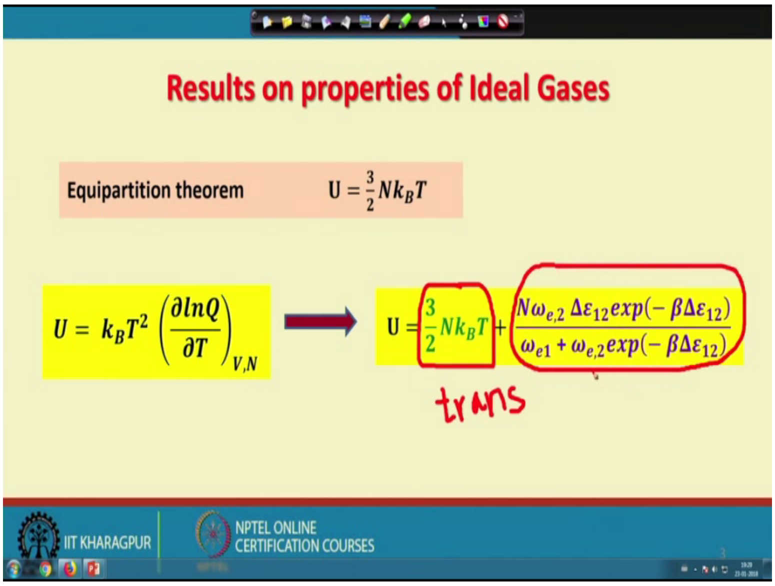
Introduction to Molecular Thermodynamics

Prof. Srabani Taraphder
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture – 28
Statistical Thermodynamics of Ideal Gases (Contd.)

Welcome back, we shall continue our discussion, on how we can use the framework of statistical thermodynamics, to understand the how we can correlate the contribution of underlying translational motion and internal structure in the case of an ideal gas, and we have already seen here that how we can write down the ideal gas equation starting from the hamiltonian of the system, and here the basic exercise that we are performing is how to calculate the canonical partition function for this N particle system, and from there we are using the prescription of connecting capital Q that is a canonical partition function to the overall Helmholtz free energy of the system, when the ideal gas is being maintained at a constant temperature volume and a number of particles.

(Refer Slide Time: 01:18)



Results on properties of Ideal Gases

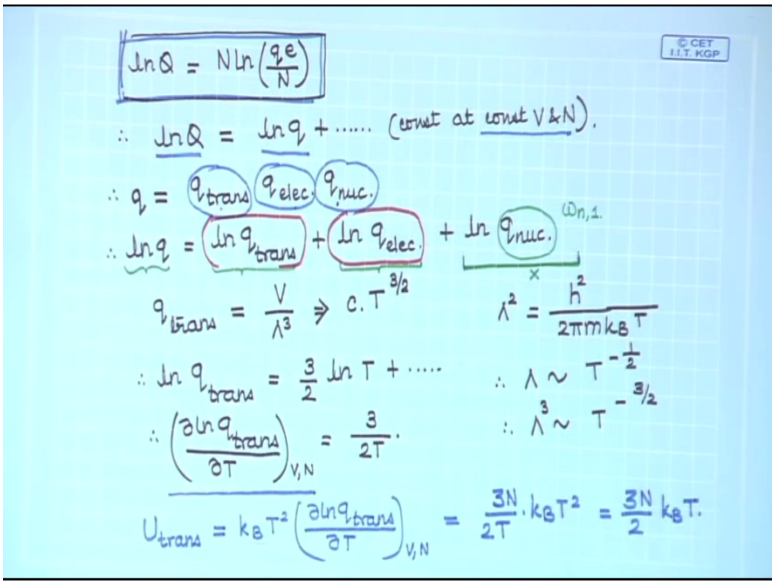
Equipartition theorem $U = \frac{3}{2} N k_B T$

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} \rightarrow U = \boxed{\frac{3}{2} N k_B T} + \boxed{\frac{N\omega_{e,2}\,\Delta\varepsilon_{12}\exp(-\beta\Delta\varepsilon_{12})}{\omega_{e1} + \omega_{e,2}\exp(-\beta\Delta\varepsilon_{12})}}$$

trans

The next property that we are going to look at is the internal energy, which from the equipartition theorem is known to be given by this expression, and that is nothing but the joules law, which says that for an ideal gas the internal energy is a function of temperature and temperature only, and for this purpose we have already started to look at how to obtain the internal energy, starting from the canonical partition function q.

(Refer Slide Time: 01:49)



© CET I.I.T. KGP

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

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

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

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

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

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

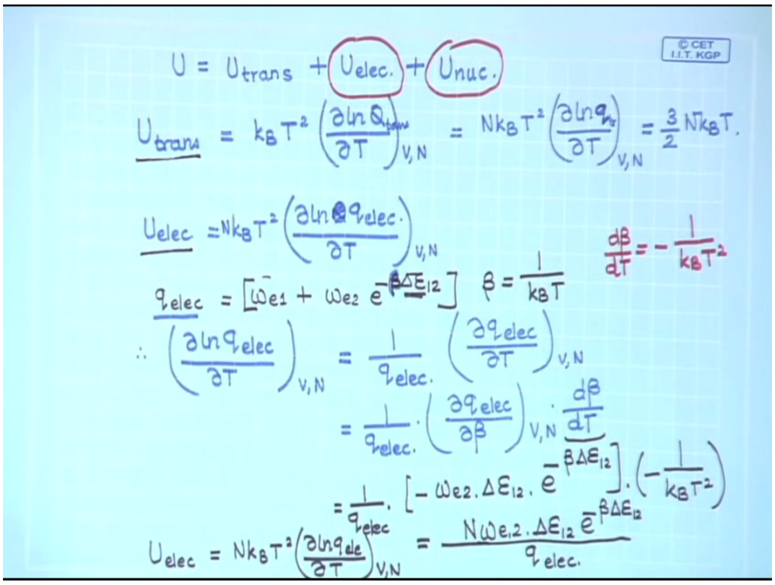
$$\therefore \left(\frac{\partial \ln q_{trans}}{\partial T}\right)_{V,N} = \frac{3}{2T}. \qquad \therefore \Lambda^3 \sim T^{-3/2}$$

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

And here we have seen that l and q is related to small q, and at constant volume and number of particles the dependence of l n q on temperature arises entirely because of l n small q, and then we started looking at the different contributions of different degrees of freedom to overall small q, q trans, q electronic and q nuclear.

Therefore under the condition of constant volume and number of particles, we understand that any dependence on temperature of this l n small q, will come either from this or from this term, and then we set out by writing the explicit expression for q trans, and found out that del l n q trans del T under the condition of constant volume and number of particles is 3 by 2T, now we will now go ahead and try and find out what is the corresponding contribution to the overall internal energy, now U trans is given by k B T square, into del l n q trans by del t, under in the condition of constant volume and number of particles and therefore, what I will write is this is nothing but 3 by 2 T into k B T squared and of course, I have a capital N from in front. So, that turns out to be 3 n by 2 k B t.

(Refer Slide Time: 03:53)



$$U = U_{trans} + \boxed{U_{elec.}} + \boxed{U_{nuc.}}$$

$$\underline{U_{trans}} = k_B T^2 \left(\frac{\partial \ln Q_{trans}}{\partial T}\right)_{V,N} = N k_B T^2 \left(\frac{\partial \ln q_{tr}}{\partial T}\right)_{V,N} = \frac{3}{2} N k_B T.$$

$$\underline{U_{elec}} = N k_B T^2 \left(\frac{\partial \ln q_{elec.}}{\partial T}\right)_{V,N} \qquad \frac{d\beta}{dT} = -\frac{1}{k_B T^2}$$

$$\underline{q_{elec}} = \left[\omega_{e1} + \omega_{e2}\, e^{-\beta \Delta \varepsilon_{12}}\right] \qquad \beta = \frac{1}{k_B T}$$

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

$$= \frac{1}{q_{elec.}} \cdot \left(\frac{\partial q_{elec}}{\partial \beta}\right)_{V,N} \cdot \underline{\frac{d\beta}{dT}}$$

$$= \frac{1}{q_{elec}} \cdot \left[-\omega_{e2} . \Delta\varepsilon_{12} . e^{-\beta \Delta \varepsilon_{12}}\right] . \left(-\frac{1}{k_B T^2}\right)$$

$$U_{elec} = N k_B T^2 \left(\frac{\partial \ln q_{ele}}{\partial T}\right)_{V,N} = \frac{N \omega_{e,2} . \Delta\varepsilon_{12}\, e^{-\beta \Delta \varepsilon_{12}}}{q_{elec.}}$$

So now what I have here is this interesting observation that in my overall u, I have contribution from U trans plus U electronic and also if possible U nuclear. So, what is U trans? U trans is given by k B T square del l n capital q, by del T under constant volume and number of particles right, and I show that this is nothing but N k B T square into del l n small q del T V N, and I have been able to show using the explicit temperature dependence of this small q term, here because of translation. So, this is trans this is also q trans, and what I find is that this is 3 by 2 in k B t. So, this is a result that we get from the equipartition theorem, but we also have some term other terms appearing here.

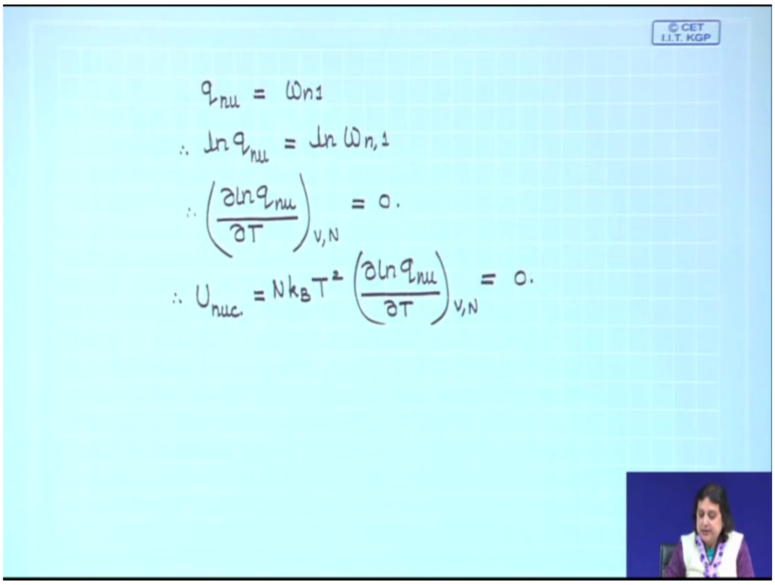
So, let us look at individually what this terms are and we find that U electronic, that is now being given by k B T square del l n capital Q or small q electronic, del T taking this derivative of constant volume and number of particles with a capital N in front, and in order to understand this what I should be doing is I should be writing down what small q electronic is, that we already know is w E 1 plus w E 2 into E to the power of minus beta delta epsilon 1 2, therefore, if I take l n of this term, I will be taking l n of this entire summation, then I am going to look at the temperature dependence of the logarithm of q electronic now why should this term be dependent on q electronic and that is because; obviously, I have this factor beta here, where did I get this number from? This number we have obtained from the solution of the Schrodinger equation, and the solution has been obtained for an isolated system for 0 kelvin temperature.

So, that part is not temperature dependent, but explicitly the appearance of the term beta, which is 1 by k T that governs the temperature dependent property of q electronic and therefore, I can say that del l n q electronic del T if I take this derivative under the condition of constant volume and number of particles that is equal to 1 by q electronic into del q electronic del t, under constant volume and number of particles right, but as you see q electronic is a function of beta. So, for the sake of doing the algebra, it is found that it is easy to write it as del q electronic del beta under the condition of constant volume and number of particles into d beta d t, right now what is the beta d T we already know that beta is 1 by k t. So, I must be having d beta d T as minus 1 by k B T square right, and now what is del q electronic del beta that can be easily figured out from this expression

So, if I put this back what I have is, 1 by q electronic multiplied by the del, del beta of this term the first term is independent of beta. So, that drops out and I have contribution from the second term, and the contribution is minus omega E 2 into delta E 1 2 into exponential minus beta delta epsilon 1 2, right and then I have a multiplication again coming from this term and that is minus 1 by k B T square. So, what does it give me, this gives me that U electronic that is equal to N k B T square, into del l n q electronic del T keeping volume and number of particles constant, that would be given by 1 by n omega E 2, then delta epsilon 1 2 e to the power of minus beta delta epsilon one 2 into q electronic right.

So, we have been able to show what U transes and what U electronic is, now think about what is q nuclear.

(Refer Slide Time: 09:44)



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

$$\therefore \ln q_{nu} = \ln \omega_{n,1}$$

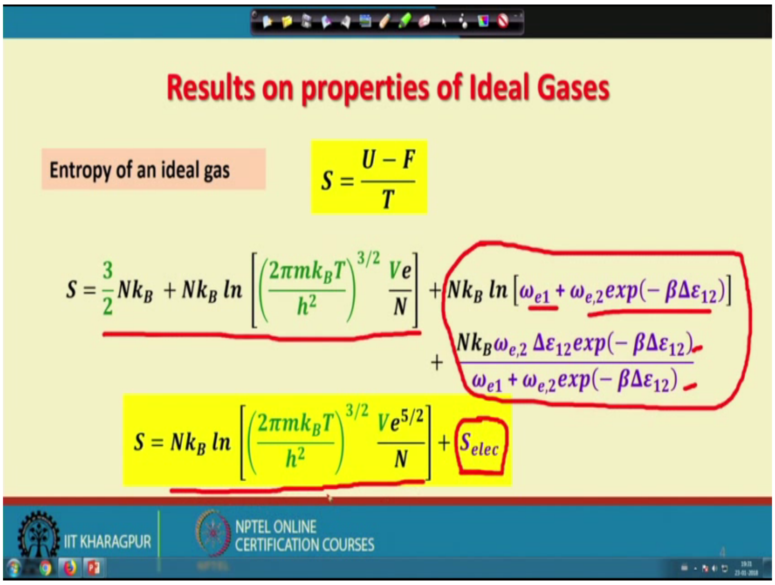
$$\therefore \left(\frac{\partial \ln q_{nu}}{\partial T}\right)_{V,N} = 0.$$

$$\therefore U_{nuc.} = N k_B T^2 \left(\frac{\partial \ln q_{nu}}{\partial T}\right)_{V,N} = 0.$$

So, once again q nuclear in this case is a constant term therefore, l n q nuclear is a logarithm of this constant term therefore, del l n q nuclear by del T under constant volume of number of particles that is going to be equal to 0 therefore, I can say that U nuclear here by assuming as a 0 of energy the ground nuclear energy state, I understand that there will be no contribution to the overall internal energy as measured in the by setting the ground nuclear energy state to be equal to 0. So, this would be given by capital N k B T square del l n q nuclear del T V N and this is 0. So, what is the net internal energy of the system then, the net internal energy of the system now is been given by an expression like this.

Now, this is something very, very interesting because as we see that in this expression, I have first this green term that appears corresponding to q trans. So, that is the contribution of the translational motion of the particles in the system of the capital N atoms in the system, and there is another term over here that is proportional to capital n. So, for each particle I have this term appearing in over here, and this term is the correction to this equipartition value that appears because of the presence of a microscopic structure of the constituent atoms of the ideal gas. So, what we find here is we not only reproduce the equipartition theorem, but also, we find out the correction that will be introduced as a result of the existence of the underlying microscopic structure of the atoms.

(Refer Slide Time: 12:11)



Results on properties of Ideal Gases

Entropy of an ideal gas

$$S = \frac{U - F}{T}$$

$$\underline{S = \frac{3}{2}Nk_B + Nk_B\, ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{Ve}{N}\right]} + Nk_B\, ln\left[\omega_{e1} + \omega_{e,2}exp(-\beta\Delta\varepsilon_{12})\right] + \frac{Nk_B\omega_{e,2}\,\Delta\varepsilon_{12}exp(-\beta\Delta\varepsilon_{12})}{\omega_{e1} + \omega_{e,2}exp(-\beta\Delta\varepsilon_{12})}$$

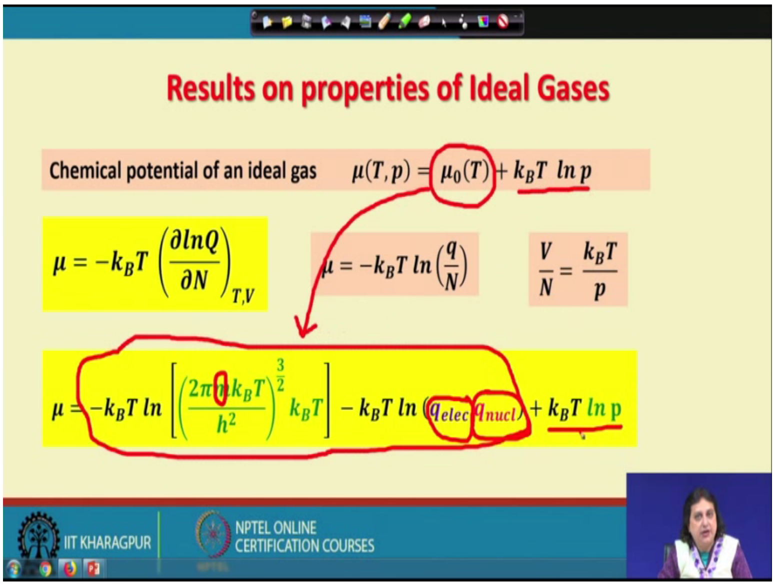
$$S = \underline{Nk_B\, ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{Ve^{5/2}}{N}\right]} + \boxed{S_{elec}}$$

The next thing that I will quickly go through is the entropy of an ideal gas, now the entropy of an ideal gas can now be determined very easily by looking by knowing the fact that I know U in terms of l n q from l n q I know F from l n q. So, if I take the difference and divide it by t, I should be getting the entropy S by definition when you do this little bit of algebra this is the expression that you get. So, what I have done is I have used the expression for U that I have derived over here I have use expression of f, and then taken the difference and this is what I write and I am going to collect some of the numbers separately and give you the final expression as this.

So, let us have a look at what these different terms are, I have taken this 3 by 2 n k B inside. And so, these 2 terms combine together to give me the first storm that I see here, and these 2 terms that appear here, they combined together to give me what I call is the S electronic or the electronic contribution to the overall entropy of the system, now why do I say. So, if we look at what S electronic is, we see that all the terms here which appeared here which have been shown in the purple color, these are dependent on the electronic structure of the underlying atom, as a result we would say that the contribution of the electronic structure is coming through these terms, and this is defined as S electronic.

Now, what is it that I have here; obviously, all the terms that I see here are coming from the overall translational motion of the atom as a whole within the volume V at a temperature t, and that is the contribution of this translational motion to the overall entropy of the system for n such atoms, and this equation is known as the sackur tetrode equation, and we will look have a look at the specific use of the sackur tetrode equation especially to understand what is known as Gibbs paradox, but that we will do later, at this point let me also try to reproduce another property of the ideal gas which we have repeatedly seen in our earlier exposure to the ideal gases, that is a chemical potential of an ideal gas.

(Refer Slide Time: 15:08)



Results on properties of Ideal Gases

Chemical potential of an ideal gas $\mu(T,p) = \mu_0(T) + k_BT\ \ln p$

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

$$\mu = -k_BT\ \ln\left(\frac{q}{N}\right)$$

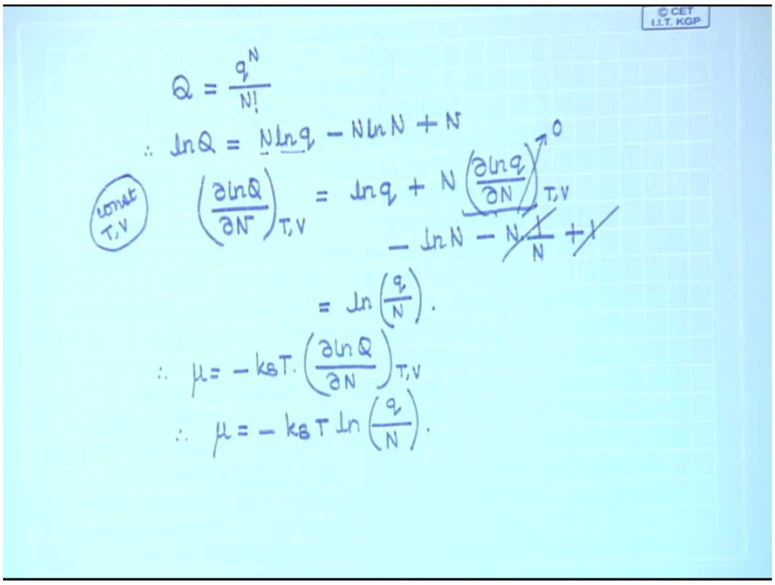
$$\frac{V}{N} = \frac{k_BT}{p}$$

$$\mu = -k_BT\ \ln\left[\left(\frac{2\pi m k_BT}{h^2}\right)^{\frac{3}{2}} k_BT\right] - k_BT\ \ln\left(q_{elec}\, q_{nucl}\right) + k_BT\ \ln p$$

So, your preliminary studies on thermodynamics must have included this expression, where you see that mu the chemical potential is a function of temperature and pressure in general, and in the case of an ideal gas this can be written as mu naught T that is the chemical potential of the gas at a temperature t, under standard conditions of standard pressure one bar plus an incremental part which is k B T l n p. So, if the gas is present at a temperature T and volume and pressure p, in that case I should be able to separate out the entire chemical potential into 2 terms, one is what that is dependent on temperature only and it is a fixed value under standard condition of 1 bar pressure, and there is an additional term which depends on the temperature and the pressure condition under which the gas is present, and the question that I asked over here is as follows, is it possible for me to start from the expression of capital Q and small q that I have used here, and explain why an ideal gas should be having a chemical potential that the whose expression separates out into two terms like this.

So, what is mu naught T in order to answer that question, what we are going to do is once again we are going to use the definition of mu. So, what is the definition of mu? The definition of mu is this is related to a derivative of l n q with respect to capital N keeping temperature and volume constant in the canonical ensemble, and then you multiply it with minus k t, and this is what you get as a chemical potential of a single component ideal gas which is maintained at a constant temperature and volume, now if I want to evaluate this for the ideal gas.

(Refer Slide Time: 17:12)



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

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

const T,V

$$\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V} = \ln q + N \cancel{\left(\frac{\partial \ln q}{\partial N}\right)_{T,V}}^{\,0} - \ln N - \cancel{N \frac{1}{N}} + \cancel{1}$$

$$= \ln\left(\frac{q}{N}\right).$$

$$\therefore \mu = -k_B T \cdot \left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}$$

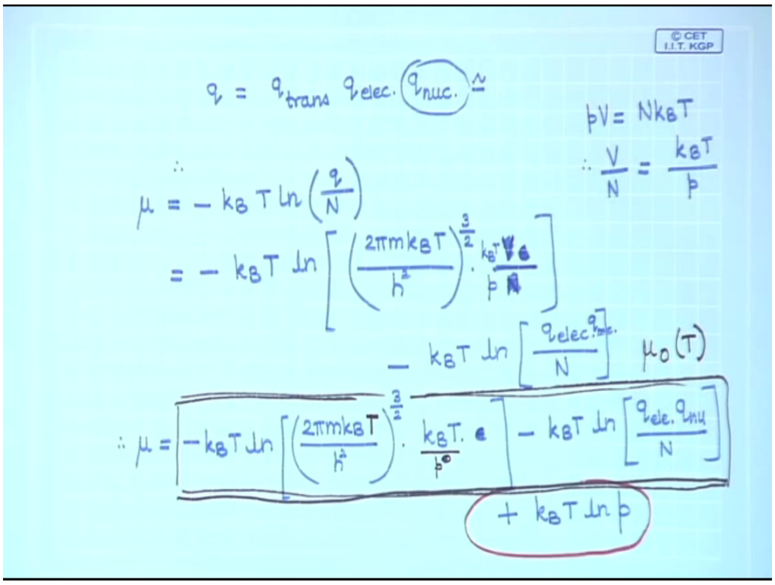
$$\therefore \mu = -k_B T \ln\left(\frac{q}{N}\right).$$

I once again I write down that capital Q is equal to small q to the power of n divided by n factorial. So, what is l n q that is the quantity that I require.

So, this can be written as capital L n q minus N l n N plus N, now under the condition of constant temperature and volume, I am going to find out what del l n q del N is. So, I am looking for this particular derivative, and this would be given by the following condition, that I can write down that this is given by l n q plus N del l n q del N TV minus l n N minus N into 1 by N plus 1. So, what I have done is in the first term I kept N constant I took a derivative with respect 2 n keeping this constant. So, this is what I get, then I kept n constant took a derivative of this with respect to capital N then I took the derivative of these terms and this is what I get.

So, the result is del L n q del N TV, that is equal to l n these terms cancel out. And so, you all you have is this is equal to small q by N, if that is. So, then, what is mu? Mu is given by minus k B t, del l n q del N T V and therefore, I can use this result and say that mu is equal to minus k B T l n small q by N right. So, it is possible for me to write down that expression that mu is equal to minus k t, then natural logarithm of q by n now please remember that in this expression, I have assumed that this is 0; obviously, small q it is written for one particle and it is independent of capital n. So, that is a reason why I have been able to write it as 0, the next thing that I will do here is as follows I am going to write down once again the explicit expression for small q.

(Refer Slide Time: 20:10)



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

$$pV = Nk_BT$$

$$\therefore \frac{V}{N} = \frac{k_BT}{p}$$

$$\therefore \mu = -k_BT \ln\left(\frac{q}{N}\right)$$

$$= -k_BT \ln\left[\left(\frac{2\pi m k_BT}{h^2}\right)^{\frac{3}{2}} \cdot \frac{k_BT\, e}{p}\right]$$

$$- k_BT \ln\left[\frac{q_{elec}\, q_{nuc.}}{N}\right] \qquad \mu_0(T)$$

$$\therefore \mu = \boxed{-k_BT \ln\left[\left(\frac{2\pi m k_BT}{h^2}\right)^{\frac{3}{2}} \cdot \frac{k_BT \cdot e}{p^{\circ}}\right] - k_BT \ln\left[\frac{q_{ele.}\, q_{nu}}{N}\right]}$$

$$\boxed{+ k_BT \ln p}$$

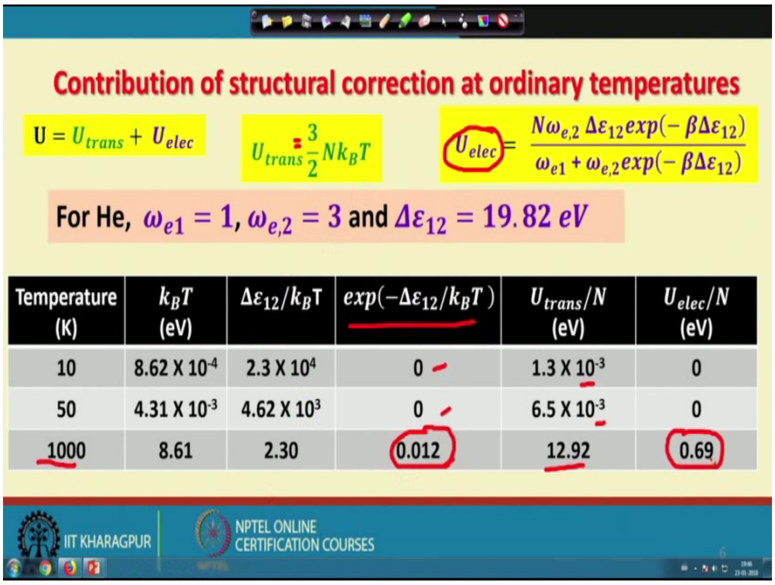
So, small q is equal to something like q trans far monatomic gas, q trans, q electronic and q nuclear, now q nuclear is a constant term therefore, for the purpose of for our purpose we can neglect that. So, I am going to neglect it as a constant term therefore, I should be able to write mu as minus k B T l n small q by capital N and the resulting expression is small q is 2 pi m k B T by h square whole to the power of 3 by 2 into V E by capital n, right and then I have minus k B T l n q electronic by capital N this term. So, this is a translational part, this is the this is the electronic part, may be for the sake of clarity I can retain the q nuclear there no harm done.

Now, please let us try and have a look at what are the terms that we have here, I know that V by N this must be having certain relationship as far as the ideal gas is concerned, I know that p V is equal to capital N k B T therefore, under the condition where here I can write that V divided by N must be equal to k B T by p right. So, what I do is instead of V by n, I will write this as k B T by p, now what I do is I take out this pressure dependent term. So now, mu is written as minus k B T l n 2 pi m k T by h square to the power of 3 by 2 into k B T into e, and then sorry this E will not be there because I am writing small q, and then minus k B T l n q electronic into q nuclear by n, then plus k B T l n p, because I had p here in the denominator there was a negative sign here so, that gives me plus k B T l n p.

Now let us have a look at the 2 types of terms that we have obtained here, I have some term over here plus I have some other term which has appeared as an additional correction to it. So, this term is the k B T l n p that we expect to have some moderate moderation on the value of mu over and above what we see here, now whatever appears within this square box that is dependent on temperature, and as you see that this I could have written as k B T by p naught, where p naught is equal to one bar and in that case this is nothing but mu naught T as defined in the literature, and therefore, what we have been able to do is using the relationship between volume and pressure and the N and T we have been able to show that well my mu is going to be comprised of 2 terms, the first term is essentially dependent on temperature and the intrinsic properties of the system like m q electronic and q nuclear, and what I am left with is this term k B T l n p, which basically tells me what mu naught T is this is nothing but whatever appears here and we obtain this k B T l n p as an additional term. So, what we have learned from here is as follows.

So, using the formalism of statistical thermodynamics or molecule a thermodynamics, we find that each and every thermodynamic function has a correction to it, that appears from the underlying microscopic structure and this correction occurs over and above a term that is coming from the contribution, of a structuralist particle that is the basic constituent of my system.

(Refer Slide Time: 25:46)



Contribution of structural correction at ordinary temperatures

$U = U_{trans} + U_{elec}$

$U_{trans} = \frac{3}{2} N k_B T$

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

For He, $\omega_{e1} = 1, \omega_{e,2} = 3$ and $\Delta\varepsilon_{12} = 19.82\ eV$

Temperature (K)	$k_B T$ (eV)	$\Delta\varepsilon_{12}/k_B T$	$exp(-\Delta\varepsilon_{12}/k_B T)$	U_{trans}/N (eV)	U_{elec}/N (eV)
10	8.62×10^{-4}	2.3×10^{4}	0	1.3×10^{-3}	0
50	4.31×10^{-3}	4.62×10^{3}	0	6.5×10^{-3}	0
1000	8.61	2.30	0.012	12.92	0.69

So, is this correction important. So, in order to understand that let us take this example, where we under try to understand the importance of the structural correction to the internal energy in the case of a monatomic ideal gas, where we know that U trans is nothing but 3 by 2 n k T and U electronic is dependent on the underlying microscopic structure of the atom. Now let us consider this example where we have helium atoms. So, for helium gas the constituent particle is a helium atom for which spectroscopy is tell you that it has a singly degenerate ground electronic state, and a triply degenerate first excited electronic state, and the difference between the ground and the first excited electronic states is given by around 20 electron volt.

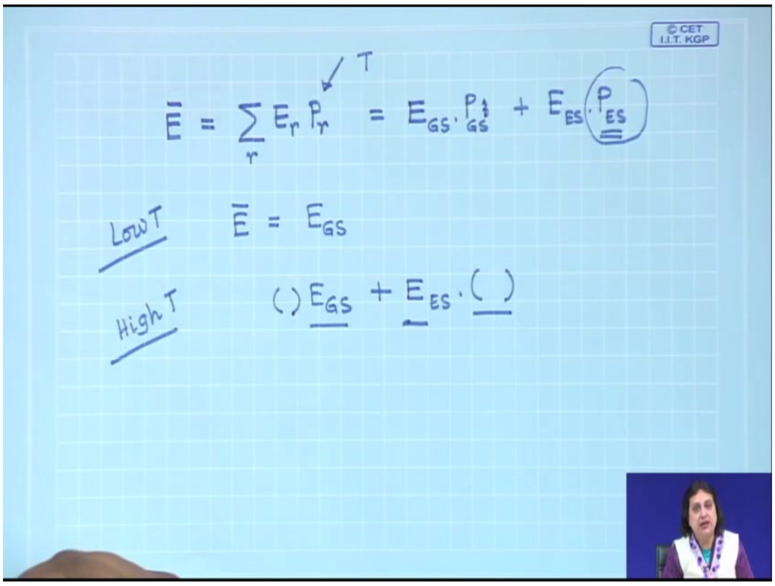
Now, then what we can do is we can do a little bit of calculations, and this calculations are as follows we look at 3 different temperatures 10 kelvin 50 kelvin and 1000 kelvin, and then we know what is the amount of thermal energy k T at each of these temperatures, and we find that delta E delta epsilon 1 2 by k T this quantity is actually a large number at 10 kelvin, even it still remains large even at 50 kelvin, but it becomes a finite number at thousand kelvin. So, what is the consequence of this, the consequence of this is that this exponential term as written out here, these are virtually 0 at the temperatures low temperatures of 10 to 50 kelvin and this is about 10 to the power of minus 2 at 1000 Kelvin.

So, what is the consequence of having this small yet finite value of this term x this exponential term to the contributions that we see here. So, if I find out you trans then I find that at 10 kelvin you transes about 10 to the power minus 3 electron, volt and then if I go to 50 kelvin it remains in the same range it is just that this pre factor changes, but essentially just because these exponential terms are essentially 0 therefore, the contribution to U electronic by n, this is going to be 0, now when I come to 1000 kelvin what happens is U trans is now about 13 electron volt, but as you see that there is some small, but finite correction coming from the underlying electronic structure, which is about point 7 electron volt.

So, what is it that we have learnt from these numbers these numbers tell me that well at low temperatures the microscopic states, that are being accessed by the system at essentially the ground electronic state of the atom, and the ground nuclear energy state of the atom and then whatever translational motion it executes at those temperatures, that is what uses up the corresponds to the total internal energy of the system in the case of a monatomic ideal gas.

Now, as you go on increasing the temperature of the system, what happens is now at much higher temperature the population of the first excited electronic state becomes appreciable, now what is U, U is the average energy of the system.

(Refer Slide Time: 29:40)



$$\bar{E} = \sum_r E_r \overset{\swarrow T}{P_r} = E_{GS} \cdot P_{GS} + E_{ES} \cdot \boxed{\underline{\underline{P_{ES}}}}$$

Low T $\quad \bar{E} = E_{GS}$

High T $\quad (\;)\, \underline{E_{GS}} + \underline{E}_{ES} \cdot \underline{(\;)}$

Now, average energy is nothing but given by the energy of the r th state multiplied by the probability of the r th state, and we know that this probability is dependent on temperature, at low temperature this probability is very, very small and therefore, E bar is approximately. So, if I can write this as this is E electronic energy ground state into, probability of observing the system in the ground state plus E first excited state into probability of observing it in the first excited state at low temperature, this probability is very, very small as a result this is dominated by the ground state energy, but at very high temperature what happens is the probability of occupation of the first excited electronic state increases, as a result then in addition to the ground state energy we have some energy values coming up from the first excited state, multiplied by some number which tells me the fraction of population present in the first excited state.

So, this will be the fraction of population in the ground state multiplied by the ground state energy plus, a fraction of the population in the excited state corresponding to the and multiplied by the for first excited electronic energy, as a result you start seeing the correction terms appearing in the in terms of the internal energy. So, we have now achieved quite a lot and what we will do is we in the last lecture for the ideal gases, we will talk about testing what we have obtained, will use the sackur tetrode equation and see if we have preserved the extensive property of entropy, and will also check for the extensive property of quantities like internal energy and so on and so, forth and that will be the end of our discussion on monatomic ideal gases, and we will extend these concepts to check for the correctness of the formalism for diatomic ideal gases.

Thank you.