Fundamentals of Statistical Thermodynamics

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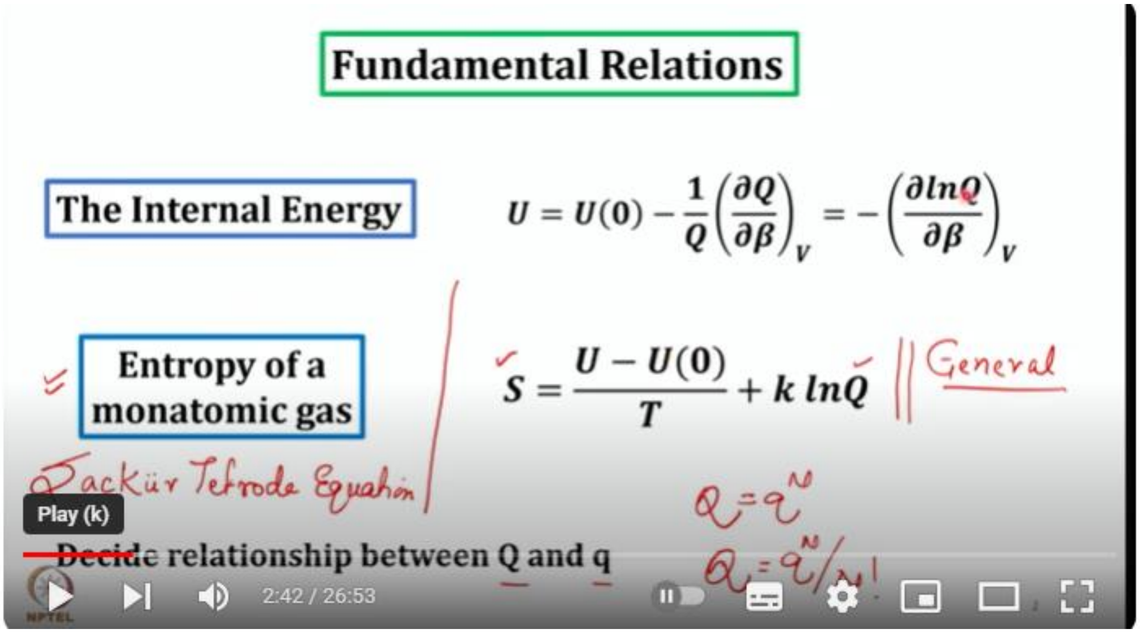
Lecture 60: Recap-2

Welcome back to the concluding part of the course on Statistical Thermodynamics. In the previous lecture, we revisited some of the concepts with which we started. We understood molecular partition function, we also understood canonical partition function, we understood the significance of first starting with non-interacting systems and then switching over to interacting systems. We also talked about the ensembles and then we talked about connection of canonical partition function with the molecular partition function. Various equations which connect internal energy or entropy are here U is equal to U° minus 1 by q δq by δβ at constant v or δlog q by δβ at constant volume. And then this is a general equation not specifically applicable to monatomic gas.

See Slide Time: 2:42



Fundamental Relations

The Internal Energy $U = U(0) - \frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V = -\left(\frac{\partial lnQ}{\partial \beta}\right)_V$

✓ **Entropy of a monatomic gas** ✓ $S = \frac{U - U(0)}{T} + k\, ln\check{Q}$ || General

Sackür Tetrode Equation

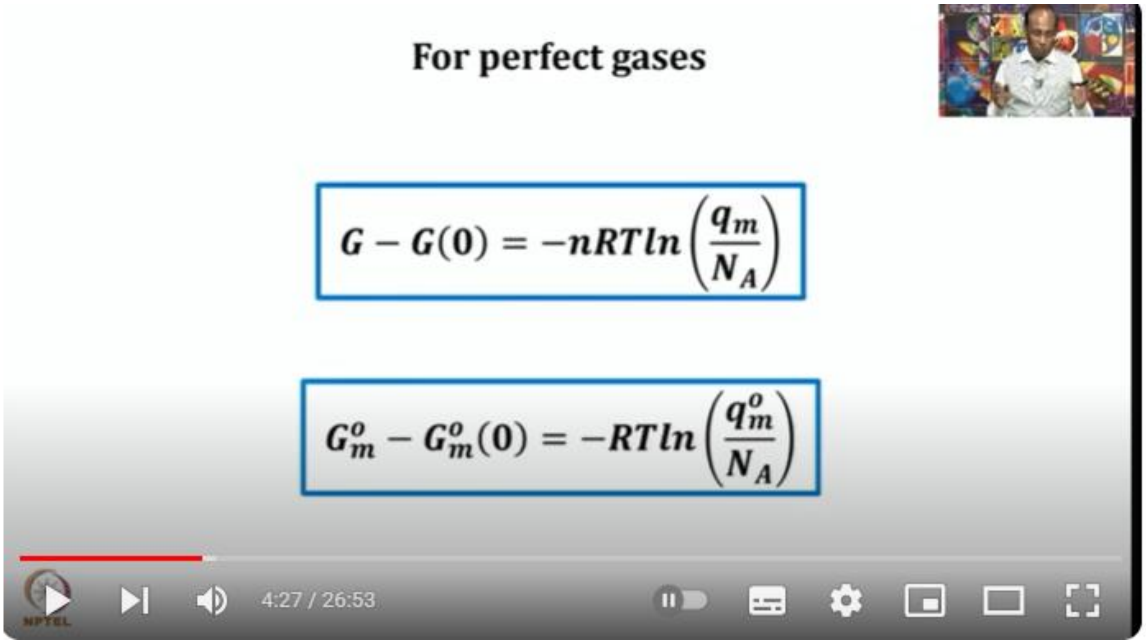
~~Decide~~ relationship between $\underline{Q}$ and $\underline{q}$

$Q = q^N$

$Q = q^N/N!$

General equation that S can be connected to canonical partition function, but then we have to be careful to decide the relationship between q and q that is whether you want to use q is equal to q raise to the power n or you want to use q is equal to q raise to the power n by n factorial. And later on, we extend we can extend this equation to derive another equation for entropy of a monatomic gas and that you remember we called as sackur tetrode equation that is different, but this is the general expression for the entropy connecting entropy with internal energy and canonical partition function. The relation of internal energy with canonical partition function is also given in this slide. We kept on further developing more relations for example, connection of canonical partition function with Helmholtz free energy which was a minus a 0 is equal to minus k T log q very important relation for Gibbs free energy.

See Slide Time: 4:27



For perfect gases

$$\boxed{G - G(0) = -nRT\ln\left(\frac{q_m}{N_A}\right)}$$

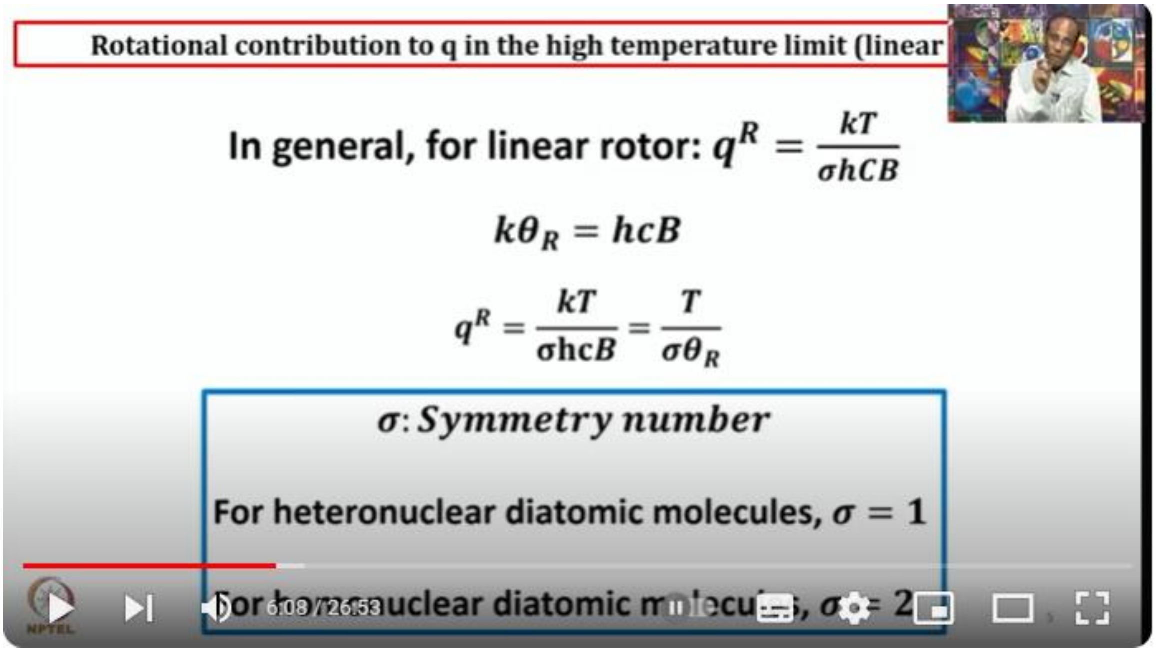
$$\boxed{G_m^o - G_m^o(0) = -RT\ln\left(\frac{q_m^o}{N_A}\right)}$$

Gibbs free energy is one of the most important thermodynamic quantity in chemical or statistical thermodynamics. Why I say Gibbs free energy is one of the most important thermodynamic quantities because whenever we say criteria of spontaneity the first thing that comes to mind is that the reaction will proceed in the direction in which the Gibbs free energy decreases and it will come to an equilibrium where ΔG becomes 0 at constant temperature and pressure and that is why this expression for Gibbs free energy becomes very very important. Later on, we connected canonical partition function with enthalpy and pressure almost all thermodynamic quantities now have been connected with the canonical partition function and we have already discussed how to recover molecular partition function from canonical partition function. Then in order to simplify the processes simplify the equations we thought that let us first of all consider only perfect gases. We know the differences between perfect gases and real gases.

In perfect gases no intermolecular interaction. In real gases deviation from ideality and that deviation from ideality comes due to onset of intermolecular interaction. So, for gases we derive this equation G minus G (0) is equal to minus nRT log n or you consume n and convert G to G_m. We also invoked the standard state condition. The advantage of invoking standard state condition with Gibbs free energy is that you can then later on you can then later on connect this with ΔG (0) is equal to minus RT log k. That is the advantage of connecting G with the standard state condition. Let me again briefly tell what is a standard state? Standard state means the substance should be pure pressure should be 1 bar temperature can be m. Translational contribution to partition function we already discussed in the previous lecture, but when the molecule is a diatomic. If the molecule is monatomic, it will have only translational degree of freedom. It may also have electronic contribution, but usually the electronic energy levels are far separated.

So, therefore, that contribution is nearly 1. Once you deal with the diatomic or triatomic or polyatomic molecule now you will have translational contribution, rotational contribution, vibrational contribution, electronic contribution. We discussed that for rotational contribution you can deal with linear rotor you can deal with non-linear rotor. For linear rotor we derived this expression q_r is equal to k T by σ h c b σ is the symmetry number k is constant Boltzmann constant h is constant Planck's constant c is constant speed of light. That means, you have this rotational constant b b is h cross by 4 π c_i and T is temperature.

See Slide Time: 6:08



Rotational contribution to q in the high temperature limit (linear

In general, for linear rotor: $q^R = \frac{kT}{\sigma hCB}$

$$k\theta_R = hcB$$

$$q^R = \frac{kT}{\sigma hcB} = \frac{T}{\sigma\theta_R}$$

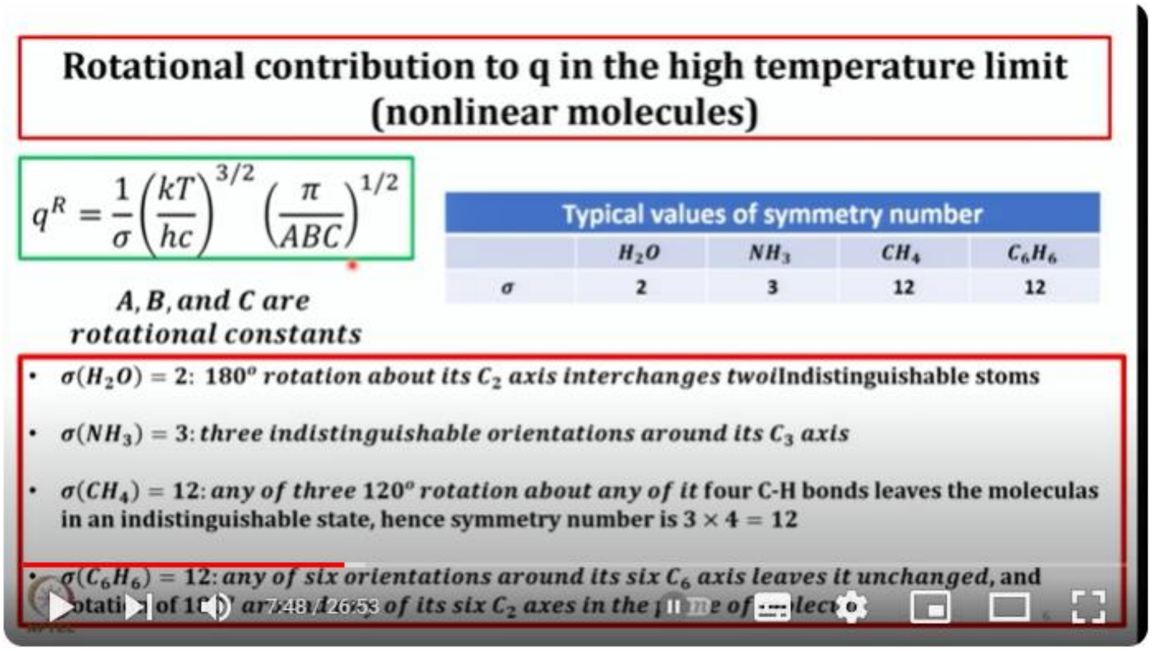
σ: Symmetry number

For heteronuclear diatomic molecules, $\sigma = 1$

For homonuclear diatomic molecules, $\sigma = 2$

We also brought in the importance of rotational temperature that this equation is valid if the temperature is higher than rotational temperature. So, this was the expression for a linear rotor, but the molecule for example, if it is a triatomic molecule then the triatomic molecule can also be non-linear. For example, you have water you have h d o these are non-linear molecules. So, if the molecules is non-linear then we discussed that the molecular partition function takes up this form q r is equal to 1 by σ into k T by h c raise to the power 3 by 2 into π by a b c square root here a b c are rotational constants for the rotation of molecule in three dimensions. The significance of symmetry number cannot be ignored and the symmetry number of several molecules at least four molecules are given over here.

See Slide Time:7:48



Rotational contribution to q in the high temperature limit (nonlinear molecules)

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2}$$

A, B, and C are rotational constants

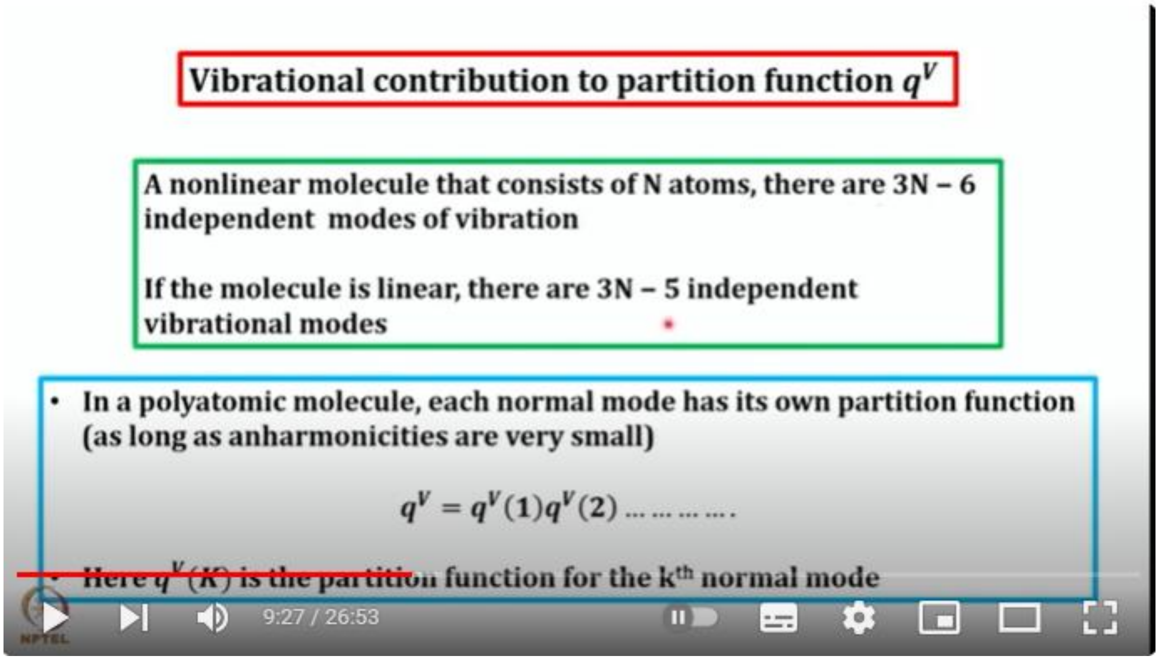
Typical values of symmetry number

	H_2O	NH_3	CH_4	C_6H_6
σ	2	3	12	12

- $\sigma(H_2O) = 2$: 180° *rotation about its* C_2 *axis interchanges two*Indistinguishable stoms
- $\sigma(NH_3) = 3$: *three indistinguishable orientations around its* C_3 *axis*
- $\sigma(CH_4) = 12$: *any of three* 120° *rotation about any of it* four C-H bonds leaves the moleculas in an indistinguishable state, hence symmetry number is $3 \times 4 = 12$
- $\sigma(C_6H_6) = 12$: *any of six orientations around its six* C_6 *axis leaves it unchanged*, and [illegible]otati[illegible] of 1[illegible] ar[illegible] *of its six* C_2 *axes in the* [illegible] *of* [illegible]lec[illegible]

So, we knew how to evaluate how to calculate the rotational contribution. If you carefully examine this equation k is constant h is constant σ is constant for a molecule c is constant and if you fix constant temperature π is constant that means, rotational contribution will depend upon a b c and what is b b is h cross by 4 π c_i I is equal to μ r^2 that means, you need the bond length and you need the reduced mass. With that kind of information, you can calculate the rotational contribution. After rotational contribution we started discussing vibrational contribution because when you go beyond atom you have molecule molecules in molecule the atoms can vibrate also around their bond. We talked about how many normal modes of vibration are there for example, for a non-linear molecule we discussed that if there are n atoms then 3 n minus 6 independent modes of vibration and 3 n minus 5 independent vibrational modes if the molecule is linear.

See Slide Time: 9:27



Vibrational contribution to partition function q^V

A nonlinear molecule that consists of N atoms, there are 3N – 6 independent modes of vibration

If the molecule is linear, there are 3N – 5 independent vibrational modes

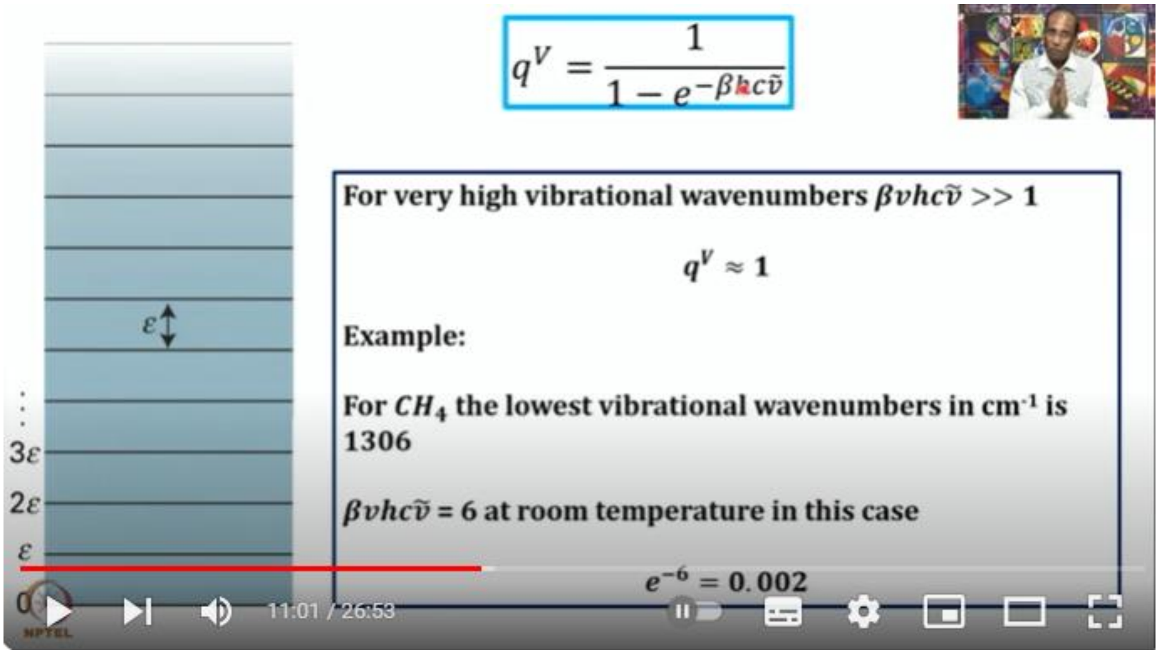
- In a polyatomic molecule, each normal mode has its own partition function (as long as anharmonicities are very small)

$$q^V = q^V(1)q^V(2)\ldots\ldots\ldots\ldots.$$

- Here $q^V(K)$ is the partition function for the kth normal mode

As we talked earlier that the overall partition function is multiplicative that means, if there are several normal modes of vibration then the vibrational partition function is equal to the vibrational contribution due to first normal mode into vibrational contribution due to second normal mode into so on so on. So, overall q v will be equal to q_{v1} into q_{v2} into q_{v3} and so on all right. To derive an expression for a non-linear molecule for vibrational contribution to partition function we took a very simple case and what was that simple case is to take uniform ladder of energy levels. Look into this diagram this is a uniform ladder of energy level what is that uniform ladder of energy level is the energy separation between two states is constant and then in that case the q_v turns out to be equal to 1 over 1 minus exponential minus β h c ν bar β is 1 over k T in terms of energy orders amongst translational rotational vibrational electronic the order is like this first translational then the next higher is rotational the next higher is vibrational the next higher is electronic. This is also going to be the order of temperature to achieve excitation for translational rotational vibration electronic.

See Slide Time: 11:01



$$q^V = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}}$$

For very high vibrational wavenumbers $\beta v hc\tilde{\nu} >> 1$

$$q^V \approx 1$$

Example:

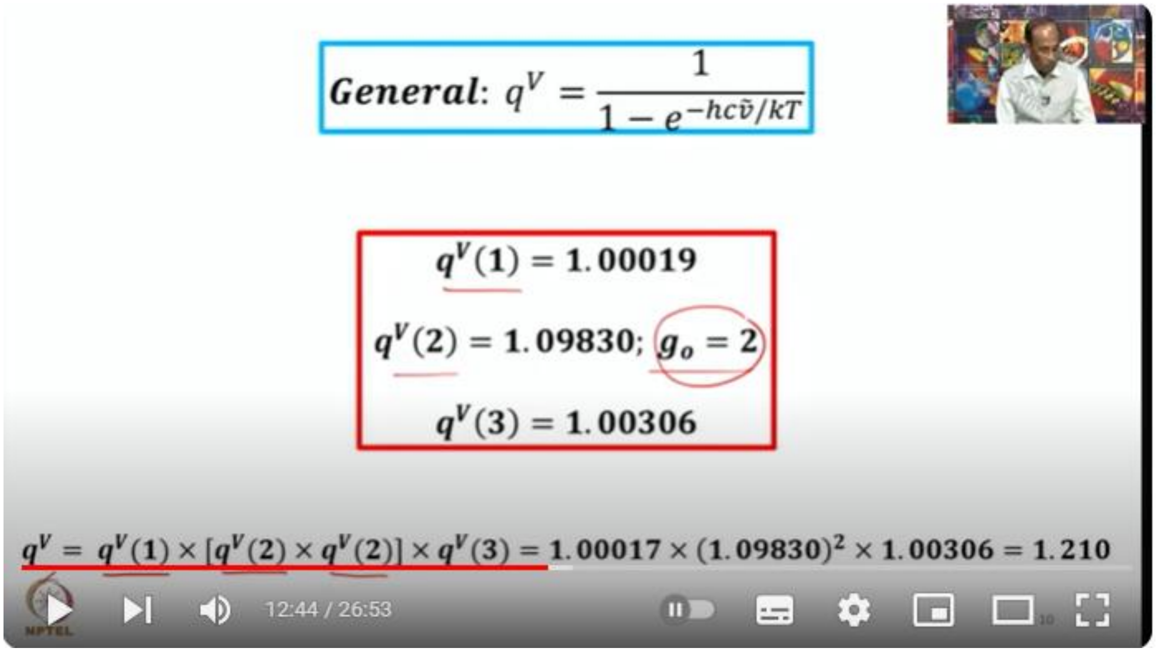
For CH_4 the lowest vibrational wavenumbers in cm^{-1} is 1306

$\beta v hc\tilde{\nu} = 6$ at room temperature in this case

$$e^{-6} = 0.002$$

Under normal conditions of temperature the energy is not sufficient to excite the molecules particles to higher or upper vibrational levels. If most of the molecules are in the ground state of the vibration in that case your vibrational contribution to partition function usually will be very close to 1. Keeping this in mind and also recognizing that there is a temperature called characteristic vibrational temperature the partition function can also be expressed in terms of characteristic vibrational temperature provided the temperature is high. Then this is another elaboration of the statement that the overall partition function is multiplicative here you have first normal mode which is the number is 1.000194 second mode the molecular partition function the number is 1.09830, but this is doubly degenerate third one 1.0030 the overall vibrational partition function will be first one into second one and since second degeneracy is two it will appear twice, but in a multiplicative mode then you have the third one overall value is 1.210.

See Slide Time: 12:44



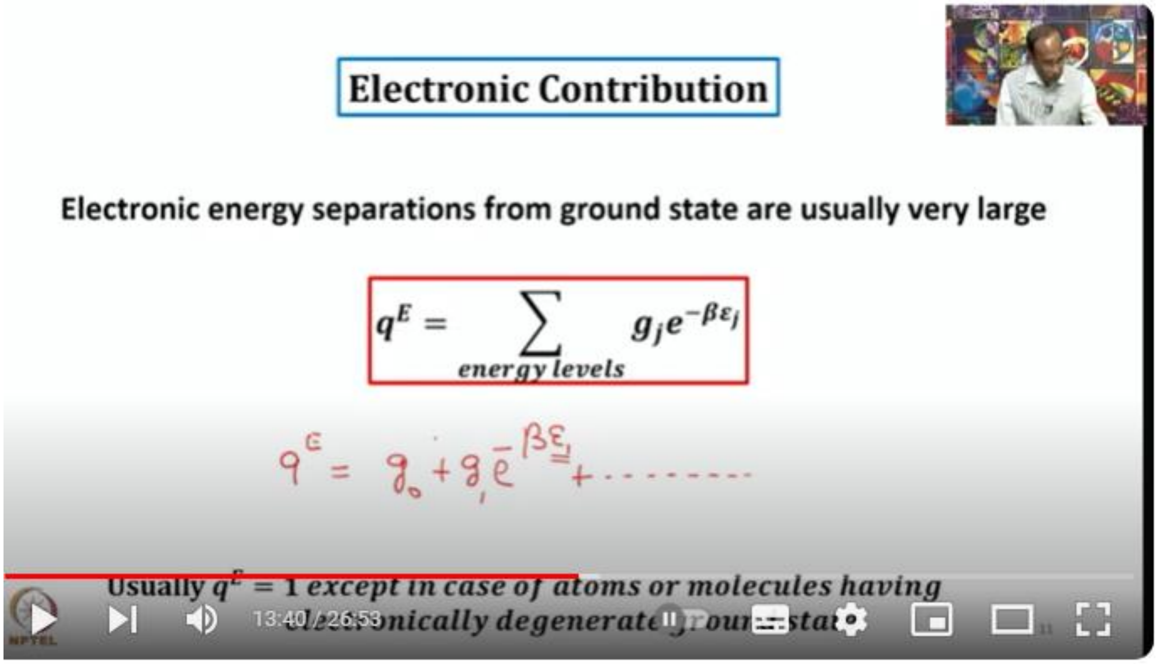
$$\boxed{\textbf{General}: q^V = \frac{1}{1 - e^{-hc\tilde{\nu}/kT}}}$$

$$\boxed{\begin{gathered} q^V(1) = 1.00019 \\ q^V(2) = 1.09830;\ g_o = 2 \\ q^V(3) = 1.00306 \end{gathered}}$$

$$q^V = q^V(1) \times [q^V(2) \times q^V(2)] \times q^V(3) = 1.00017 \times (1.09830)^2 \times 1.00306 = 1.210$$

Still, you see the value of the vibrational contribution to partition function is close to 1 only that means, not many molecules' particles they are excited to upper vibrational states under normal temperature conditions and since we discussed that the next higher energy levels the separation is electronic. So, therefore, if I expand this I have q electronic is equal to G_0 plus G_1 exponential minus βE 1 plus so on and since these values are very high usually the electronic contribution to the partition function is equal to degeneracy of the ground state keep that in mind.

See Slide Time:13:40



Electronic Contribution

Electronic energy separations from ground state are usually very large

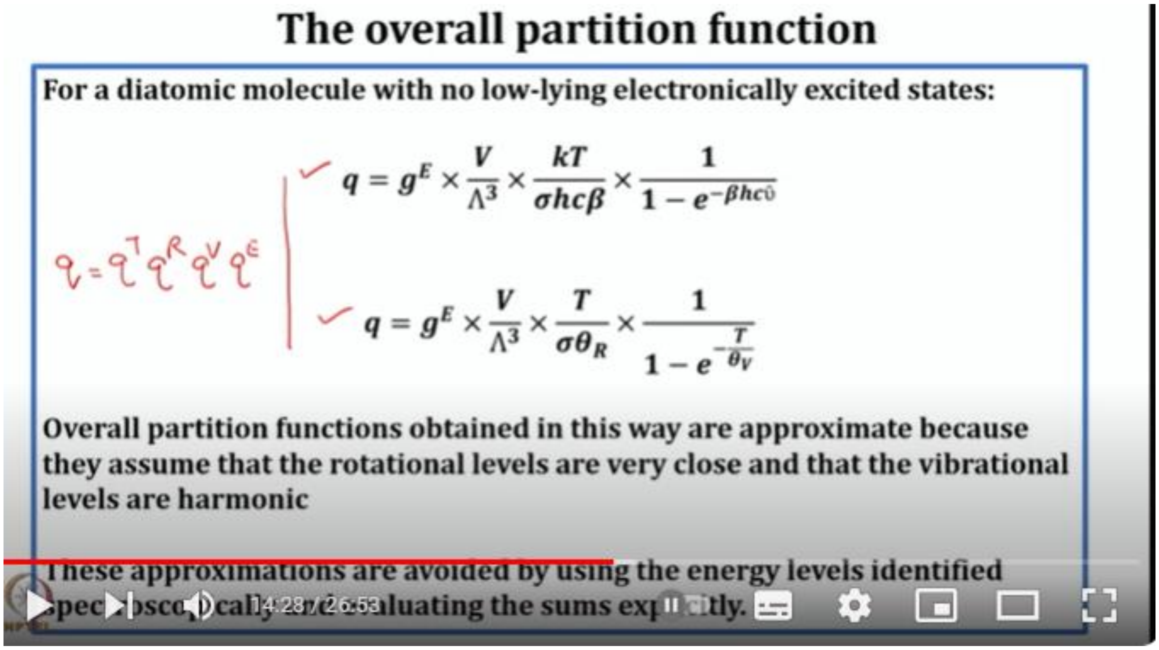
$$\boxed{q^E = \sum_{energy\ levels} g_j e^{-\beta\varepsilon_j}}$$

$$q^E = g_0 + g_1 e^{-\beta\varepsilon_1} + \cdots\cdots$$

Usually $q^E = 1$ except in case of atoms or molecules having electronically degenerate ground state

Now overall partition function overall q is equal to q translational q rotational q vibrational q electronic and when you substitute their expressions you will have either this or you want to express in terms of characteristic rotational and vibrational temperature you have another one. So, that means, whenever you are dealing with a certain problem in which the molecule has all degrees of freedom translational degree of freedom rotational degree of freedom vibrational degree of freedom electronic degree of freedom you will need to know the overall partition function therefore, you will need to evaluate q^T q^R q^V q^T. While evaluating q^R you need to know whether the rotor is linear or it is non-linear because the expressions for linear rotor and non-linear rotor partition function is different. Then further we connected the molecular partition function with the mean energy translational contribution for one dimension was 1 by 2 k T and for a molecule free to move in three dimensions it was 3 by 2 k T. If the temperature is not high the rotational contribution to mean energy turned out to be a complicated expression, but if the temperature is very high, we find out it is equal to k T.

See Slide Time: 14:28



The overall partition function

For a diatomic molecule with no low-lying electronically excited states:

$$q = q^T q^R q^V q^E$$

$$q = g^E \times \frac{V}{\Lambda^3} \times \frac{kT}{\sigma hc\beta} \times \frac{1}{1 - e^{-\beta hc\tilde{\nu}}}$$

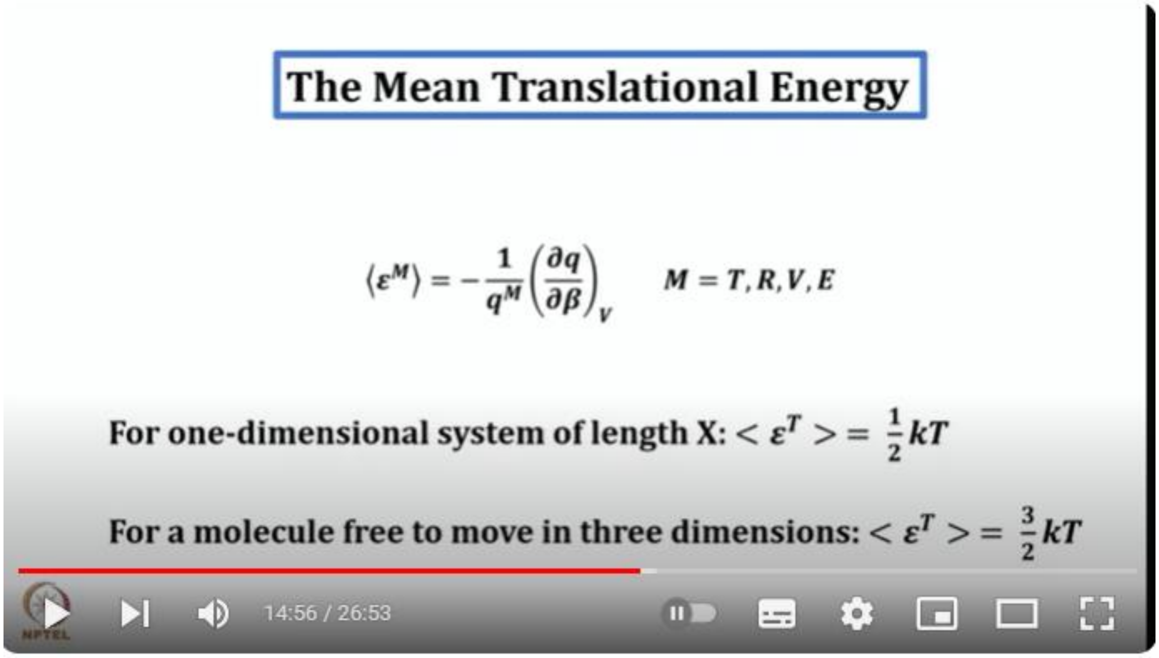
$$q = g^E \times \frac{V}{\Lambda^3} \times \frac{T}{\sigma\theta_R} \times \frac{1}{1 - e^{-\frac{T}{\theta_V}}}$$

Overall partition functions obtained in this way are approximate because they assume that the rotational levels are very close and that the vibrational levels are harmonic

These approximations are avoided by using the energy levels identified pec[illegible]osco[illegible]cal[illegible]aluating the sums exp[illegible]itly.

For vibration simply if the temperature is very high then it is equal to k T otherwise at other temperatures, we derived another equation where mean vibrational energy can be evaluated this is in the high temperature limit. Once you have information on mean energy mean energy and internal energy are correlated with each and times mean energy is equal to total energy and total energy E is connected to U as U minus U (0) and C_v is connected to U that means, C_v is connected to E here you can see that. And since β is equal to 1 by k T if you have any derivative with respect to temperature you can further transform it to another equation where the expression is derivative with respect to β. So, therefore, you can use this expression or you can use this expression to obtain heat capacity with several considerations to translation rotation vibration electronic. We came up with an expression which could be used to estimate the constant molar volume heat capacity this was a very important observation that when the temperature let us say for a gas you consider a gas in gas the molecules gas molecules will always have translational degree of freedom that means, 3 by 2 R contribution will always be there and if it is a linear rotor you keep on increasing the temperature another R contribution will come.

See Slide Time: 14:56



The Mean Translational Energy

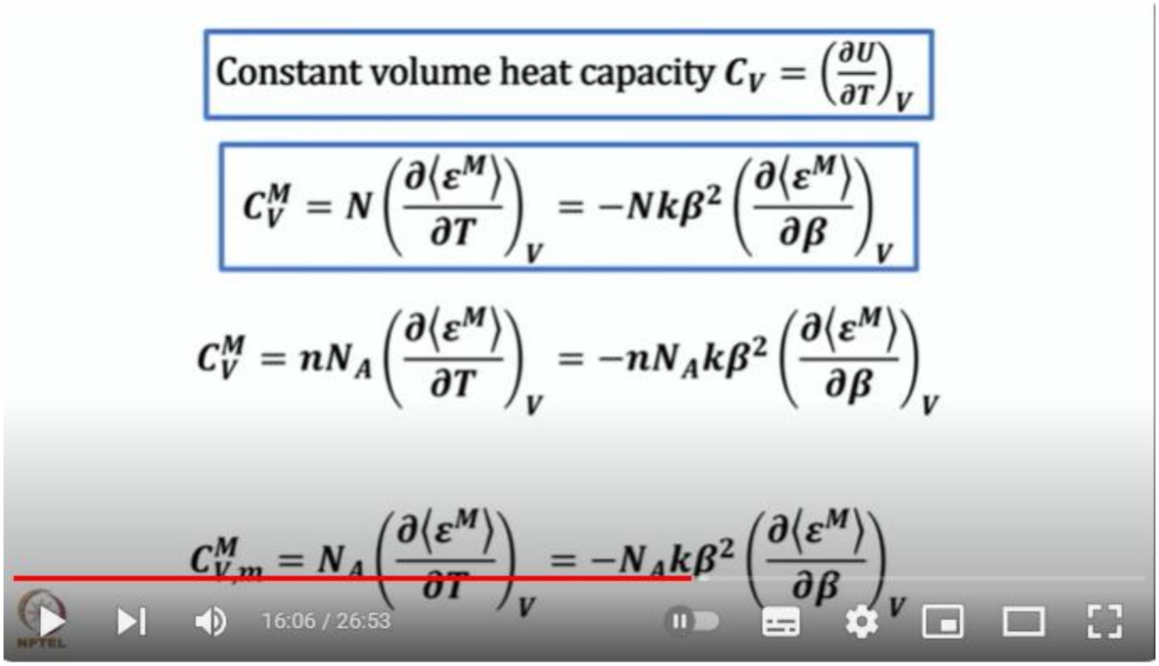
$$\langle \varepsilon^M \rangle = -\frac{1}{q^M}\left(\frac{\partial q}{\partial \beta}\right)_V \qquad M = T, R, V, E$$

For one-dimensional system of length X: $< \varepsilon^T > = \frac{1}{2}kT$

For a molecule free to move in three dimensions: $< \varepsilon^T > = \frac{3}{2}kT$

If you further keep on increasing then another R contribution come for a diatomic molecule and if you consider diatomic molecule and you further keep on increasing temperature then diatomic molecule will undergo dissociation and once diatomic molecule undergo dissociation diatomic means two atoms will convert diatomic in the sense diatomic molecule will be like X_2 will dissociate to 2X and you will have two times translational contribution because atoms will have only translational contribution. Finally, having discussed all other thermodynamic quantities we ended up by connecting molecular partition function with equilibrium constant remember that equilibrium constant is very important thermodynamic quantity because it tells us how much product is formed not only academically, but industrially also it is a very important thermodynamic quantity. We established this relation of equilibrium constant with the molecular partition function and ΔE° which is the difference in the zero-point energies that means, in order to evaluate equilibrium constant what information do we need to have we need to know the molecular partition function and this molecular partition function is product of translation, rotation, vibration and electronic. We also need to know what is the value of ΔE° that is the difference in zero-point energies. After connecting to K, the equilibrium constant as I said that equilibrium constant is one of the remarkable thermodynamic quantities because if I go back, you have equilibrium constant connected to ΔG ΔG° is equal to minus RT log k.

See Slide Time: 16:06



Constant volume heat capacity $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$$C_V^M = N\left(\frac{\partial\langle\varepsilon^M\rangle}{\partial T}\right)_V = -Nk\beta^2\left(\frac{\partial\langle\varepsilon^M\rangle}{\partial \beta}\right)_V$$

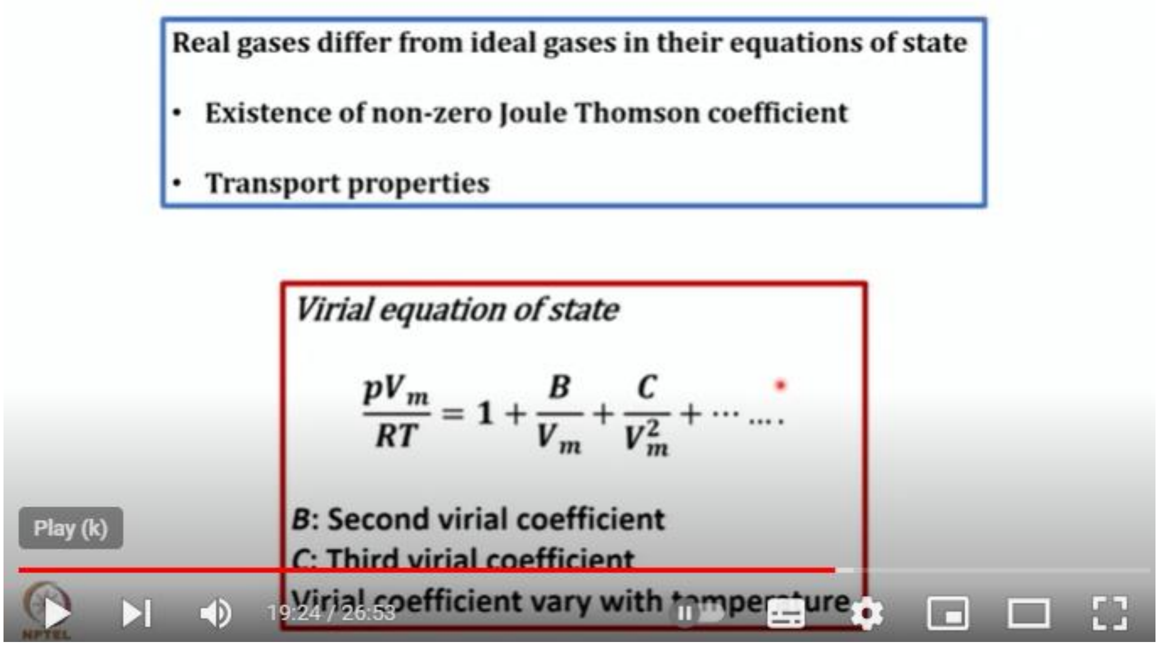
$$C_V^M = nN_A\left(\frac{\partial\langle\varepsilon^M\rangle}{\partial T}\right)_V = -nN_Ak\beta^2\left(\frac{\partial\langle\varepsilon^M\rangle}{\partial \beta}\right)_V$$

$$C_{V,m}^M = N_A\left(\frac{\partial\langle\varepsilon^M\rangle}{\partial T}\right)_V = -N_Ak\beta^2\left(\frac{\partial\langle\varepsilon^M\rangle}{\partial \beta}\right)_V$$

Another very important thermodynamic relation Log k ΔT at constant pressure is Δvan't half H° by RT square. We realize the significance of equilibrium constant here once we have knowledge about equilibrium constant we can talk about spontaneity of the process and once we have equilibrium constant as a function of temperature, we can get enthalpy change of the reaction that is the beauty of thermodynamics that sometimes without doing experiments you can even calculate the things. So, here the equilibrium constant that I mentioned this equilibrium constant it can be determined by calorimetric methods it can be determined by spectroscopic methods. So, that means, this highlights that even if we get the equilibrium constant by means of spectroscopy, we can get enthalpy change. Enthalpy change a property which is usually determined from calorimetry after equilibrium constant up to that point we were dealing with the ideal systems.

Now, how to deal with non-ideal systems because majority of the things are non-ideal. Ideality only arises under special conditions for example, when we talk about the gases the gases start behaving ideal when the pressure is very very low because then the molecules are very far apart from each other and we know that the real gases they differ from the ideal gases because in the real gases there is onset of intermolecular interactions. There what we did was we introduced virial coefficients the equation of state called virial equation of state was PV_m by R T is equal to 1 plus b by m plus c by V_m square etcetera etcetera where b is the second virial coefficient c is the third virial coefficient and these virial coefficients have information about intermolecular interactions. You can compare remember ideal gas equation PV is equal to n R T versus Van der Waals equation. In Van der Waals equation you brought in a and b which correspond to attraction and repulsion representations.

See Slide Time:19:24



Real gases differ from ideal gases in their equations of state

- **Existence of non-zero Joule Thomson coefficient**
- **Transport properties**

Virial equation of state

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots \ldots$$

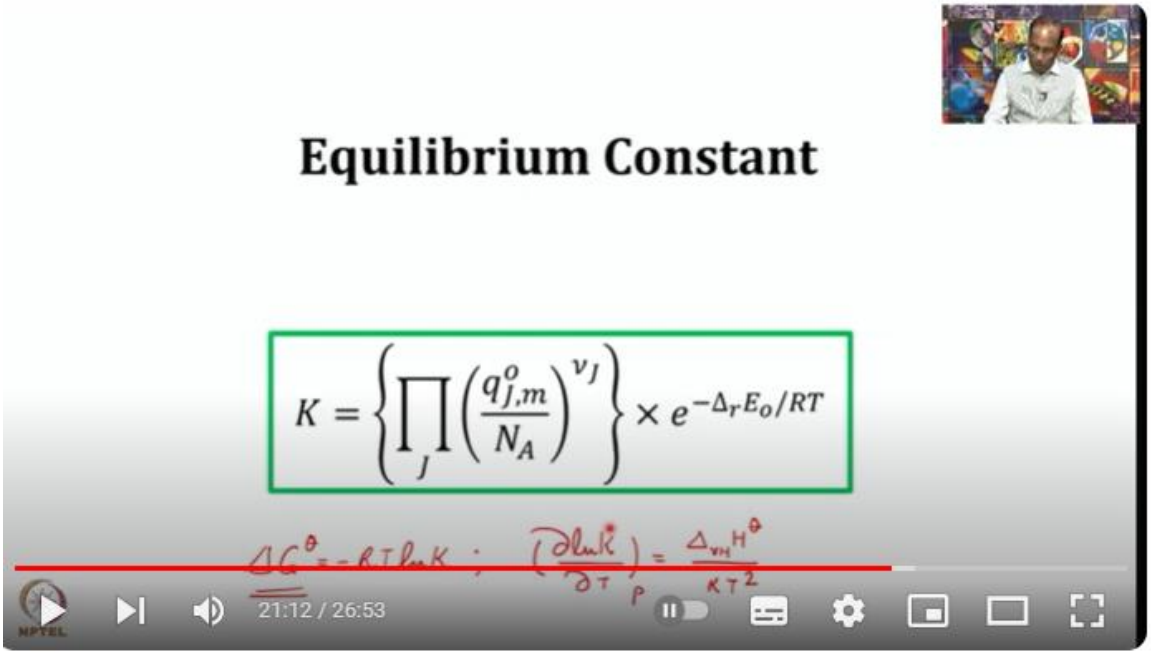
B: Second virial coefficient

C: Third virial coefficient

Virial coefficient vary with temperature

So, similarly here the virial coefficient b virial coefficient c these are indicators of intermolecular interactions or the deviations from ideality. Most of the discussion that we had was based upon Maxwell Boltzmann distribution. We extended the discussion and brought in compartmentalization to give another angle to our discussion and derived the Bose Einstein distribution function. The treatment was similar, but the final result although looks nearly similar, but differs slightly. In the treatment of Bose Einstein distribution function, we did not put any restriction of Pauli exclusion principle.

See Slide Time: 21:12



Equilibrium Constant

$$\boxed{K = \left\{\prod_J \left(\frac{q^o_{J,m}}{N_A}\right)^{\nu_J}\right\} \times e^{-\Delta_r E_0/RT}}$$

$$\underline{\underline{\Delta G^\theta}} = -RT\ln K \; ; \; \left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta_{rH} H^\theta}{RT^2}$$

Restriction of Pauli exclusion principle was introduced in Fermi direct distribution where we did not put more than two particles more than two electrons in the same cell. Here also the treatment the final look of the equation the final look of the equation is nearly the same as that for the Maxwell Boltzmann or Bose Einstein distribution function although with the some deviation. Later on, we brought in some discussion on how to deal with the liquids and there we talked about radial distribution function. With the discussion on radial distribution function, we then wanted to check how the scenario will be in the solid state. Due to the limited availability of time in this course we could only restrict our discussion up to radial distribution function. For more advanced level of understanding the further advanced level of statistical thermodynamics will be required. We started with an aim of understanding statistical thermodynamics that means the link between individual molecular properties and bulk thermodynamic properties. We achieved the journey target journey goal by first understanding molecular partition function, canonical partition function then recovering molecular partition function from canonical partition function and connecting with all the thermodynamic quantities. So, we discussed Gibbs free energy, Helmholtz free energy, enthalpy, pressure, heat capacity, internal energy, equilibrium cost. Once we have information about these thermodynamic quantities then we have a complete characterization rather thermodynamic characterization of the system under investigation. I hope this course was useful to you with an understanding that all these thermodynamic quantities can be obtained by employing spectroscopy. Wish you all the best and thank you very much.

Thank you.