$C_v = C_{v,COM} + \underline{C_{v,rot}} + \underline{C_{v,vib}} + C_{v,elec} + C_{v,nucl}$$

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And similarly we should be able to see that the C v the overall specific heat of the system are also going to have two additional contributions in terms of C v rot and C v vib.

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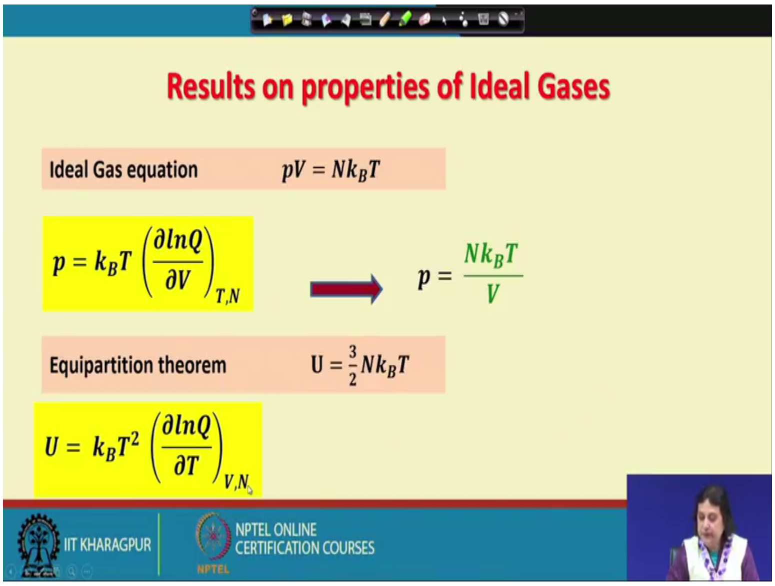

Results on properties of Ideal Gases

Ideal Gas equation $pV = Nk_BT$

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

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

$$U = k_BT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$$

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In the next part of my lecture today what I am going to do is I am going to try and reproduce some of the well known results in the case of an ideal gas. I will show you the expressions for the monatomic ideal gas case and I would urge you to go back and try it out yourself for the diatomic case. So, the first thing that we would like to talk about is the ideal gas equation.

Now, in the ideal gas equation which is a derived from experimental data it is said that if you measure the pressure of a gas at a given volume and at a given temperature for a certain amount of the gas the number of particles is fixed, then the pressure satisfies the pressure resultant pressure of the gas satisfies a functional relationship and that is given by pV is equal to N k T.

Now, once again I have already discussed the derivation of this to you before and I will do so again by looking at the kind of results that we have got for the monatomic ideal gas case and try to see how we can do a little bit of algebra to arrive at this relationship. In order to do this the first thing to realize would be that the pressure is given in terms of k B T del ln Q del V T N. Now, if I go back and write down what capital Q is for an ideal gas that is small q to the power of N divided by N factorial therefore, we could show that ln Q is equal to capital N q small q e by N under sterling's approximation. If I can do this then if I want to find out what is the derivative of this quantity with respect to volume I have to look at the right hand side and try to understand where does the volume appear.

As you see the only term where the volume would appear is small q. So, I would say that ln Q is something like capital N ln small q plus other terms which are independent of volume. Please remember that we are going to take this derivative as del ln Q del V T N. So, we are going to dump here all the terms that depend on N that depends on T, but does not depend on the volume. Now, if I do this then what is del ln Q del V T N? Once I have fixed T and N this whatever terms appear here they are independent of V and they do not affect what I the way I take a derivative here and there because for my mathematical purpose whatever terms are there these are constants therefore, I can write this as capital N del ln small q del V T N.

Now, for a monatomic ideal gas we have been able to show that small q is equal to V by lambda cube into q electronic and q nuclear. Now, where does the dependence on V appear? The dependence on V appears through this explicit appearance of capital V, as a result I would say that if I assume that q electronic and q nuclear these are constant terms with respect to volumes in that case I can write down ln q that is equal to ln V plus other terms that I need not be bothered about and therefore, what is del ln q? Del V del ln q del V keeping T and N constant. Now, turns out to be 1 by V. Therefore, I can go back and look the definition of pressure, pressure is equal to k B T del ln Q del V keeping temperature and number of particles constant that is equal to Nk B T into del ln small q by del V TN and I find that this is nothing, but Nk B T divided by V.

So, we have been able to show that if I use this definition of p in that case it is straightforward to find that the major contribution to pressure comes from the translational part because in q trans you had a direct dependence on V, and that is what is giving you this kind of a term that is nothing, but the ideal gas equation. Please remember while deriving this we have assumed that these terms are independent of the volume this is more or less a reasonable approximation for the kind of temperatures, normal temperatures that we talk about. Now, let us next go ahead and try to see if from the formalism that we have derived over here if we can show the equipartition theorem, whether equipartition theorem is important the importance of equal partition theorem from the theoretical formalism that we have proposed here. So, the equipartition theorem tells you that the internal energy of the system is 3 by 2 Nk T at a given temperature T or in other words in as proposed by Joules law the internal energy of an ideal gas is a function of temperature and temperature only.

Now, let us try and see if we can at all reproduce this property from our formulation.

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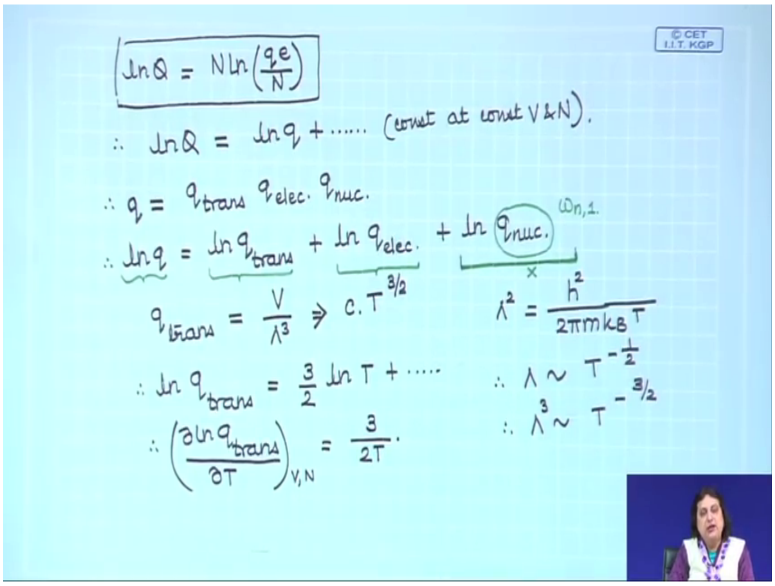

$$\boxed{\ln Q = N \ln\left(\frac{qe}{N}\right)}$$

$$\therefore \ln Q = \ln q + \ldots\ldots \text{ (const at const } V \,\&\, N\text{)}.$$

$$\therefore q = q_{trans}\, q_{elec.}\, q_{nuc.}$$

$$\therefore \underbrace{\ln q} = \underbrace{\ln q_{trans}} + \underbrace{\ln q_{elec.}} + \underbrace{\ln \boxed{q_{nuc.}}}_{\times} \quad \omega_{n,1}.$$

$$q_{trans} = \frac{V}{\Lambda^3} \Rightarrow c.\,T^{3/2} \qquad \Lambda^2 = \frac{h^2}{2\pi m k_B T}$$

$$\therefore \ln q_{trans} = \frac{3}{2}\ln T + \ldots\ldots \qquad \therefore \Lambda \sim T^{-\frac{1}{2}}$$

$$\therefore \Lambda^3 \sim T^{-3/2}$$

$$\therefore \left(\frac{\partial \ln q_{trans}}{\partial T}\right)_{V,N} = \frac{3}{2T}.$$

So, for this purpose once again. I am going to use the result that ln capital Q is equal to capital N ln small qe by N. And what is U? U is given by this expression that is k B T square into del ln q del T V N. So, I need to understand what is the derivative of ln Q with respect to temperature keeping volume and number of particles constant and once I know this derivative I will multiply it with k B T square and the result will give me the internal energy.

Now, when I look back at this particular expression that I have written down for ln Q, I understand that shear I need to find out the temperature dependent part that and the rest of the part should remain constant at a given N and V. So, here I can write down that ln Q is dependent on ln small q plus some other terms which are constant at constant volume and number of particles. Now, let us have a look at what small q is therefore, small q we know that this is equal to q trans into q electronic into q nuclear therefore, small ln q that will have additive contributions from these 3 terms because it is the log quantity that I am looking at q nuclear.

Now, in this expression can I find out where the temperature dependent terms come? I already know that q nuclear is nothing, but the degeneracy of the ground nuclear energy state which is a constant for a given system. Therefore, if I keep the volume and the number of particles constant in that case this term is not going to have any dependence on temperature therefore, if I am looking at the temperature dependence of this quantity I should be bothered about temperature dependence of this quantity and this quantity and I can safely neglect this part. Now, if I looked at what the expression for q trans is that is V by lambda cube right and this I can write that this is sum constant if I use the expression for lambda I know that lambda squared is equal to h square divided by 2 pi m k T.

So, what is lambda? Lambda goes as T to the power of minus half therefore, lambda cubed should go as T to the power of minus 3 by 2. As a result I would say under the condition of constant temperature and pressure a constant volume and number of particles I can have this as written as something into T to the power of 3 by 2. Therefore, ln q trans that will be written as 3 by 2 ln T plus certain other terms which are constant at constant volume and number of particles and therefore, del ln q trans del T keeping volume and number of particles constant that is going to give you 3 by 2 T.

In the next part of my lecture I am going to use the kind of results to express what will be the contribution of the overall translational motion to the internal energy of the system.

Thank you.