Introduction to Molecular Thermodynamics
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Lecture - 29
Statistical Thermodynamics of Ideal Gases (Contd.)

Welcome in today's class, we will revise and summarize what all we have learnt about the statistical thermodynamics of ideal gases, where as you have seen, that we are mainly focusing on gases which are comprised of atoms, such as helium or argon or diatomic molecules, such as carbon monoxide, nitric oxide, HCl or HBr which can be classified as Heteronuclear diatomic molecules, or gases like hydrogen, deuterium, oxygen etc, which can be clubbed under the common name of Homonuclear diatomic molecules.

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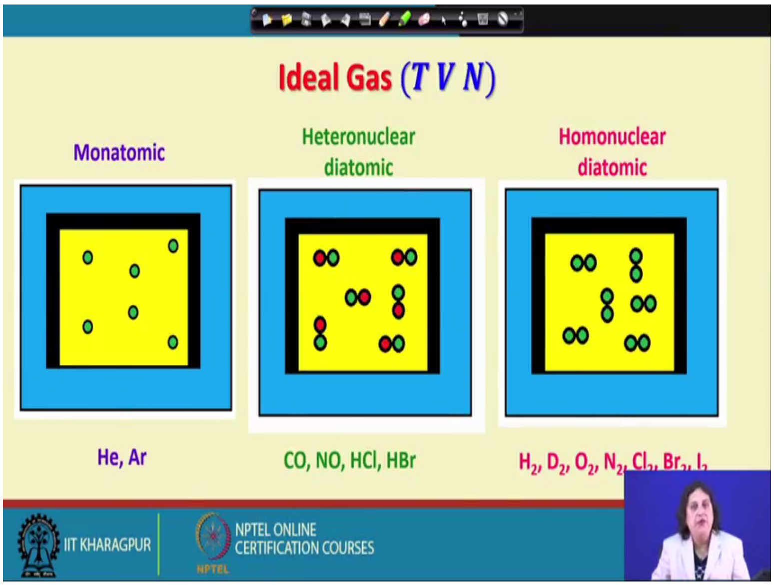

Ideal Gas $(T\ V\ N)$

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

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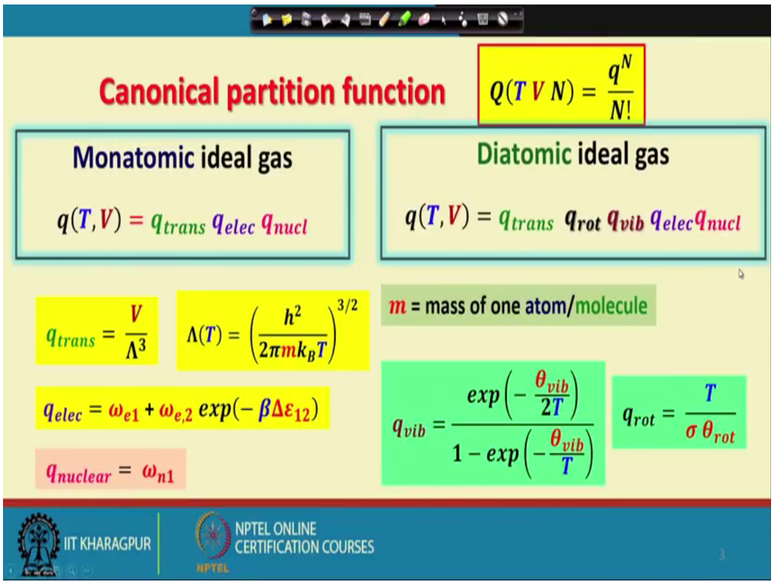

Canonical partition function

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

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 that, the microscopic information regarding any of these systems is actually collected and contained in what is known as the canonical partition function?

So, what is this canonical partition function? If you maintain the ideal gas at a given temperature volume and with a constant number of particles either atoms or molecules, in that case if you start from the Hamiltonian of the system, you can write down all informations regarding the underlying accessible microscopic states, along with their associated probabilities in the form of this canonical partition function and as shown here, this is what the expression for this canonical partition function is;

So, as you see in addition to depending on this capital N the number of particles it depends on the small q, that is the single particle partition function and we know that for monatomic ideal gases small q will derive contributions from the overall translational motion of the atom, and the underlying electronic and nuclear structure for a monatomic ideal gas whereas, if you have a diatomic ideal gas then 2 additional terms will come into the picture, which are due to the rotation of the molecule about an axis and also the vibration of the chemical bond, that is connecting the 2 atoms that are constituting the molecule of the gas.

And we have discussed in detail like, how we can calculate each of these quantities given the situation and in general we know that, if we know the thermodynamic quantities like

V T and the number of particles, in that case we are able to find out q trans q electronic q nuclear provided you have information regarding the microscopic structure in terms of the underlying energy states of the electronic and nuclear nature, and also the transition energy between the first and the ground and the first excited electronic state.

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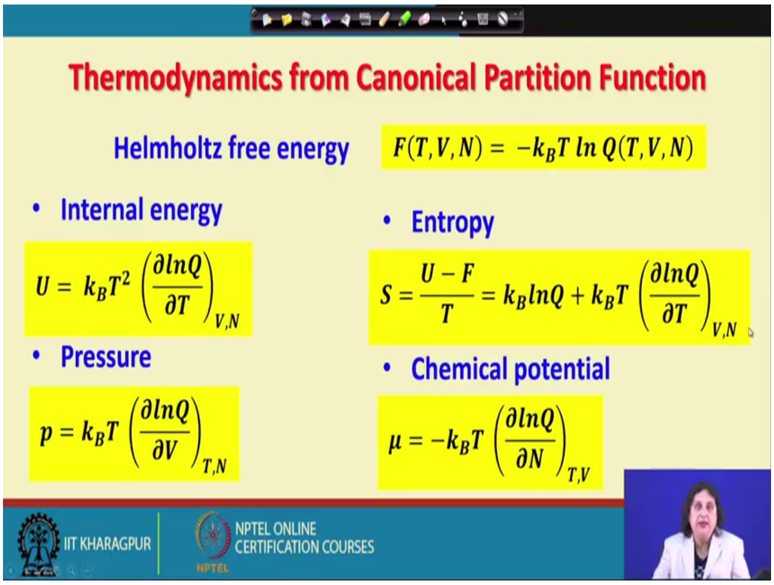

Thermodynamics from Canonical Partition Function

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

- **Internal energy**

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

- **Pressure**

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

- **Entropy**

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

- **Chemical potential**

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

With this background in mind, then we can we have already talked about how to obtain the thermodynamics from the canonical partition function and as you know that, all the thermodynamic properties that are of interest in our case can be derived, if you know the dependence of lnQ on properties like, temperature, volume or the number of particles.

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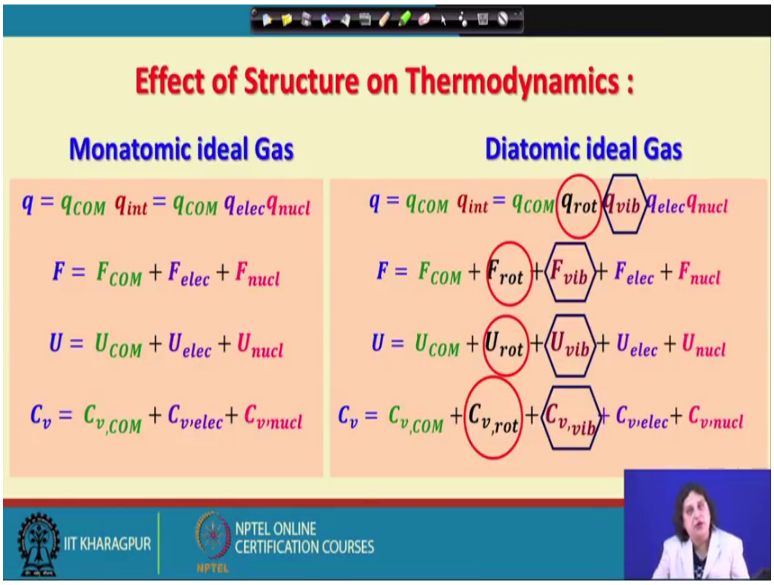

Effect of Structure on Thermodynamics :

Monatomic ideal Gas

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

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

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

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

Diatomic ideal Gas

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

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

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

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

So, with this background in mind what we have also pointed out, that the underlying structure plays an important role in overall thermodynamics, that is because the presence of this underlying structure gives add additional corrections.

So, the corrections that add up to the dominant term in each of these thermodynamic properties and we have seen that in the case of monatomic ideal gas, simply because we can partition the overall single particle canonical partition function into the contribution from the center of mass, that is structureless and the internal the structure all the thermodynamic properties, that we could derive they also had explicit contributions arising from these 3 factors, which added together to give us the net thermodynamic property.

Now, if we look at what happens in the case of the monatomic ideal gases in the case of the diatomic ideal gases, what we find is in this case, because of the presence of these 2 extra terms that you see here, there are 2 extra terms which are appearing in all the thermodynamic properties, which can be attributed to the effect of discrete energy levels present at this present for the rotational and the vibrational degrees of freedom for the diatomic case and as a result we would say, that well the presence of these 2 extra terms for example, q rot gives the it is corresponding extra terms in each of the thermodynamic properties that we have shown here, similarly the presence of q vib leads to this vibrational contribution to each of the thermodynamic properties that we see.

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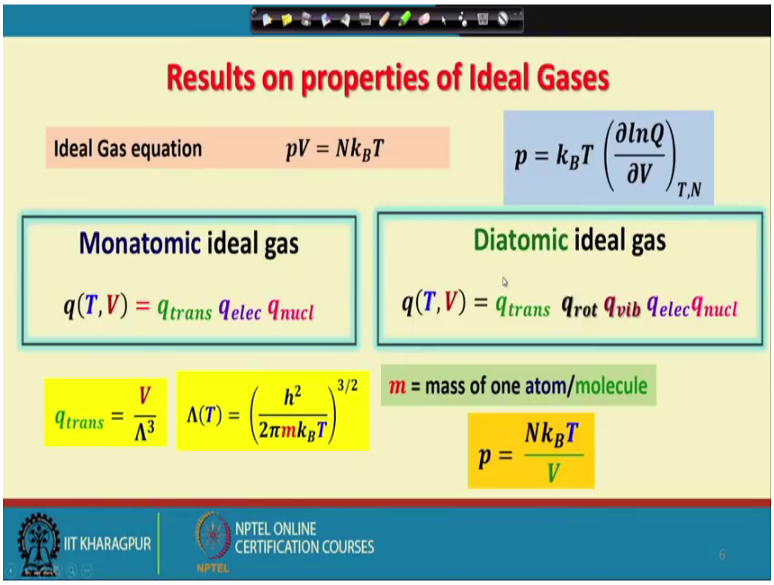

Results on properties of Ideal Gases

Ideal Gas equation $pV = Nk_BT$

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

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

$$p = \frac{Nk_BT}{V}$$

Now, we have seen all that and now, let us try and understand what happens, if I want to derive the ideal gas equation starting from the canonical partition function. Now, we have already seen in the last lecture, that the pressure is related to the derivative of lnQ with respect to volume keeping temperature and the number of particles constant. Now, if I think about what the way the structure of small q on which this capital Q depends, we find that in both the cases the explicit volume dependence of the small q term, comes through this translational partition function.

So, in the case of the monatomic ideal gas, this corresponds to the national motion of the single atom in the given box and here. It corresponds to the translational motion of the molecule as a whole, represented in terms of the translational motion of the center of mass in the confining volume, under the given condition of temperature.

Now, what we find here is it is possible, then to write down what the q trans is irrespective of whether, we are dealing with a monatomic ideal gas or a diatomic ideal gas and this is given in terms of the volume of the gas divided by the cube of the thermal wavelength lambda, where we have already seen that the thermal debroglie wavelength lambda depends on temperature and the mass of each particle and therefore, the way the monatomic and the diatomic gases will differ from each other will be in terms of this the quantity m.

Now, if we use this, then taking a natural logarithm of q trans and then estimating the derivative directly gave us the pressure in terms of NkBT by V. We have already done this derivation. So, what I wanted to emphasize over here, is that the pressure when I derive the pressure, the result that I get this is the same as far as the monatomic ideal gas or the diatomic ideal gas is concerned.

And that is because, both of them have identical terms giving rise to the corresponding to the translational motion in the volume V and therefore, I would expect that the pressure term, that I see here would be NkBT by V, in both the cases irrespective of whether, I am looking at the translational motion of an atom or the translational motion of a diatomic molecule.

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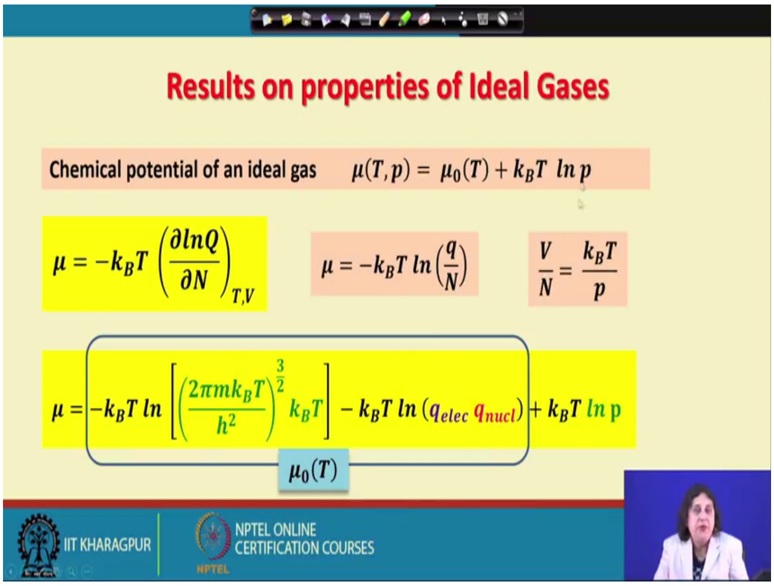

Results on properties of Ideal Gases

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

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

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

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

$$\mu = \underbrace{\boxed{-k_BT\, ln\left[\left(\frac{2\pi m k_BT}{h^2}\right)^{\frac{3}{2}} k_BT\right] - k_BT\, ln\,(q_{elec}\, q_{nucl})}}_{\mu_0(T)} + k_BT\, ln\, p$$

Similarly, we have also checked if the theoretical development, that I have been presenting here for molecular thermodynamics of ideal gases can reproduce the known form of chemical potential of an ideal gas, where we know that if I want to predict, what the chemical potential of the ideal gas is going to be at a given temperature and pressure. This is dependent on, what the chemical potential of the gas is at a temperature T under standard conditions of one bar pressure plus an additional term, that depends on the pressure at which I am going to observe the chemical potential of the ideal gas. Now, we have already carried out this derivation and indeed we have been able to show, that starting from the definition of chemical potential in terms of ln capital Q, then it is possible to find out what exactly the form of chemical potential would be in terms of the parameters like, mass of each particle temperature then q electronic, q nuclear etc.

Now, here what once again I would like to highlight is that, this expression has given me one set of terms, that is independent of pressure and dependent on temperature only and it also depends on the kind of system that we are working on. So, very easily I can say that, this must be the chemical potential at one bar pressure at a given temperature T.

So, when I have one bar pressure by definition, this small p is p by p naught, and where p naught is the standard pressure of 1 by one bar therefore, I put this equal to 0. So, this must be the mu naught now, what I have here is this additional term kBTlnp, which reproduces correctly the form that I expected from our prior knowledge of thermodynamics.

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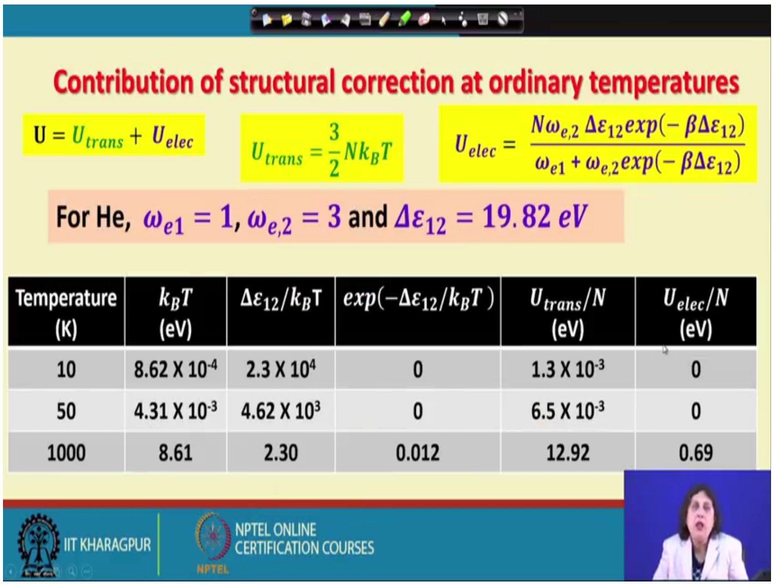

Contribution of structural correction at ordinary temperatures

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

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

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

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

We also looked at the predictions of the internal energy for an ideal gas and compared the predictions of our theory, that we are presenting here, with what we know from for example, equal partition theorem or joules law. And here what we found is that for a monatomic ideal gas like, helium if you know the underlying microscopic structure and the energy values associated it is found, that not 2 high temperatures the internal energy of the system is essentially corresponding to the translational energy. And at low temperatures the correction terms appearing, because of the underlying electronic structure is negligibly small, but if you go to very high temperatures, then what you will find is you will find that the contributions from this correction terms appearing, because of the underlying macroscopic structure of the gas is becoming significant.

So, as you understand that, if you go for temperatures like 1500 Kelvin or 2000 Kelvin, this number is going to become larger and larger and will start competing at very large temperatures with the translational contribution. So, basically the message here, is as follows. If we are at a few 100s of Kelvin, in that case the internal energy of the gas is dominated by the translational energy, translational contribution to the internal energy. And the translational contribution as we have seen here, this is dependent on KT right and therefore, and there is no other dependents in here like, volume does not appear therefore, U is a function of temperature and temperature only.

It is only at very high temperature, that we start seeing an additional correction term in the form of U electronic, but at a normal temperatures a few 100 of Kelvin these correction terms are not important and therefore, whatever experiments that we do are good enough to it will be explained with the equipartition theorem. With this background in mind, let us now go ahead and try and talk about this property.

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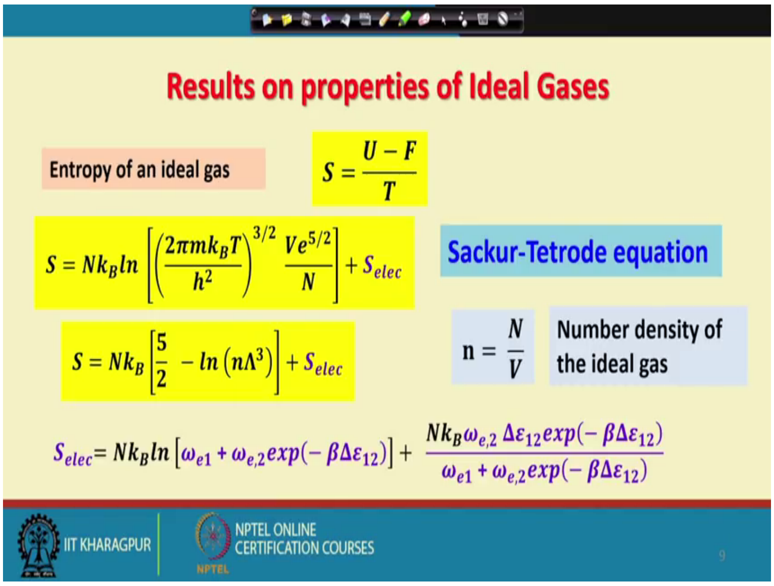

Results on properties of Ideal Gases

Entropy of an ideal gas

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

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

Sackur-Tetrode equation

$$S = Nk_B\left[\frac{5}{2} - ln\left(n\Lambda^3\right)\right] + S_{elec}$$

$$n = \frac{N}{V}$$

Number density of the ideal gas

$$S_{elec} = Nk_B ln\left[\omega_{e1} + \omega_{e,2} exp(-\beta\Delta\varepsilon_{12})\right] + \frac{Nk_B\omega_{e,2}\,\Delta\varepsilon_{12} exp(-\beta\Delta\varepsilon_{12})}{\omega_{e1} + \omega_{e,2} exp(-\beta\Delta\varepsilon_{12})}$$

The entropy of an ideal gas the way we will calculate this quantity is at this point, we know what U is what f is in terms of lnQ from lnQ. So, S is equal to U minus F divided by T.

A few lectures back, I asked you to work this out and this would be the expression for entropy as calculated starting from the current model of the canonical partition function for this monatomic ideal gas and here, what we find is this S electronic, this is a term which is a correction to the big term that you see here, that depends on the underlying electronic structure of the atom, as you can see very well the all the terms that are appearing here, they are connected to q trans, that is they are connected to the contribution to entropy from the translational motion of the atom in the box, and this is the contribution from the underlying electronic structure, and this equation is known as the Sackur-Tetrode equation, and in today's class we are going to use this equation a lot and so, it is very important that we understand what are the different quantities that are involved.

Let me write down explicitly, what S electronic is? What you must note over here, is that in this particular expression I have S electronic is proportional to NkB, because this appears as a pre-factor for both the terms, that you see here. Now, then I have 2 terms all of which depends on parameters that are associated with the electronic structure of the atom present in the system and of course, it is temperature dependence comes through the appearance of beta. Now, once I understand what S electronic is I find that in order to be able to use the Sackur-Tetrode equation, I would like to simplify it a little bit and this is what I shall be doing.

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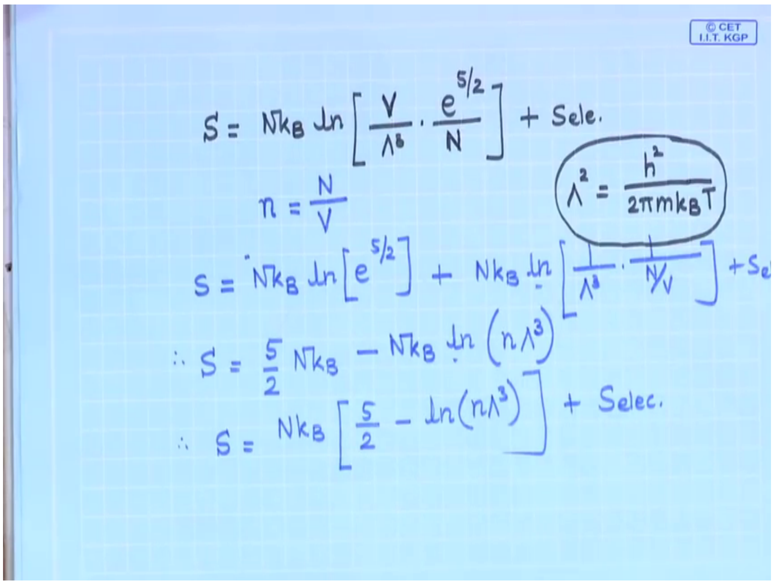

$$S = Nk_B \ln\left[\frac{V}{\Lambda^3}\cdot\frac{e^{5/2}}{N}\right] + S_{ele.}$$

$$n = \frac{N}{V}$$

$$\boxed{\Lambda^2 = \frac{h^2}{2\pi m k_B T}}$$

$$S = Nk_B \ln\left[e^{5/2}\right] + Nk_B \ln\left[\frac{1}{\Lambda^3}\cdot\frac{1}{N/V}\right] + S_e$$

$$\therefore S = \frac{5}{2}Nk_B - Nk_B \ln\left(n\Lambda^3\right)$$

$$\therefore S = Nk_B\left[\frac{5}{2} - \ln\left(n\Lambda^3\right)\right] + S_{elec.}$$

As I understand that, instead of writing out specifically the total expression for the entropy. I can very easily write down the entropy as V by lambda cubed into e to the power of 5 by 2 divided by N this plus S electronic as I have shown here. So, what is lambda? Lambda square by definition is equal to h square divided by 2 pi m kBT and in the slide that, I was showing to you I had this net expression put in here, instead of lambda cube. Now, if I go back and try to see that well, I have V and I have N. So, what happens if I introduce this quantity small n which is capital N divided by V.

If that is So, then I can rewrite the expression of S as NkB ln e to the power of 5 by 2 plus NkB ln 1 by lambda cube into one divided by N by V. If that is So, then S turns out to be nothing but 5 by 2 NkB minus NkB ln small n into lambda cube. So, what I have done is I understand that, whatever I see here appears in the denominator. So, when I take it up a negative sign comes over here, because I have a logarithm here and therefore, I can very easily say that capital S in this case and of course, you have this plus S electronic. So, that is NkB multiplied by 5 by 2 minus ln n lambda cube plus S electronic, right?

So, as you see then, an alternative and simpler form of the Sackur-Tetrode equation involves this number density n and the thermal debroglie wavelength lambda. We are going to use this equation now, to do some of the following checks.

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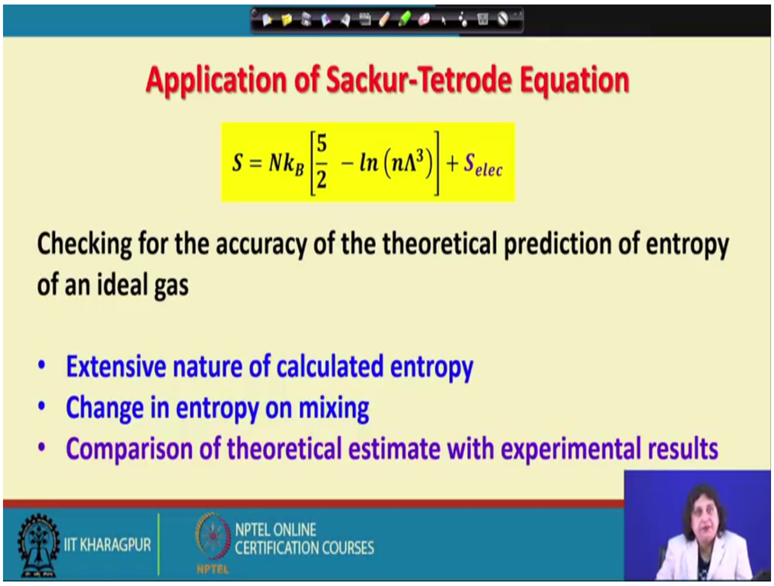

Application of Sackur-Tetrode Equation

$$S = Nk_B\left[\frac{5}{2} - ln\left(n\Lambda^3\right)\right] + S_{elec}$$

Checking for the accuracy of the theoretical prediction of entropy of an ideal gas

- Extensive nature of calculated entropy
- Change in entropy on mixing
- Comparison of theoretical estimate with experimental results

So, first we are going to check for the accuracy of the theoretical prediction of entropy of an ideal gas first by examining whether, the entropy that we are calculating here, preserves that extensivity of entropy as denoted by the basic formulation of thermodynamics.

We are also going to check, if the current formalism given in terms of the Sackur-Tetrode equation can correctly predict, what would happen when I mix 2 ideal gases irreversibly or reversibly and finally, it is possible to estimate the absolute value of entropy using the Sackur-Tetrode equation, if you know which thermodynamic state your system is present, in that case you can use these theoretical estimates and compare them with experimental results which will tell you whether, the theoretical prediction that you are making using the formalism of molecular thermodynamics is correct or not.

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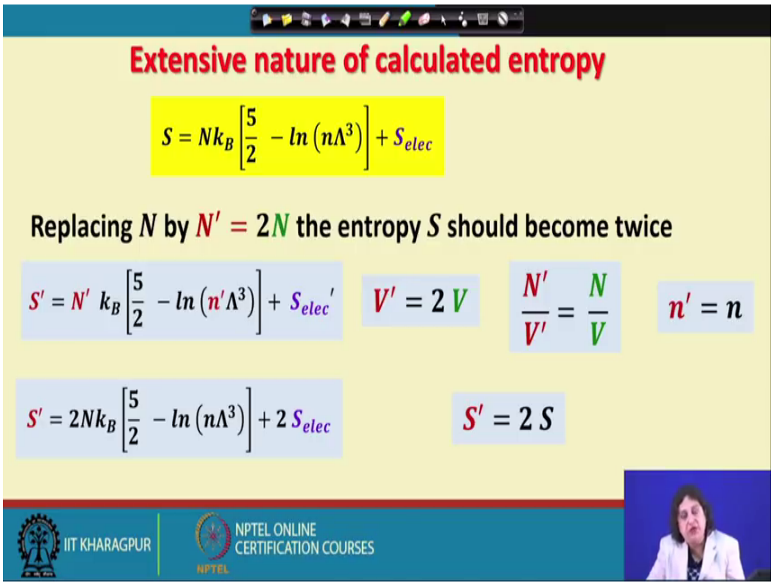

Extensive nature of calculated entropy

$$S = Nk_B\left[\frac{5}{2} - ln\left(n\Lambda^3\right)\right] + S_{elec}$$

Replacing N by $N' = 2N$ the entropy S should become twice

$$S' = N'\, k_B\left[\frac{5}{2} - ln\left(n'\Lambda^3\right)\right] + S_{elec}{}'$$

$$V' = 2\,V$$

$$\frac{N'}{V'} = \frac{N}{V}$$

$$n' = n$$

$$S' = 2Nk_B\left[\frac{5}{2} - ln\left(n\Lambda^3\right)\right] + 2\,S_{elec}$$

$$S' = 2\,S$$

So, let us take each of these one by one. So, the first thing that, we check is the extensive nature of calculated entropy. So, the first thing that, I do is in order to do this all the time we understand that, if there is a property X which is a an extensive property, in that case it must be a function of capital N in such a way that, if I replace N by N prime and N prime is equal to 2 N, then X will be replaced by X prime such that, X prime would be equal to 2 X .

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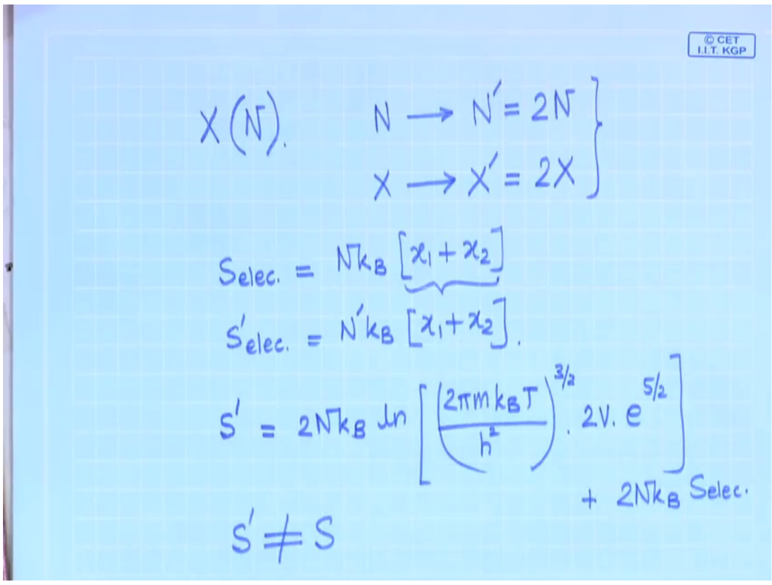

$$X(N). \qquad \left.\begin{array}{l} N \rightarrow N' = 2N \\ X \rightarrow X' = 2X \end{array}\right\}$$

$$S_{elec.} = N k_B \underbrace{[x_1 + x_2]}$$

$$S'_{elec.} = N' k_B [x_1 + x_2].$$

$$S' = 2N k_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} . 2V . e^{5/2}\right] + 2N k_B S_{elec.}$$

$$S' \neq S$$

So, that is the basic definition of an extensive property and here, we know from basic thermodynamics that entropy is an extensive property and we have used a molecular thermodynamics to find out some expression for entropy.

Now, we are going to test if the expression that, we have obtained for entropy in terms of the Sackur-Tetrode equation correctly tells me that, if I replace N by 2 N or in other words if I replace N by N prime such that, N prime is equal to 2N if I have done everything correctly, then if the Sackur-Tetrode equation is correct, then the entropy should become twice of it is original value. So, in order to do this what we do is if this is the expression for S, then what we do is we write down the expression for S prime where, in case while calculating S prime I am replacing N by N prime; obviously, the number density small n is represented by small n prime and S electronic this is also becoming S prime electronic.

Now, if you would remember that, S electronic is a term that, is NkB into one particular sum plus another particular sum and these 2 do not depend on N. So, in S electronic if I replace N by N prime. So, S prime electronic will now become N prime kB into the same x1 plus x2, correct? So, if that happens then, what I can do is I can now go ahead and replace N prime by 2N and check what is small n prime and S prime the electronic S. I realize over here that, when I float N equal to N prime in or N prime equal to 2 N the other extensive property that I have in this expression is volume, then volume goes from a value of V to V prime where, V prime is equal to 2V.

Now, let us check what happens to the ratio N by V as I understand that, N by V is equal to N prime by V prime under this condition and therefore, I should be able to say that well, the number density is not an extensive function it remains the same even if I replace N by twice it is value. Now, if I put this back.

So, I understand that here, N prime is 2N capital N prime is 2N small n prime is nothing but small n and S prime electronic is nothing but 2 S electronic and therefore, this is the expression that we would get here, and if I now compare the expression for S prime to the expression for S that, is the entropy we immediately conclude that, S prime is equal to 2 S. So, as expected the Sackur-Tetrode equation correctly preserves the extensive property of entropy as derived through the prescriptions of molecular thermodynamics.

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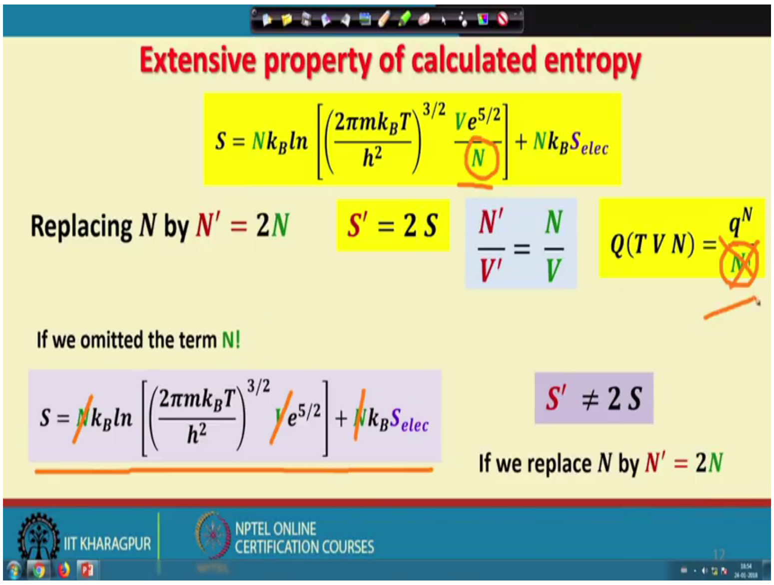

Extensive property of calculated entropy

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

Replacing N by $N' = 2N$

$S' = 2\,S$

$\frac{N'}{V'} = \frac{N}{V}$

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

If we omitted the term N!

$$S = \cancel{N}k_B ln\left[\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\cancel{V}e^{5/2}\right] + \cancel{N}k_BS_{elec}$$

$S' \neq 2\,S$

If we replace N by $N' = 2N$

Now, if I look a little closely enough, I understand that this entire analysis depends very much on the presence of this factor capital N here. Now, where did this factor capital N come from if we go back and look at the derivation, we will find that incorporation of this factor N factorial in the expression for capital Q is the reason, why in the final expression of S the term capital N appeared here. Now, what would have happened if we just did not write down this N factorial, we just wrote capital Q is equal to small q to the power of N, which means; that the corresponding expression for entropy would have been given by something like this.

Now, what would have happened if you wanted to check for the extensivity property of entropy, you would replace N by 2 N here, also you will replace N by 2 N and you will replace V by 2 V and then, S prime will turn out to be 2 NkB ln 2 pi m kBT by h square to the power of 3 by 2 into 2 V into e to the power of 5 by 2 N plus 2 NkB S electronic.

So, immediately you can see S prime is not equal to S and that is because, there will be an extra ln 2 term here, that will destroy the equality and therefore, we have made everything correct by incorporating this term N here, which in turn was introduced in this picture by the famous scientist Gibbs, who pointed out that well unless and until you are having this factorial N then you are not going to get the correct thermodynamic properties.

The other reason why Gibbs wanted to introduce this factor N factorial is that; obviously, unless you do. So, you are not taking into account of the fact that, you have identical particles constituting the gas we have already discussed it many times that, in order to avoid over counting of entropy over counting of the microscopic states of a system we should be dividing by N factorial in the case where, I have identical particles.

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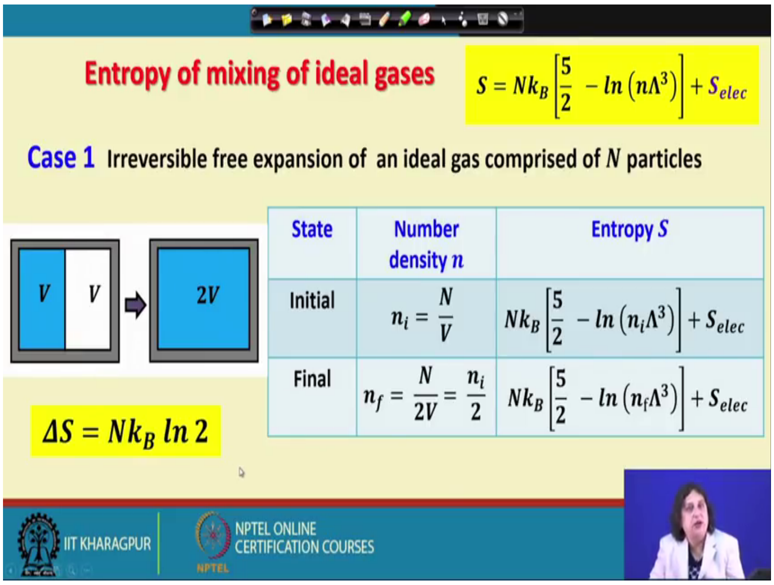

Entropy of mixing of ideal gases

$$S = Nk_B\left[\frac{5}{2} - ln\left(n\Lambda^3\right)\right] + S_{elec}$$

Case 1 Irreversible free expansion of an ideal gas comprised of N particles

State	Number density n	Entropy S
Initial	$n_i = \frac{N}{V}$	$Nk_B\left[\frac{5}{2} - ln\left(n_i\Lambda^3\right)\right] + S_{elec}$
Final	$n_f = \frac{N}{2V} = \frac{n_i}{2}$	$Nk_B\left[\frac{5}{2} - ln\left(n_f\Lambda^3\right)\right] + S_{elec}$

$$\Delta S = Nk_B\, ln\, 2$$

Now, let us next have a look at the entropy of mixing of ideal gases, and here also we are going to use the Sackur-Tetrode equation and check if the Sackur-Tetrode equation can explain the entropy of mixing of ideal gases correctly.

Now, the first case that we think about is the irreversible free expansion of an ideal gas that, are comprised of capital N particles. So, we are basically looking at the situation where, my initial system is something like this. So, I have a partition separating the entire volume into 2 equal volumes V on this side and V on the other side and this part is evacuated.

So, if I now, withdraw this partition the gas will undergo a free expansion which is an irreversible expansion and the final volume of the gas is going to be 2 V. Now, in this particular case what we have to consider the fact that in the initial state the number density is capital N particles present in a volume V of the gas of the blue gas and therefore, the initial number density is N by V.

So, using the Sackur-Tetrode equation I can write down the entropy of the system in the initial equilibrium state. Now, what is the entropy of the system in the final equilibrium state. So, for that I will have to know the final number density of the gas here, I have now capital N particles occupying a volume of 2 V therefore, I see that the number density has half and if I put it back here, and since this is essentially joules experiment where, the temperature remains constant I can argue that the lambda values are going to remain the same and within the temperature range that, we are talking about s electronic changes let us assume that, they are going to be very, very small.

Now, what do you expect we have already seen that under such, circumstances we in from thermodynamics we expect an increase in entropy and by Sackur-Tetrode equation if I use it I find that, delta s is NkBln 2 which is a positive number and therefore, correctly predicts the increase in entropy, when I allow the ideal gas to undergo an irreversible free expansion which anyway takes place under isothermal condition.

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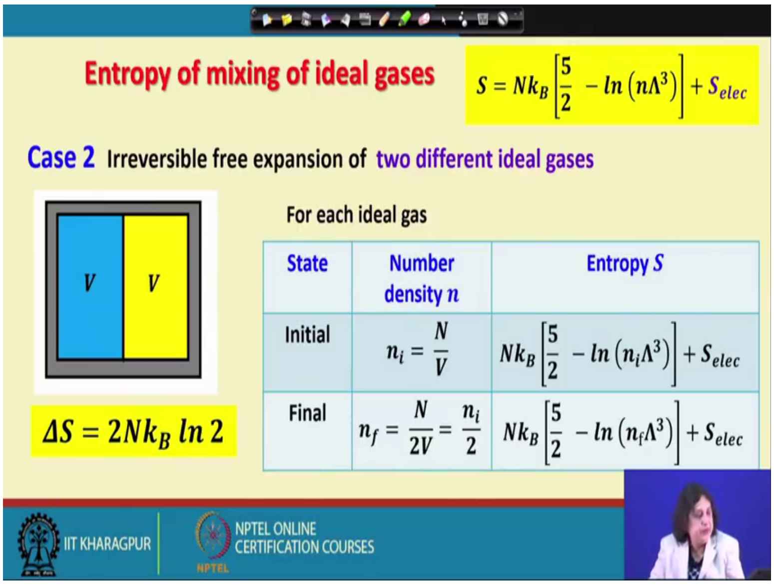

Entropy of mixing of ideal gases

$S = Nk_B\left[\frac{5}{2} - ln\left(n\Lambda^3\right)\right] + S_{elec}$

Case 2 Irreversible free expansion of two different ideal gases

$\Delta S = 2Nk_B\, ln\, 2$

For each ideal gas

State	Number density n	Entropy S
Initial	$n_i = \frac{N}{V}$	$Nk_B\left[\frac{5}{2} - ln\left(n_i\Lambda^3\right)\right] + S_{elec}$
Final	$n_f = \frac{N}{2V} = \frac{n_i}{2}$	$Nk_B\left[\frac{5}{2} - ln\left(n_f\Lambda^3\right)\right] + S_{elec}$

Now, if I have 2 different gases on 2 sides of the partition, if I withdraw the partition it is as if as far as the yellow gas is concerned, there was no yellow gas on the other side of the partition. So, it is an irreversible free expansion of the yellow gas just like, the irreversible free expansion for the blue gas and therefore, for each ideal gas I can once again repeat the same argument and therefore, I should be able to say that well here, the change in entropy is going to be positive and it is going to be twice the amount of we have seen from the case one and that is correctly predicted by the Sackur-Tetrode equation.

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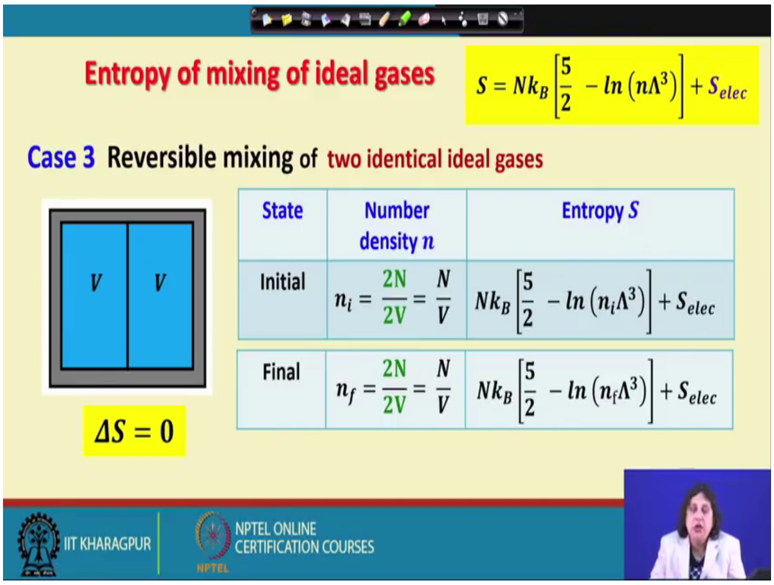

Entropy of mixing of ideal gases

$S = Nk_B\left[\frac{5}{2} - ln\left(n\Lambda^3\right)\right] + S_{elec}$

Case 3 Reversible mixing of two identical ideal gases

State	Number density n	Entropy S
Initial	$n_i = \frac{2N}{2V} = \frac{N}{V}$	$Nk_B\left[\frac{5}{2} - ln\left(n_i\Lambda^3\right)\right] + S_{elec}$
Final	$n_f = \frac{2N}{2V} = \frac{N}{V}$	$Nk_B\left[\frac{5}{2} - ln\left(n_f\Lambda^3\right)\right] + S_{elec}$

$\Delta S = 0$

So, this brings us to the final and most interesting case and this is a case of reversible mixing of 2 identical ideal gases. So, what is it that we are trying to do here, I have in the initial equilibrium state the same gas on both sides of the partition and I am reversibly withdraw the partition present in the 2 halves of the box. Now, what will happen what do you expect since, both the gases are they are the same and you have not done anything from outside rather than, just removing the partition you do expect that, there should not be any change in entropy or in other words delta S is going to be 0.

Now, let us see what is predicted by the Sackur-Tetrode equation, we find that the initial state I have capital N particles of the ideal gas on this side and capital N particles of the gas on the other side and therefore, I have a total of 2 N particles of the blue type divider and present in a volume of 2 V therefore, the initial number density is N by V and accordingly that, initial entropy of the system is given by this.

Now, when I allow the reversible mixing under isothermal condition what is the final density? The final number density once again is N by V and therefore, Sackur-Tetrode equation correctly predicts that, the delta s in such case is going to be equal to 0 and therefore, you once again see the importance of the appearance of the capital N term inside the log and unless you have that, correction it is not possible to reproduce all these informations.

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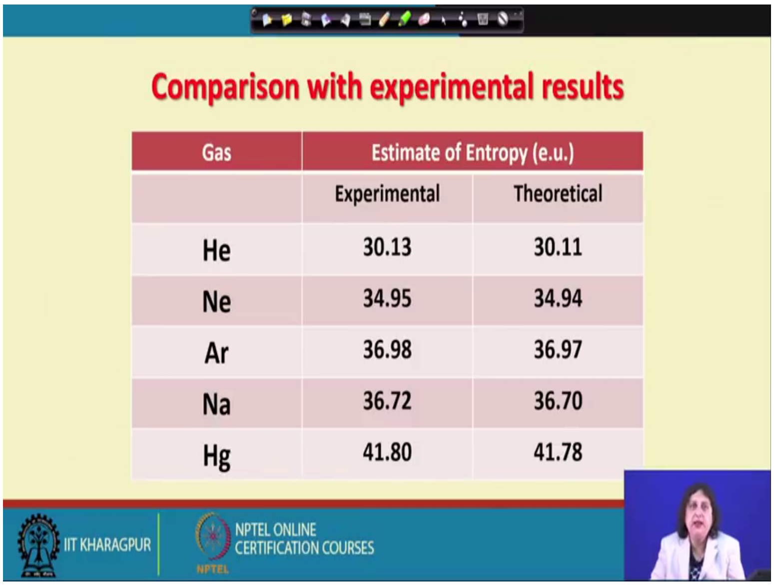

Comparison with experimental results

Gas	Estimate of Entropy (e.u.)	
	Experimental	Theoretical
He	30.13	30.11
Ne	34.95	34.94
Ar	36.98	36.97
Na	36.72	36.70
Hg	41.80	41.78

And finally, if one compares the estimated values of entropy as obtained from the Sackur-Tetrode equation to the ones obtained experimentally as you can very well see from the data presented here that, there is an astonishing agreement between the theoretical prediction and the experimental results.

So, this brings us to the conclusion that, the formalism that we have proposed through the molecular thermodynamics. So, statistical thermodynamics is actually an accurate one it not only gives us a molecular derivation of the ideal gas law the form of chemical potential of the an ideal gas or why the temperature dependent term? Why the internal energy will be dominated by a term proportional to temperature at normal temperatures?

It is also capable of reproducing the essential properties of entropy of an ideal gas and it agrees very well with the experimental data. So, that for any theoretical framework is an enormous achievement and in the next class we will see how these considerations can be extended to understand the properties of diatomic gases ideal gases where, the structure is also playing underlying structure is also playing an important role by having this additional contribution of rotational and vibrational structure.

Thank you.