Introduction to Molecular Thermodynamics
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Lecture – 31
Statistical Thermodynamics of an Ideal Gas

Welcome, we will continue our discussion on the application of basic principles of molecular thermodynamics of statistical thermodynamics to an ideal gas.

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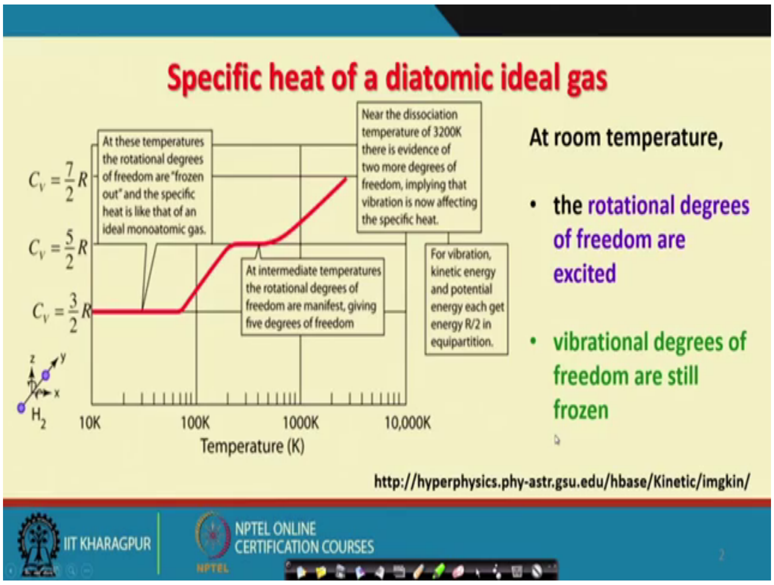

Specific heat of a diatomic ideal gas

At these temperatures the rotational degrees of freedom are "frozen out" and the specific heat is like that of an ideal monoatomic gas.

Near the dissociation temperature of 3200K there is evidence of two more degrees of freedom, implying that vibration is now affecting the specific heat.

At intermediate temperatures the rotational degrees of freedom are manifest, giving five degrees of freedom

For vibration, kinetic energy and potential energy each get energy R/2 in equipartition.

At room temperature,

- the rotational degrees of freedom are excited
- vibrational degrees of freedom are still frozen

http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/imgkin/

And you have already seen how the fundamental concepts developed by the molecular thermodynamics use developed within the frameworks of molecular thermodynamics can be used to successfully explain the variation of specific heat of the atomic ideal gas. And also explain why it why it should be different from mono atomic ideal gases, and under what condition the structure, the presence of a structure in a diatomic molecule is going to be reflected in the thermodynamic property of it is that that is measured at the microscopic level.

Today, we are going to talk about another very interesting case which I label as the curious case of hydrogen gas. Now why do I say that is a curious gas case? If you look back at the fundamental properties of hydrogen gas, in terms of the hydrogen molecules, we find that the disassociation constant is about 432 kilo joules per mol.

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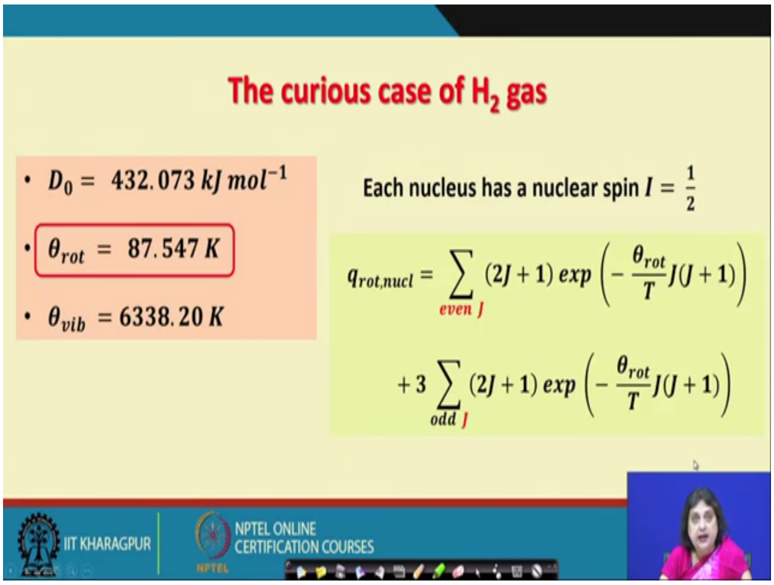

The curious case of H_2 gas

- $D_0 = 432.073\ kJ\ mol^{-1}$
- $\boxed{\theta_{rot} = 87.547\ K}$
- $\theta_{vib} = 6338.20\ K$

Each nucleus has a nuclear spin $I = \frac{1}{2}$

$$q_{rot,nucl} = \sum_{even\ J} (2J+1)\ exp\left(-\frac{\theta_{rot}}{T}J(J+1)\right)$$

$$+3\sum_{odd\ J} (2J+1)\ exp\left(-\frac{\theta_{rot}}{T}J(J+1)\right)$$

And then we also find that ahah the theta rot and theta vib the rotational and vibrational temperatures for this system these are known. But what is interesting over here if you compare the values of theta rot observed here to the once that we have discussed so far, you find that theta rot for hydrogen is a very large number.

If you would remember, for hcl this was roughly about 15 kelvin, and for k 2 vapor this was less than one kelvin. And therefore, when you think about hydrogen gas, and it has such a high rotational temperature, it gives rise to certain unique behavior that we are going to be interested in. Now in the case of the homo nuclear hydrogen gas, we understand that each nuclears has a nuclear spin of half and correspondingly we have discussed in detail how we can write down the overall contribution to the partition functions single parti particle partition function from a symmetry allowed combination of the rotational energy states with the nuclear energy states. So, following those prescriptions we find that this contribution to the single particle partition function is going to be comprised of 2 parts.

And therefore, you understand that in the case of hydrogen gas all the thermodynamic properties are going to be having 2 different contributions; one arising from the symmetric contri symmetric associated with the symmetric nuclear wave functions, the other one is associated with the anti-symmetric nuclear wave function. Now what is the consequence? People actually were aware of these difference in the underlying molecular structure for a long time, even before the emergence of the of quantum mechanics.

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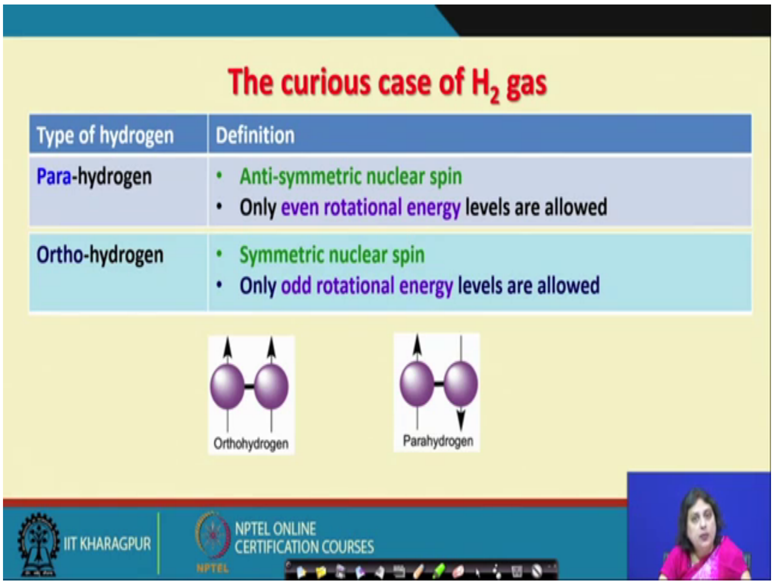

The curious case of H_2 gas

Type of hydrogen	Definition
Para-hydrogen	• Anti-symmetric nuclear spin • Only even rotational energy levels are allowed
Ortho-hydrogen	• Symmetric nuclear spin • Only odd rotational energy levels are allowed

So, in this case, the chemists in particular they were aware of 2 types of hydrogen molecule one is called the para hydrogen; which now we understand is associated with the anti-asymmetric nuclear spin wave function, and accordingly, we have only even rotational energy levels allowed for the system. And for the ortho hydrogen, we have a symmetric nuclear spin, and only odd rotational energies are is are allowed. And so, this is the schematic representation, where in the para hydrogen all I am trying to say is that if one is associated with ah some alpha as a nuclear function a nuclears spin function, then and the other one is having beta; in that case, it is the anti-symmetric combination of these 2, nuclear spin function alpha beta minus beta alpha divided by root 2 that represents the nuclear wave function for the para hydrogen. And the ortho hydrogen on the other hand, can have 3 different representations corresponding to 3 different symmetry allowed a wave nuclear wave function.

Now accordingly we can just go back and use the q rot to find out the average number of ortho and para hydrogen molecules at a given temperature T.

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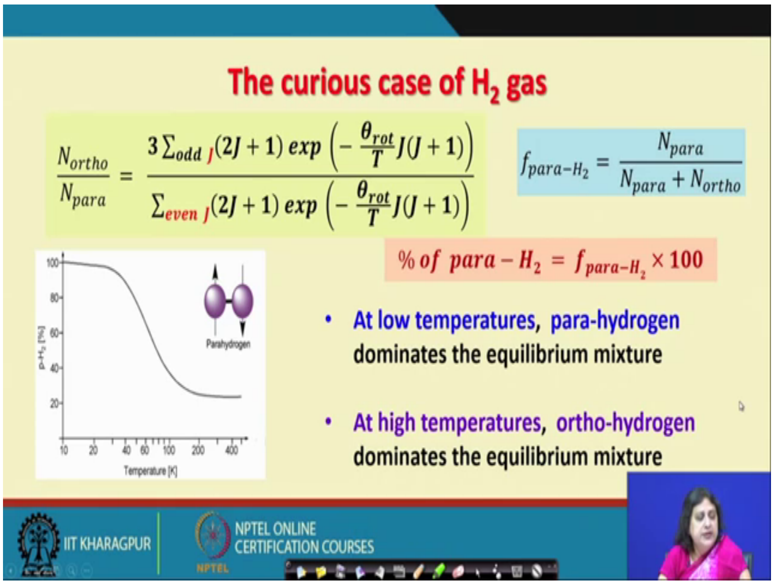

The curious case of H_2 gas

$$\frac{N_{ortho}}{N_{para}} = \frac{3\sum_{odd\ J}(2J+1)\, exp\left(-\frac{\theta_{rot}}{T}J(J+1)\right)}{\sum_{even\ J}(2J+1)\, exp\left(-\frac{\theta_{rot}}{T}J(J+1)\right)}$$

$$f_{para-H_2} = \frac{N_{para}}{N_{para}+N_{ortho}}$$

$$\%\ of\ para-H_2 = f_{para-H_2} \times 100$$

- At low temperatures, para-hydrogen dominates the equilibrium mixture
- At high temperatures, ortho-hydrogen dominates the equilibrium mixture

So, as you see that this ratio, that is going to be dependent on at what temperature, we are making the measurement ok, and then we can very easily say that well for a given temperature, I can always predict what is going to be the fraction of para hydrogen molecules in the assembly of ortho and para hydrogen. And accordingly, I can calculate the percentage of para hydrogen molecule in a given system. From the known fraction, now simply because this ratio of N ortho and N para are dependent on temperature.

Therefore, I should get this percentage of para hydrogen in equilibrium with ortho hydrogen at different temperatures, this must be a function of temperature. So, this is what is plotted over here. So, as you see that this percentage of para hydrogen is a strong function of temperature, initially at very low temperature my system is comprised mostly of para hydrogen. And then as you increase temperature, the percentage of para hydrogen decreases.

And finally, when you are near about the room temperature, what you find is the equilibrium mixture of ortho and para hydrogen is nearly 25 percent para hydrogen, and it is dominated by the ortho hydrogen. And therefore, we can conclude by looking at this theoretical calculation that, if I have a equilibrium mixture of the ortho and para hydrogen, then at low temperature the para hydrogen is going to dominate, the population of the equilibrium mixture. But when I go to high temperatures, then the dominant contribution will come from ortho hydrogen in the equilibrium mixture.

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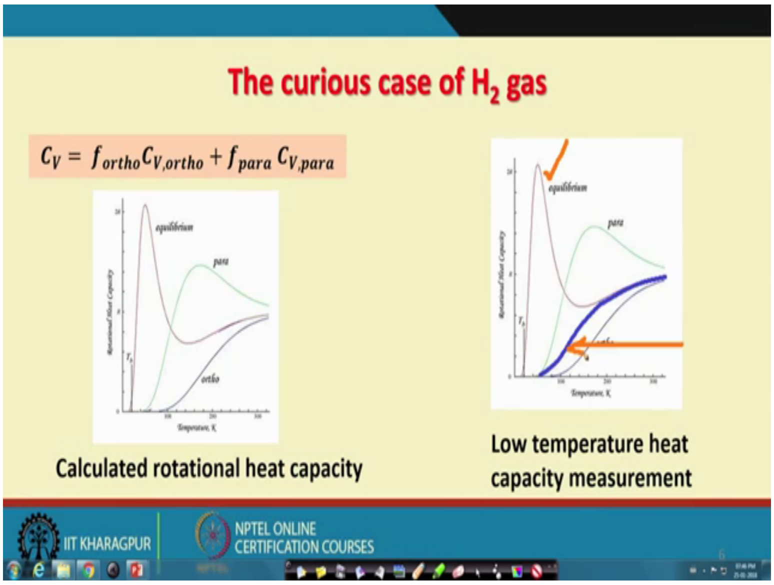

The curious case of H_2 gas

$C_V = f_{ortho} C_{V,ortho} + f_{para}\, C_{V,para}$

Calculated rotational heat capacity

Low temperature heat capacity measurement

With this background in mind then, obviously, one can calculate using the formalism oh ah molecular thermodynamics, what is going to be the overall specific heat of molecular hydrogen gas present at a given temperature, within confined within a volume. So, as you see that that would be given by the fraction of the ortho hydrogen multiplied by whatever is the pre-prediction of Cv for the ortho hydrogen as obtained from the q rot nuclear plus.

The corresponding quantity from the para hydrogen. And if I do that then these are the results of the rotational contribution to the overall specific heat of hydrogen molecule. So, what you have here at a given temperature T, a low temperature T then we understood that if the mixture is entirely comprised of para hydrogen, this is how the Cv will vary with temperature. Had it been entirely comprised of the ortho hydrogen? This is how the specific heat would change with temperature.

But since we know that the under realistic condition, if there is an equilibrium at that temperature between the ortho or para. And especially if we are looking at a very low temperature, then for this equilibrium mixture, it can be very easily calculated that this is going to represent the variation of Cv for the ah equilibrium mixture. But now we see if we do a measurement at low temperature the experimental data is what you see here through this white dark blue line.

So, this is the prediction of theory that you see for the equilibrium; where you have shown that if there is an equilibrium between the ortho and para hydrogen at a low temperature, where it is dominated by the para hydrogen, this should be the variation. But in the experiments this is what you get. So, basically this experiment was carried out long back in the very early days of quantum mechanics. And therefore, people started asking this question is quantum mechanics valid I mean this is something that we are observing.

And very clearly Description of the underlying molecular structure of hydrogen molecule using the results of quantum mechanics, apparently was unable to explain the experimental data. So, where was the problem. So, this actually led to a lot of debate and a lot of thought and scientific investigations where invested in solving this problem. And this is what was found out to be a clue to the solution of this problem.

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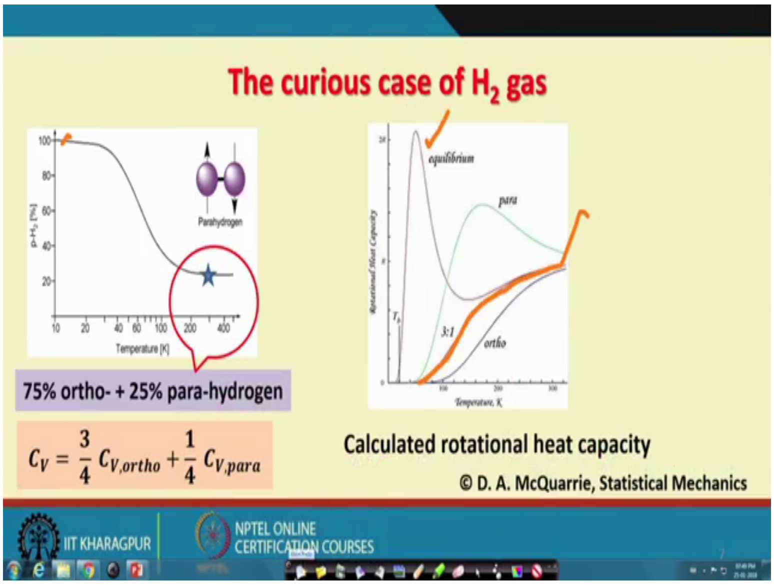

The curious case of H_2 gas

75% ortho- + 25% para-hydrogen

$$C_V = \frac{3}{4} C_{V,ortho} + \frac{1}{4} C_{V,para}$$

Calculated rotational heat capacity

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Now, here this particular picture that I have shown here, this assumes that at every temperature the percentage of para hydrogen is a function of temperature. And at a given temperature, this is the percentage of para hydrogen if para hydrogen is residing at equilibrium with ortho hydrogen in that temperature.

Now if so happens that you can think of well, this is the composition at room temperature, where I have 75 percent ortho, and 20 and 25 percent para hydrogen. Now for this mixture, let me say that if I calculate the corresponding rotational contribution to

Cv, what will happen? So, I will take 75 percent of the Cv for the pure ortho hydrogen. Plus, 25 percent of the Cv of the para hydrogen, add them 2 up and get the Cv for an equilibrium mixture, had it been 75 percent ortho? And 25 percent para. Now the result of the calculation was extremely interesting. This is the result of the variation of Cv with temperature when we use this 3 is to one combination at low temperature.

So, at that very low temperature this is what you have expected had there been an equilibrium between the ortho and the para hydrogen as predicted at this low temperature. But actually, what we find is that by during the experimental measurement, the experimental data actually very easily very nicely is reproduced by this 3 is to one mixture, which we expected to survive only at very high temperature in equilibrium. So, what is happening here? So, if I go back and look a little more closely into additional experimental data.

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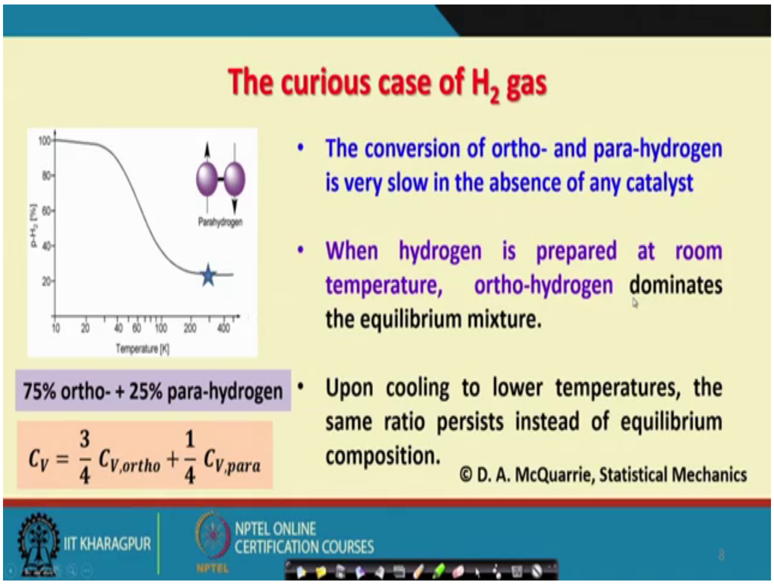

The curious case of H_2 gas

- The conversion of ortho- and para-hydrogen is very slow in the absence of any catalyst
- When hydrogen is prepared at room temperature, ortho-hydrogen dominates the equilibrium mixture.
- Upon cooling to lower temperatures, the same ratio persists instead of equilibrium composition.

75% ortho- + 25% para-hydrogen

$$C_V = \frac{3}{4}\, C_{V,ortho} + \frac{1}{4}\, C_{V,para}$$

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What we find is that the conversion of ortho and para hydrogen is actually very, very slow if there is no catalyst used. And when hydrogen is prepared at room temperature, we prepare a mixture where ortho hydrogen is dominating the equilibrium mixture. Now while performing the specific heat experiment at low temperature, you cool down the system to lower temperature, but what happened is, when you took it to the lower temperature, then the same ratio relative amount of ortho and para persisted.

So, what we have at that low temperature for the heat capacity measurement was not the equilibrium mixture at that particular temperature, but a meta stable mixture which had 75 percent ortho and 25 percent para. So, obviously, one would question that this explanation is going to be valid provided you do something else.

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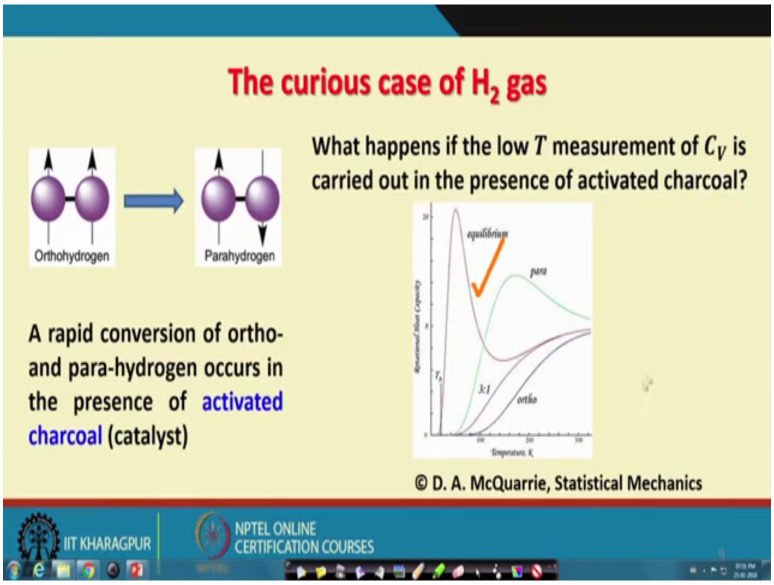

The curious case of H_2 gas

What happens if the low T measurement of C_V is carried out in the presence of activated charcoal?

A rapid conversion of ortho- and para-hydrogen occurs in the presence of activated charcoal (catalyst)

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And what is that particular experiment that was carried out? It was found from the literature of chemistry, that a rapid conversion of ortho and para hydrogen occurs in the presence of activated charcoal as a catalyst. Now if the measurements of ah specific heat of hydrogen at low temperature was carried out in the presence of activated charcoal, then you would expect that the population of ortho will rapidly get converted to para at low temperature, even if I am having a low temperature. And then if you do the measurement, what you find is that the experimental data agree very well with how the specific heat should vary with temperature at very low temperatures if there is an equilibrium mixture.

So, this is one of the major triums of the framework of molecular thermodynamics, which told us that not only we can explain how the specific heat ah of the given atomic molecule will vary with temperature, but we could look very closely at the 2 different types of nuclear spins is present in molecular hydrogen, and then correlate the observed experimental data to the calculated results obtained using the fundamental framework of molecular thermodynamics. And I would also like to highlight over here, that this kind of behavior you can very easily understand that it.

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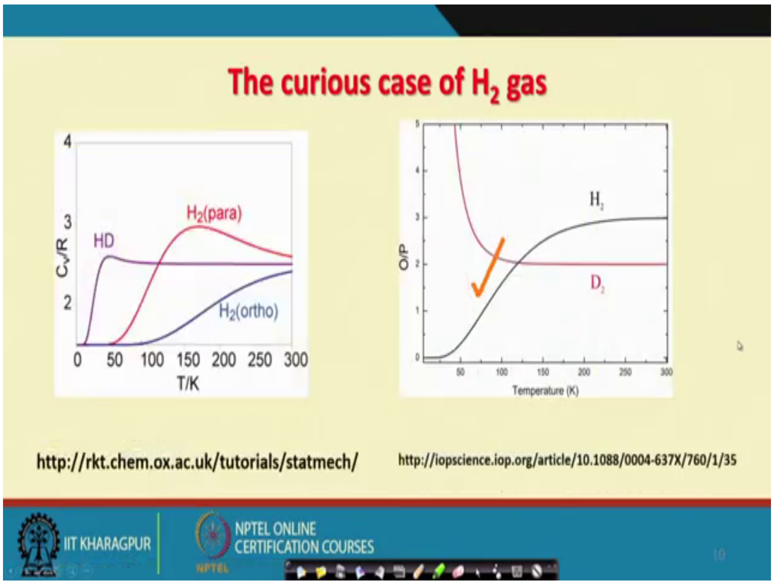

The curious case of H_2 gas

http://rkt.chem.ox.ac.uk/tutorials/statmech/

http://iopscience.iop.org/article/10.1088/0004-637X/760/1/35

Also extends to the cases of specific heat measured at low temperatures for not only hydrogen molecule, but also for HD gas or hydrogen and H 2 and D 2 gas.

So, all these informations that you see here; which results of measurements, they can be justified within the framework of molecular thermodynamics. So, in this lecture, as we are discussion the use of statistical thermodynamic or molecular thermodynamics to explain experimental data, let us pick up another experimental data that we know very well for an ideal gas mixture.

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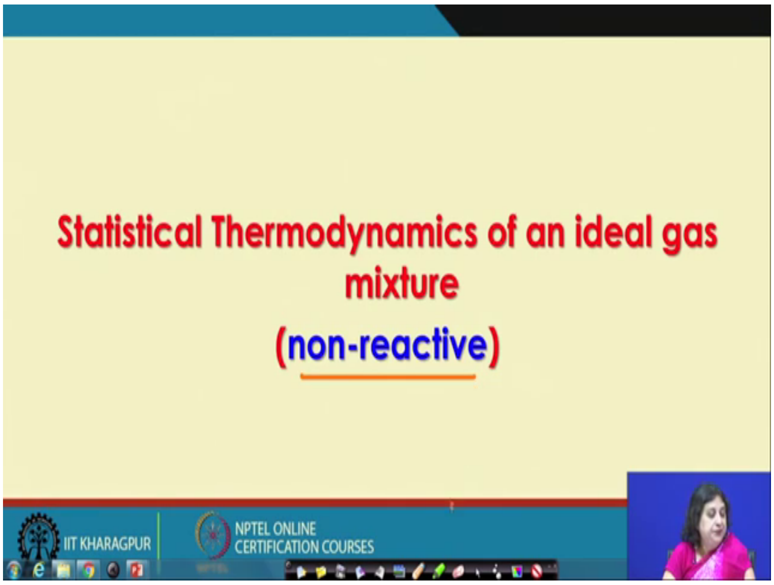

Statistical Thermodynamics of an ideal gas mixture

(non-reactive)

Now here I have highlighted the fact that, I am going to pick up a experimental data or the law that has been formed by looking at a very large body of experimental data; where I have a mixture of ideal gases, and the components do not interact with each other. So, there is no chemical reaction present.

So, in this case the kind of system that I am talking about can be outlined like this .

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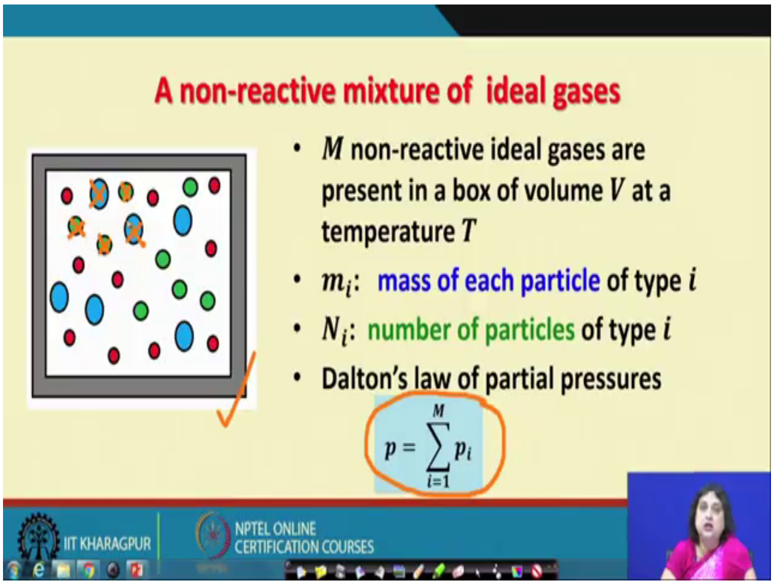

A non-reactive mixture of ideal gases

- M non-reactive ideal gases are present in a box of volume V at a temperature T
- m_i: mass of each particle of type i
- N_i: number of particles of type i
- Dalton's law of partial pressures

$$p = \sum_{i=1}^{M} p_i$$

So, I have a non-reactive mixture ideal gases, where a typical microscopic state looks like this. So, I have in this picture how many different types of ideal gases? I have one comprised of these red molecule, I have another one comprised of these green molecules. And I have the third type comprised of this blue molecules. In general, we would say that, one such gas mixture will be comprised of capital m ideal gases, and there will be contained in a box of volume v at a temperature T. Now since this box is surrounded by a rigid impermeable wall, therefore, I would say that the thermodynamics state of the mixture is very well represented in terms of a canonical example. Now ah here let me adopt this notation that M i is the mass of each particle of type i.

Which means here in my case i varies from 1 2 3. So, here I will have 3 types of masses N 1 for this, N 2 for this, and N 3 for this. Now I also understand that for each type of particle i, there will be some number of particles present which I call N i. So, here in this part I have 1, 2, 3, 4, 5, 6, 7, 8, 9, 10. 10 molecules for of type 1, that is the red molecule, therefore, in my case N 1 is equal to 10. Similarly, you can count 1, 2, 3, 4, 5, 6, N 3 that is for the blue molecule, which is equal to 6 and so on and so forth.

Now, the daltons law of partial pressure tells us that you can in principle measure the pressure of the gas. That is present under this condition, and if this mixture is present under the condition of a given temperature and given total pressure, then this is going to be a sum of the individual partial pressures pi, now what is the definition of pi? Pi is, if I had the same box of volume v maintained at the temperature t, but not having this mixture it is let us say that it is filled with only the red molecules. So, these molecules will not be there, then if I could measure the pressure of this gas, this would be P 1 for the red gas which I given index of 1. So, if I could get this partial pressure P 1 P 2 P 3 etcetera.

Under the identical conditions of constant temperature, then I would say the constant the total pressure of this mixture ideal gas mixture is going to be equal to a sum of their partial pressure. Now the question that I am asking here is as follows; is it possible for us to use the formalism that we have developed within molecular thermodynamics to derive a relationship like this. And that is exactly what I am going to do in the next few slides in this lecture.

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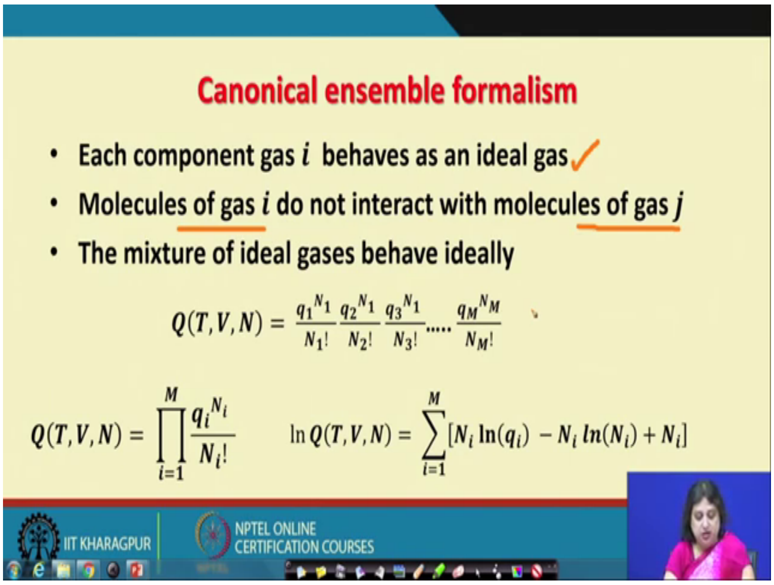

Canonical ensemble formalism

- Each component gas i behaves as an ideal gas ✓
- Molecules of gas i do not interact with molecules of gas j
- The mixture of ideal gases behave ideally

$$Q(T,V,N) = \frac{q_1^{N_1}}{N_1!}\frac{q_2^{N_1}}{N_2!}\frac{q_3^{N_1}}{N_3!}\cdots\frac{q_M^{N_M}}{N_M!}$$

$$Q(T,V,N) = \prod_{i=1}^{M}\frac{q_i^{N_i}}{N_i!} \qquad \ln Q(T,V,N) = \sum_{i=1}^{M}[N_i \ln(q_i) - N_i \ln(N_i) + N_i]$$

So, here there are certain assumptions which are very, very important, I understand that each of the component gases they behave like an ideal gas. And also, I understand that the molecules of gas I do not interact with the molecules of gas j. So, that the mixture on the whole acts as an ideal gas mixture.

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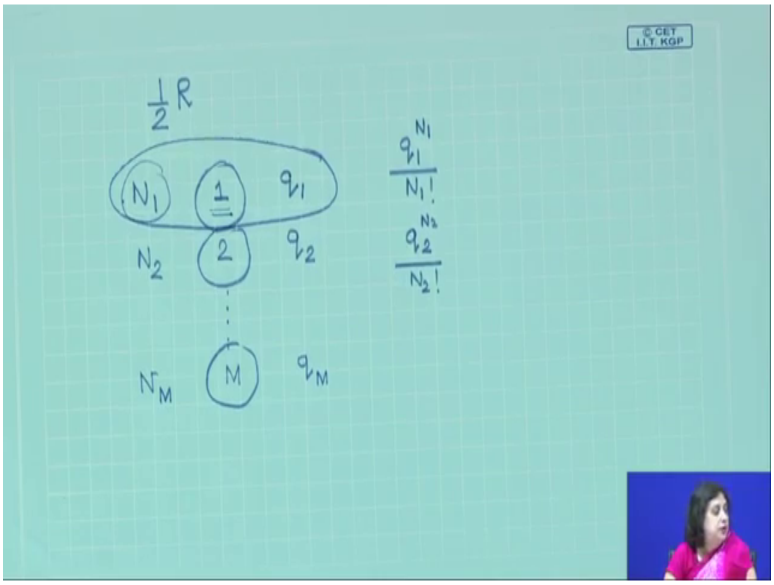

And therefore, now I have in my mixture N one particles of type one for which the single particle partition function can be written as q 1, I have N 2 particles of type 2 for which the single particle partition function can be written as q 2 and so on and so forth ok. If you I have capital N different types of particles, then the associated single particle partition function is going to be q 1. And since for each type I have identical N 1 particles corresponding to the type i, therefore, for this type the single particle partition function taking this N 1 identical particles together is going to be q 1 divided by N 1 factorial. Similarly, for the type 2 this is going to be q 2 to the power of N 2 divided by N 2 factorial.

Now, what happens since the molecules of type one are independent of molecules of type 2 and so on and so forth, therefore, I can write down the total canonical particle partition function for the system like this. And this means what? In general, in the short hand notation, I should be able to write down capital Q as a product of these numbers, where I have for the ith ah type of particle, qi raised to the power of ni divided by ni factorial.

Now if I have mixture of ideal gases that I am handling at microscopic level, we understand that each of the ni values are going to be very large like, we mix one mole of hydrogen with 3 moles of nitrogen. So, that is how many hydrogen molecules? Avagadro number of hydrogen molecules, and 3 times the avagadro number of nitrogen molecules.

So, each of these numbers ni are very, very large. And therefore, while calculating the logarithm of capital Q i can use the (Refer Time: 23:09) approximation. With that I arrive at this kind of an expression for l N cube. So, what is the consequence? Obviously, whenever I am using the formalism of molecular thermodynamics within the canonical (Refer Time: 23:25), then I actually require capital Q.

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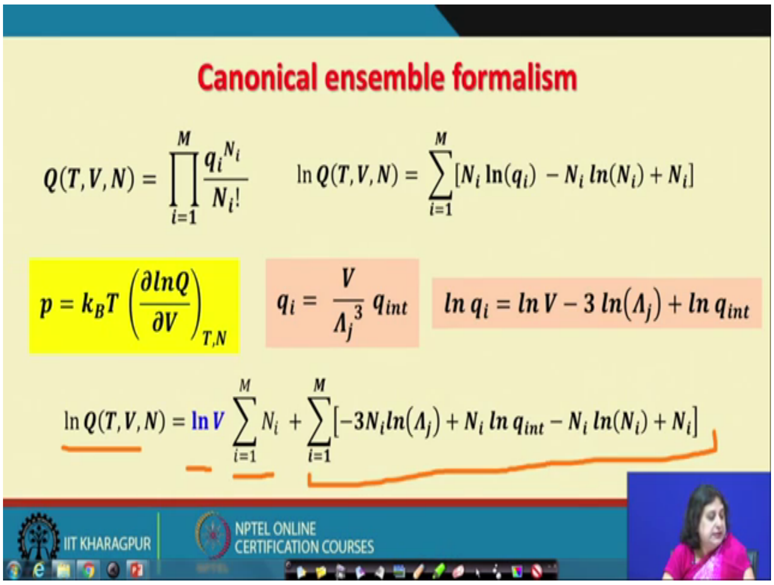

Canonical ensemble formalism

$$Q(T,V,N) = \prod_{i=1}^{M} \frac{q_i^{N_i}}{N_i!}$$

$$\ln Q(T,V,N) = \sum_{i=1}^{M} [N_i \ln(q_i) - N_i \ln(N_i) + N_i]$$

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

$$q_i = \frac{V}{\Lambda_j^3} q_{int}$$

$$\ln q_i = \ln V - 3\ln(\Lambda_j) + \ln q_{int}$$

$$\underline{\ln Q(T,V,N)} = \ln V \sum_{i=1}^{M} N_i + \underbrace{\sum_{i=1}^{M}[-3N_i \ln(\Lambda_j) + N_i \ln q_{int} - N_i \ln(N_i) + N_i]}$$

So, when I go ahead and calculate the pressure of this mixture, then I need to understand how l and q explicitly depends on volume. Now if I examine the expression for l and q, what I find here is that l and q is nothing but contributions coming from this term, this term and this term. And the and the last 2 terms are independent of volume.

So, I have to focus on what small qi is, and this small qi is this term multiplied by whatever internal structure that the system has. Therefore, I would say that the explicit volume dependence on lnq arises from this lnv term. And therefore, if I go ahead and calculate the pressure, then what will happen is, I should be able to write down lnqtvn as lnv multiplied by this sum, plus atom that is independent volume ok. And it is a constant at a given temperature, and the total number of particles, is that happens then I can rewrite this expression do a little algebra.

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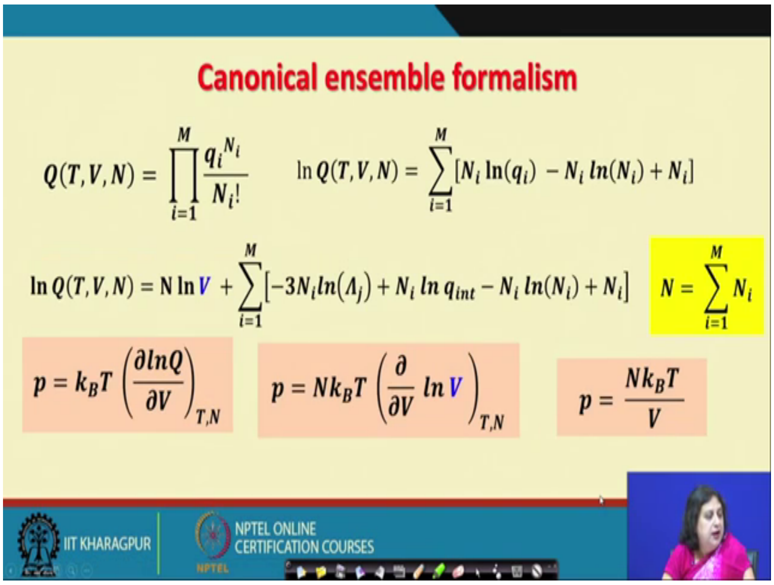

Canonical ensemble formalism

$$Q(T,V,N) = \prod_{i=1}^{M} \frac{q_i^{N_i}}{N_i!} \qquad \ln Q(T,V,N) = \sum_{i=1}^{M} [N_i \ln(q_i) - N_i \, ln(N_i) + N_i]$$

$$\ln Q(T,V,N) = \mathrm{N} \ln V + \sum_{i=1}^{M} [-3N_i ln(\Lambda_j) + N_i \, ln \, q_{int} - N_i \, ln(N_i) + N_i] \qquad N = \sum_{i=1}^{M} N_i$$

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

And we write this expression, I introduce this number capital N which is a sum of all the individual Parti number of individual particles present in the system.

And then, I can say that lnqtvn is N lnv plus atom that does not depend on volume explicitly, and is a constant at constant temperature and total number of particles. Now when this happens, when I calculate pressure, so, obviously, pressure is given by del v of lnv with this P factor. And I find that pressure now is given by as before it is capital N kbt by v, but here this capital N is not the total number of particles of one type, but rather it is the total number of particles taken all the different N types together ok.

So, once I understand this, what I find is that I have a achieved the following. I started by saying that this is an ideal gas mixture, I have different N different types of particles, therefore, I could write the canonical partition function like this, and then I will write the total pressure of this ideal gas mixture as this where N is nothing but this quantity. So, let us put this back in the expression and this is what you are going to get. Once you get that you please remember that we will assume that each component gas in this gas mixture also behaves ideally.

So, in that case I must be able to say that if each component gas was present at the same temperature, at for the same volume occupying the same volume, and they were still N in particles of the type I then what would have been the pressure that pressure would have been pi.

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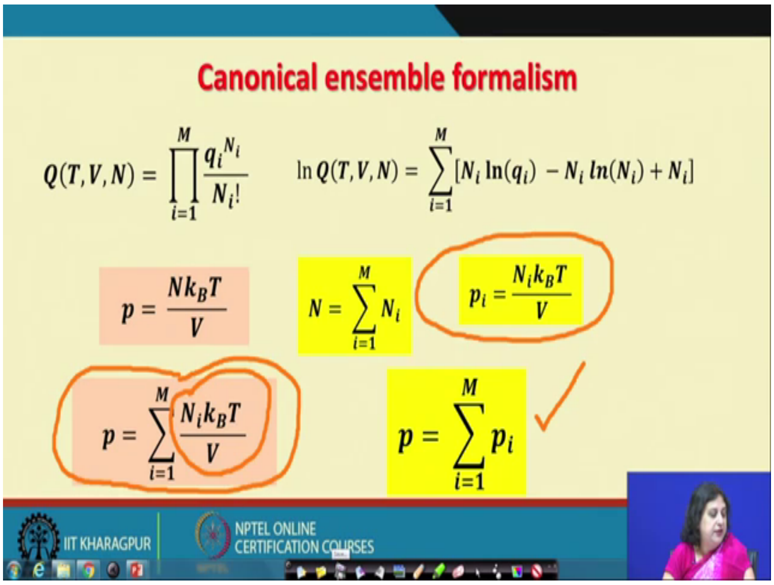

Canonical ensemble formalism

$$Q(T,V,N) = \prod_{i=1}^{M} \frac{q_i^{N_i}}{N_i!} \qquad \ln Q(T,V,N) = \sum_{i=1}^{M} [N_i \ln(q_i) - N_i \ln(N_i) + N_i]$$

$$p = \frac{Nk_BT}{V} \qquad N = \sum_{i=1}^{M} N_i \qquad p_i = \frac{N_ik_BT}{V}$$

$$p = \sum_{i=1}^{M} \frac{N_ik_BT}{V} \qquad p = \sum_{i=1}^{M} p_i \checkmark$$

This by definition is the partial pressure of the ith component. Now look back what is it that we have achieved over here. We have achieved in writing down the total pressure of the system as a sum of this quantity. And this quantity is nothing but the partial pressure of each of the components present in the system by definition. And then what you do is combine you these 2, and write this down and that is nothing but daltons law of partial pressure. So, here the key to understanding the derivation, is that you have N different types of particles which are not interacting with each other. Now for a given type, you have anion molecules or anion atoms which are identical to each other. So, you must be very careful when you write down the total canonical partition function of the system.

And the rest of it is daily routine, and in knowing the definition of the partial pressure, that you can obtain the daltons law. So, what we have learnt from this particular lecture is a fact that if I have an ideal gas, starting from the Hamiltonian, I can model the microscopic state of the molecules or the atoms present in the system. And then using the formalism of molecular thermodynamics within the canonical (Refer Time: 28:43) I can try and reproduce many of the experimental results, that are known in the literature, that were derived from different kinds of experiments. And apparently there was no connection between each other except for the fact that all these working systems obeyed the ideal gas law.

Therefore, the success of molecular thermodynamics principles that we are discussing here is that we can start by microscopic modeling of an assembly of atoms or molecules, and go ahead and have a look at how these molecules this assembly of a very large number of molecules; for example, I can given temperature and constant volume, can give rise to specific thermodynamic properties like a specific temperature dependence of the heat capacity of ideal gases, or the daltons law of partial pressure, or even the very curious case of molecular hydrogen gas.

Thank you.