Introduction to Chemical Thermodynamics and Kinetics
Dr. Arijit Kumar De
Department of Chemistry
Indian Institute of Science Education and Research, Mohali

Lecture – 09
First law – part 4

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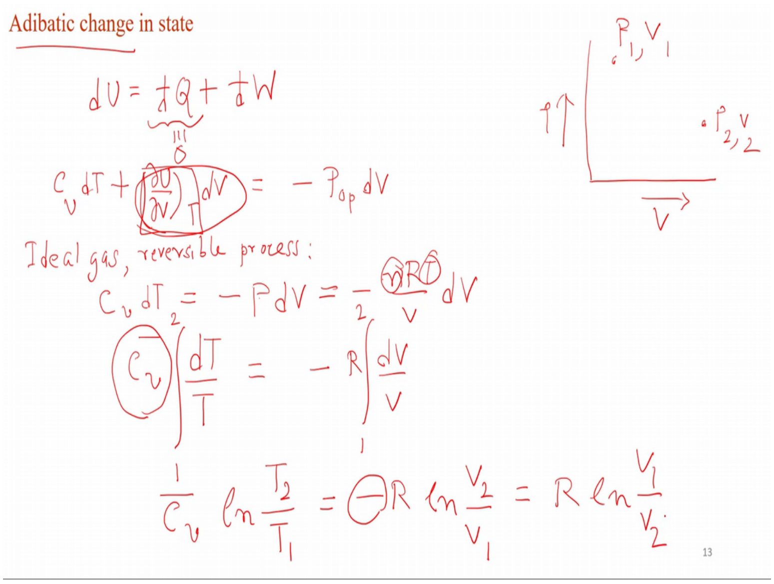

Adibatic change in state

$$dU = \underbrace{\text{đ}Q}_{\substack{\shortparallel \\ 0}} + \text{đ}W$$

$$C_V\,dT + \left(\frac{\partial U}{\partial V}\right)_T dV = -P_{op}\,dV$$

Ideal gas, reversible process:

$$C_v\,dT = -P\,dV = -\frac{nRT}{V}\,dV$$

$$C_v\int_1^2 \frac{dT}{T} = -R\int_1^2 \frac{dV}{V}$$

$$\frac{1}{C_v}\ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1} = R\ln\frac{V_1}{V_2}$$

We saw that in the Joule Thomson effect the experiment was carried out in an thermally insulating chamber or sealed tube by thermally insulating we mean that the wall which separates the system from the surroundings does not allow any heat flow across it, which means heat cannot flow from the surrounding into the system or the other way in such case if a transformation happens we call that transformation as Adiabatic transformation or Adiabatic change.

Now, let us try to understand what will be the pressure volume work associated with an Adiabatic change in state now as before let us consider that the system is undergoing some change from an initial state P 1 V 1 to a final state P 2 V 2. So, using the first law we can write d U is d cross Q plus d cross W again remember that we are using d for exact differential and d cross for in exact differential because internal energy U is a state function whereas, heat denoted as Q and work denoted as W are path functions.

Now, for an adiabatic change in state d cross Q must be equal to 0 as there is no heat flow across the boundary. So, we can write using the relationship for d U that we developed using the condition when we make a change in constant volume. So, we had for d U C V d T plus del U del V T d V and on the right hand side for d cross W we have the expression for pressure volume work as usual.

Now, let us consider an ideal gas and also further consider this process is a reversible process now we already discussed that for ideal gas del U del V T this term is 0. So, we have C V d T is nothing, but minus P opposing d V, but for a reversible change remember the change is carried out by changing the external pressure infinitesimally small amount in each step which means the transformation in is done in a manner such that the system always tries to adjust with the external pressure.

So, the external pressure is nothing, but the pressure of the system itself. So, it is P d V and using ideal gas equation we can write n R T by V d V now we can just rearrange by writing C V bar where I am dividing the C V by n by number of moles which means C V bar is nothing, but the molar heat capacity at constant volume we are also bringing down the temperature here. On right hand side we have then minus R d V by V now we can integrate between the 2 limits 1 and 2 now here we have approximated that C V bar is a constant it does not depend on temperature it is an approximation. Now the frame of the integrand will be it is basically integral d x by x. So, the integral is nothing, but l n T 2 by T 1 is equal to minus R l n V 1 by V 2 now we can use this minus sign.

Remember that minus l n A by B is nothing, but l n B by A. So, we can rewrite R l n V 2 by V 1.

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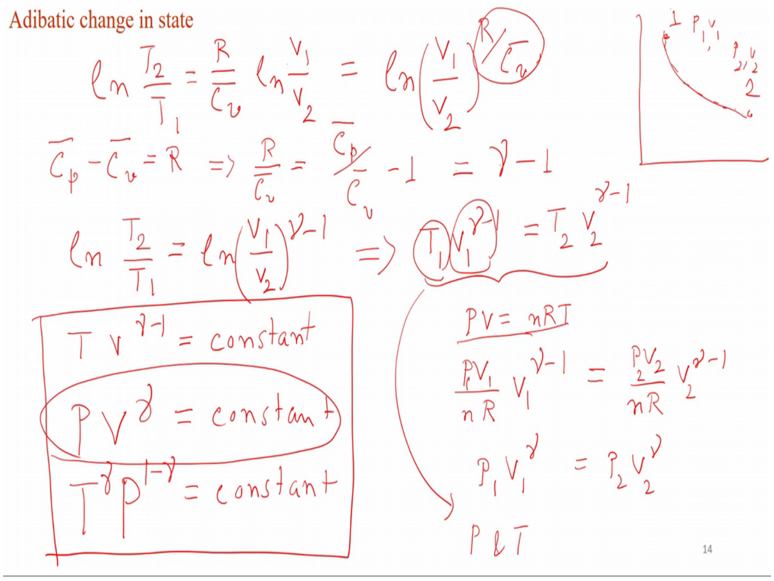

Adibatic change in state

$$\ln\frac{T_2}{T_1} = \frac{R}{\bar{C}_v}\ln\frac{V_1}{V_2} = \ln\left(\frac{V_1}{V_2}\right)^{\boxed{R/\bar{C}_v}}$$

$$\bar{C}_p - \bar{C}_v = R \Rightarrow \frac{R}{\bar{C}_v} = \frac{\bar{C}_p}{\bar{C}_v} - 1 = \gamma - 1$$

$$\ln\frac{T_2}{T_1} = \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1} \Rightarrow \underbrace{\boxed{T_1}\boxed{V_1^{\gamma-1}} = T_2 V_2^{\gamma-1}}$$

$$\boxed{\begin{array}{l} T V^{\gamma-1} = \text{constant} \\ \boxed{P V^{\gamma} = \text{constant}} \\ T^{\gamma} P^{1-\gamma} = \text{constant} \end{array}}$$

$$\underline{PV = nRT}$$

$$\frac{P_1V_1}{nR} V_1^{\gamma-1} = \frac{P_2V_2}{nR} V_2^{\gamma-1}$$

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

P & T

So, we got if we further rearrange l n T 2 by T 1 is R divided by C V bar l n V 2 by V 1 which is and the right hand side will be minus R l n V 2 by V 1 and remember we can use this minus sign by using the relationship minus l n A by B is nothing, but l n B by A. So, this relation becomes R l n V 1 by V 2. So, we can further rearrange by writing l n T 2 by T 1 is nothing, but R by C V, C V bar in this case it is a molar heat capacity V 1 by V 2 or we can actually take it through the power by using the fact A l n B is nothing, but l n B to the power A.

Now, we have to figure out this value of R divided by C V bar, since we are using ideal gas we know that the difference between the molar heat capacities for an ideal gas is nothing, but R the molar gas constant. So, we can easily figure out what is R by C V bar it is nothing, but the ratio of the molar heat capacities minus 1 and this ratio we denote as a symbol gamma. So, gamma is the ratio of molar heat capacities C P by C V molar heat capacity at constant pressure divided by molar heat capacity at constant volume.

So, we can rewrite that l n T 2 by T 1 is l n V 1 by V 2 to the power gamma minus 1 or we can get rid of this l n and write T 1 V 1 to the power gamma minus 1 is nothing, but T 2 V 2 to the power gamma minus 1. So, we get a very interesting relationship that T 1 V 1 to the power gamma minus 1 is constant remember this was very different for an ideal gas for ideal gas and for an ideal gas undergoing isothermal change.

So, we can actually develop further relation using this relationship which we just got between temporary and volume we can plug in the ideal gas equation P V equal to n R T and get relationship between say pressure and volume. So, if you write T if we substitute T and write P V by n R we get P V 1 divided by n R V 1 to the power gamma minus 1 is equal to P V 2 divided by n R V 2 to the power gamma minus 1.

So, what we get is P 1 this should be P 1 V 1 to the power gamma minus 1 is P 2 V 2 to the power gamma minus 1 this gamma minus 1 and V 1 gets multiplied to get P 1 V 1 to the power gamma is equal to P 2 V 2 to the power gamma. So, what we get is P, P to the power of gamma is constant for an adiabatic change similarly we can get a relationship between pressure and temperature you can just substitute the V in this equation by n R T divided by P using the ideal gas law and you can show that then we will get T to the power gamma P to the power 1 minus gamma is constant.

So, these are the relationships for an adiabatic change now remember for an isothermal change if we go from state 1 to state 2 from pressure P 1 V 1 to sake P 2 V 2. So, the curve looks like looks like this, but compared to that the pressure falling curve for an adiabatic change will be much steeper because gamma is greater than 1 we will come back to it why gamma is better greater than 1.

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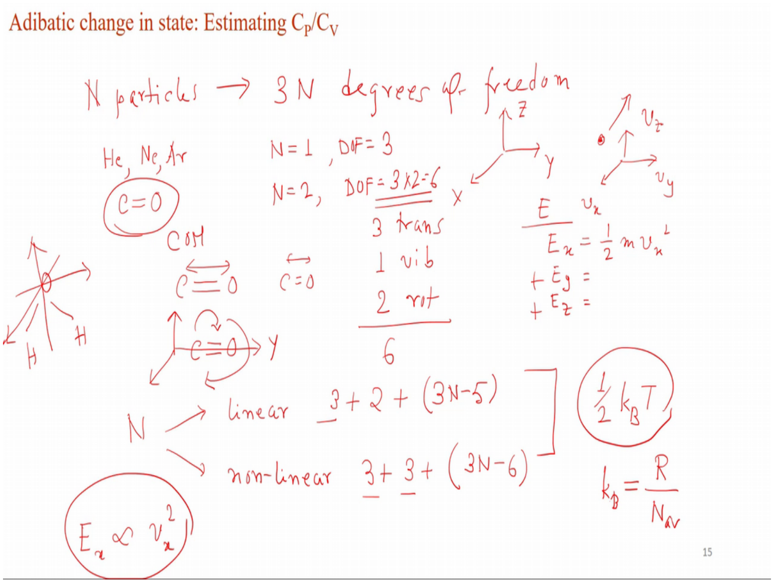
Adibatic change in state: Estimating C_p/C_V

Now, before that let us try to estimate what is the value of gamma now here we estimate the value of gamma for that we need to know a theorem which is known as equal partition theorem now for any mechanical system which has or which is composed of say n particles the system will have a total 3 N independent degrees of freedom what does it mean for example, suppose take a monatomic ideal gas or monatomic any gas say for example, any real gas like helium, neon, argon they are all one atomic gas.

So, N in this case is 1 and the total degree of freedom is 3 these 3 are actually the 3 translational motion along X Y and Z laboratory axis. So, if we call this as X, this as Y, and this as Z then any particle in this case a helium atom or neon atom can move in any arbitrary direction and the velocities can be resolved in this 3 particular direction like V x, V y and Vz. So, there will be some associated kinetic energy also along this 3 direction which you can write it as E x is half m V x square and similarly, for E y and E z whereas, the total energy is divided or written as a sum of E x plus E y plus E z.

Now if it is a diatomic molecule say for example, carbon monoxide. So, what will happen for that for that N is equal to 2. So, the degrees of freedom will be 3 N or 3 into 2 equal to 6. So, 3 R as before the translational motion which describes the motion of center of mass of this diatomic molecule, now what are the other 3 degrees of freedom.

Now carbon dioxide can also vibrate it can stretch the bond and it can compress the bond do like that. So, this vibration is another degree of freedom, we get 3 translation one vibration and this carbon dioxide can also rotate. So, if you think that the molecule is initially along aligned along the y axis then it can rotate along the z axis like this also it can rotate along x axis it can rotate along the x axis like this; however, if we rotate it along y axis there will be no change in moment of inertia because it is already aligned along y.

So, there are only 2 rotational degrees of freedom, 3 plus 1 plus 2 these are the total 6 degrees of freedom in this way we can calculate for any arbitrary system which consists of N particle and the rule of thumb is if it is a linear molecule by system usually here at call it will discuss only the molecular systems. So, for a linear molecule I will have total 3 translational degrees of freedom and then there will be 2 rotation degrees of freedom and then there will be trend minus 5 degrees of vibrational degrees of freedom.

If it is a non-linear molecule, for example if it is something like this water, then it can have it can have non 0 moment of inertia for rotation along any 3 axis you can easily figure that out because moment you try to align you cannot align the entire molecule along a particular direction because the molecule is now not linear molecule. So, you will have 3 translation 3 rotation, 6 degrees of freedom has already been taken into account.

So, you will be left with 3 N minus 6 vibrational degrees of freedom, this way we can calculate. Now the equipartition theorem tells that for any degree of freedom if the associated energy is or can be written as a sum of square term meaning in this case we saw that there are 3 translational motion and the translational kinetic energy along any direction can be written as say for example, E x was written as proportional to V x square. So, if this is the case then each degree of freedom or each motion for that contributes half k B T amount of energy towards the total internal energy of that molecule where k B is the Boltzmann constant defined by the more gas constant divided by N the avogadro number.

Now, let us take an example suppose we have a monatomic gas which is say helium or any inert gas.

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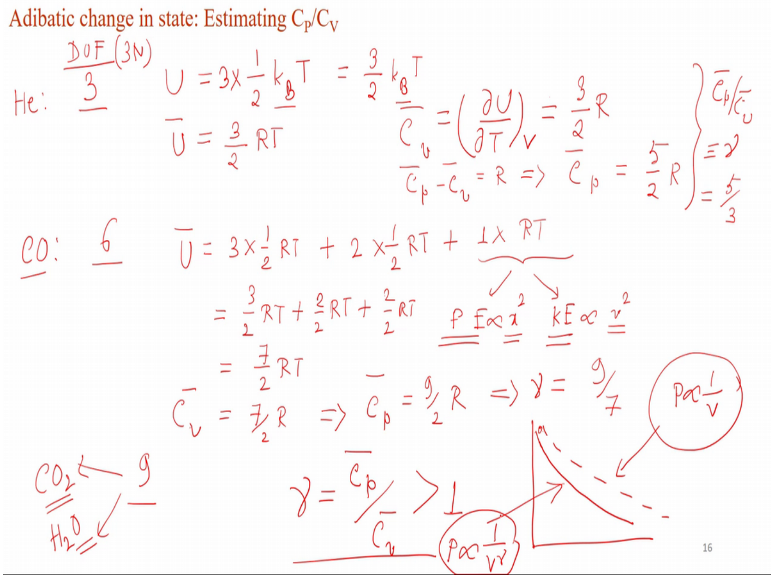

Adibatic change in state: Estimating C_P/C_V

$\underline{\text{DOF}}$ (3N)

He: $\underline{3}$ $\quad U = 3 \times \frac{1}{2} k_B T = \frac{3}{2} k_B T$

$\bar{U} = \frac{3}{2} RT$ $\quad \bar{C}_v = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} R$

$\bar{C}_p - \bar{C}_v = R \Rightarrow \bar{C}_p = \frac{5}{2} R$ $\quad \left.\right\} \bar{C}_p / \bar{C}_v = \gamma = 5/3$

CO: $\underline{6}$ $\quad \bar{U} = 3 \times \frac{1}{2} RT + 2 \times \frac{1}{2} RT + \underbrace{1 \times RT}$

$= \frac{3}{2} RT + \frac{2}{2} RT + \frac{2}{2} RT$ $\quad \underline{PE \propto x^2}$ $\quad \underline{KE \propto v^2}$

$= \frac{7}{2} RT$

$\bar{C}_v = 7/2 R \Rightarrow \bar{C}_p = 9/2 R \Rightarrow \gamma = 9/7$

$CO_2 \leftarrow \underline{9} \rightarrow H_2O$

$\gamma = \bar{C}_p / \bar{C}_v > 1$

So, the total degree of freedom is only translational degree of freedom which is 3 and we know that transition and degree of freedom can be written as sum of 3 kinetic energies where each kinetic energy along a particular direction in space is proportional to a square term in velocity. So, each kinetic energy will be equal to half k B T. So, the total energy the molecule possess will be nothing, but half k B T for each degree of freedom or 3 by 2 k B T. Now usually instead of for one molecule we write it for one mole of molecule. So, again multiplied by Avogadro number, that this k B becomes R (Refer Time: 18:07) gas constant. So, for that energy will be nothing, but 3 by 2 R T for our monatomic gas. So, the total degree of freedom was 3.

So, C V are the heat capacity at constant volume is nothing, but del U del T V which is if we take the derivative will be nothing, but 3 by 2 r. So, you can see that C P minus C V already you know is R and from that we get C P is nothing, but 3 by 2 R plus R which is 5 by 2 R. So, in this case C P by C V which is written as gamma will be 5 by 2 R divided by 3 by 2 R which is nothing, but 5 by 3. So, gamma is always greater than 1.

So, we can take another example say for example, carbon monoxide here at the total degrees of freedom there are 2 particles. So, the total degrees of freedom will be 3 N which is 6 in this case now 3 goes for translation and the translational contribution will be 3 into half R T. Now 2 goes for rotation and for each rotation it will be half R T and then there is 3 N minus 5 because it is linear. So, 3 N is 6 minus 5 is 1 contribution for the vibration.

Now, interestingly for any vibrational motion you have 2 interestings contribution from energies total energies 1 is the potential energy and 1 is the kinetic energy, remember the potential energy for an bond vibration can be written as if we approximate the vibrations are harmonic we can use Hooks law and the energy will be nothing, but half k x square or the energy is proportional to x squared. So, x square term and the kinetic energy as before is P square by twice m where P is the momentum or half m V square usually do not write m (Refer Time:20:42) reduce mass, but whatever it is that is also proportional to velocity squared.

So, each degree of freedom in this case instead of contributing half R T will contribute R T 1 half R T is coming from the potential energy and 1 R T half R T is coming from the kinetic energy. So, if you calculate in this way for carbon monoxide will have 3 by 2 R T plus this is R T or we can just write it as 2 by 2 R T and this is also R T we can also write it as 2 by 2 R T just for using calculation.

So, 3 plus 2 plus 2 is 7 by 2 R T. So, this is the U and similarly C V bar will be 7 by 2 R. So, that C P becomes 9 by 2 R and gamma which is the ratio of C P by C V becomes 9 by 2 R divided by 7 by 2 R which is 9 by 7. In that way you can also calculate carbon dioxide which is a linear molecule and H2 O which is a non-linear molecule both carbon dioxide and H2O have 3 N which is equivalent to 9 because there are 3 atoms; however, the calculation will be different for the linear and non-linear molecule. Now this discussion shows that gamma or C P by C V C P bar by C V bar is always greater than 1 which means for an isothermal change we saw that the curves looked like this because of Boyles law and the Boyles law was P was proportional to 1 over V inversely proportional to the volume. However, for adiabatic change you see that the curve will be more steeper because now it follows an equation which is P is proportional to 1 by V to the power gamma where gamma is greater than 1.

So, the fall off will be more steeper for an adiabatic case than for an isothermal case because for the isothermal the equation is P is proportional to 1 over V for the idea that the equation is P is proportional to 1 over V to the power gamma.

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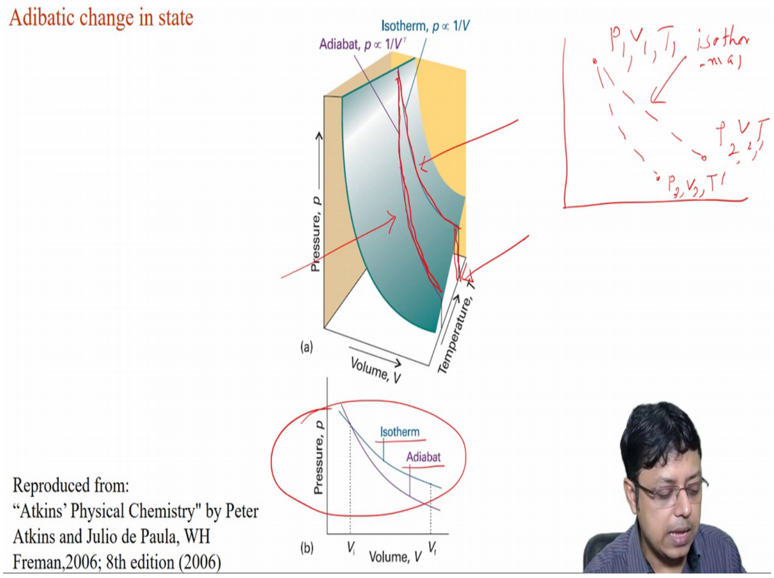

Adibatic change in state

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“Atkins’ Physical Chemistry" by Peter Atkins and Julio de Paula, WH Freman,2006; 8th edition (2006)

Now, this is the P V T surface fraud an isothermal change and adiabatic change you can see that this is a surface for a real gas we had discussed it earlier that for isotherm if this denotes the isotherm the area bars are much steeper also notice that when an isothermal change is happening it is isothermal means the temperature constant.

So, we took a slice along this temperature that is why we got a P V isotherm; however, when the adiabatic change is happening as it is changing the systems temperature is also changing. So, whatever we discussed that the system goes from P 1V 1 to P 2 V 2 for an ideal gas or any system as in an isothermal change for the adiabatic change what we just showed that the adiabatics are much steeper the system is going to a different pressure volume and not only that it is also going to a different temperature it is not maintaining it is own temperature like the isothermal change.

So, the temperature drops in this case because it is an expansion and this is a very crucial observation which we will be using now again in the pressure volume diagram here it is shown that how an isotherm and an adiabatic should be written on a pressure volume diagram the adiabatics are always much steeper it falls off much steeply as the pressure drops or as the volume increases.

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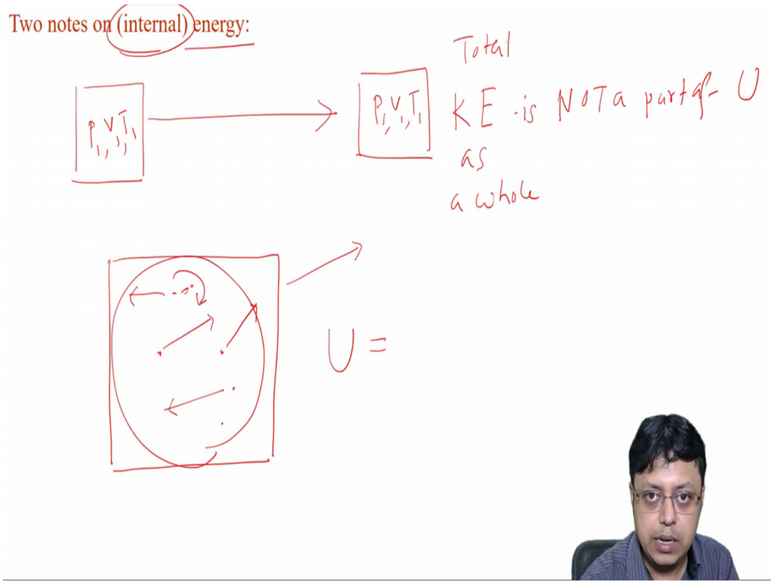
Two notes on (internal) energy:

Total KE is NOT a part of U as a whole

Now will conclude this part by noting down 2 particular important issues one is that whenever we talked about energy we said it is an internal energy meaning it is the energy associated with the system due to it is internal motion.

Now, what do you mean by that suppose we have a system which is an ideal gas content in some pressure some volume some temperature and then suppose we move the system to with some velocity. So, the inter system is now moving and the system as such will have kinetic energy; however, this energy is not a part of the internal energy or kinetic energy the total kinetic energy as a whole is not a part of U or internal energy.

So, by internal energy we mean when the molecules or the atoms whichever the system is composed of they are moving around and they are vibrating they are rotating the associated energies are cause are those associated energies constitute the internal energy U. So, internal energy of course, has a kinetic energy and rotation energy and vibrational energy and many other energies electronic energy nuclear energy, but that is internal to the system if the system moves as a whole it is kinetic energy will not be considered as the internal energy.

So, this distinction has to be kept in mind.

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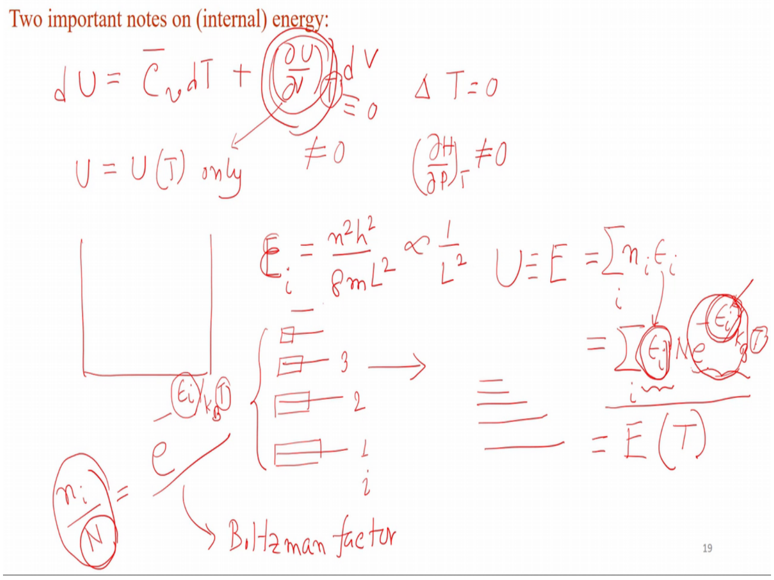

Two important notes on (internal) energy:

Secondly, which is very important we considered a process where we are changing the internal energy as a function of volume and temperature and there we got a relationship that which we just used which is C V d T plus del U del V T d V. Now the question was this was taken to be 0 for ideal gas now this was based on an experiment which was joules experiment and remember that in joules experiment joule found there was no rise in temperature delta T was 0 from that he concluded del U del V T was is 0.

However later on people carry doubt much refined experiment where they found that del U del V T is not equal to 0 much like we also discussed that del H del P T is also not equal to 0 for any real gas. Now how can you understand that for ideal gas this should be 0 or for ideal gas energy is a function of temperature only, as long as we are not changing the temperature remember del U del V T means the temperature is kept constant the internal energy does not change.

Now, we will make an analogy with the particle in a box model remember in a particle in a box one dimensional box the expression for energy is n square h square by 8 m L squared where n is the quantum number h is the Planck constant m is the mass of the particle and L the length of the box which means energy is proportional to the inverse of length square. So, if you change the length of the box of the volume as such then the energy levels should also change which means if I suppose this is the initial energy levels if I increase the L the energy levels should come closer together.

So, that is understandable then why do you say that del U del V T is 0 because as we are changing the volume the energy levels are coming closer together. Now the fallacies at any point you will have some molecules in the ground state some number of molecules or some fraction of molecules in the excited state that will be dictated by a factor which is known as the Boltzmann factor. So, if we call that for any level which we denote as I where suppose I is 1 for this is the first energy level, I is 2 for this is the excited energy level, I is 3 for this.

So, the associated energy if I write it as E i by if excited energy can be written as E i where E i is nothing, but this expression energy then we can say the number of molecules in this which are occupying this state will be proportional to that or the fraction of molecules ordered it will be nothing, but this e to the power minus E by k B T here N is the total number of molecules and this factor is known as Boltzmann factor now the fallacies here when I am changing the volume as long as the temperature is constant the number the fallacies can be resolved as this.

So, the answer why del U del V T is 0 can be answered like this the total energy of the molecule will be the number of molecules occupy in a state multiplying by the energy of that state and taking a sound over all the energy states which will be nothing, but epsilon I are writing this as first into instead of n i and write capital N e to the power of minus E i by k B T now what is happening if we keep the temperature constant then changing the volume changes E i.

However since the temperature is constant suppose we are increasing the volume then E i decreases, but then this fraction decreases at the same time this E i also decreases. So, they will somehow compensate and make the total energy independent of the change of the following which means the total energy which we wrote as U in thermodynamic language is a function of temperature only.

So, changing the following for example, increasing will actually decrease this value which means e to the power of minus E by k B T will increase; however, Ei will also decrease and then if we take the sum we can show that the sum will still be a constant which is independent of the change in volume. So, let us summarize what we discussed in this session.

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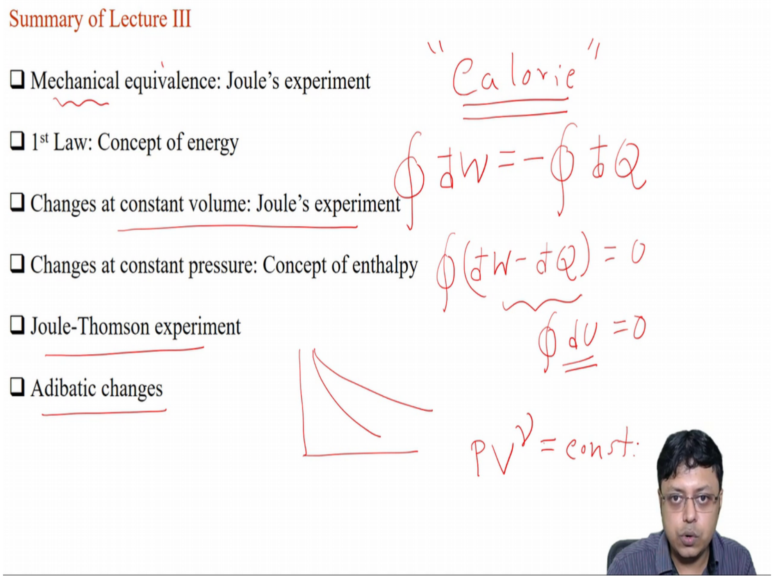

Summary of Lecture III

- ☐ Mechanical equivalence: Joule's experiment
- ☐ 1st Law: Concept of energy
- ☐ Changes at constant volume: Joule's experiment
- ☐ Changes at constant pressure: Concept of enthalpy
- ☐ Joule-Thomson experiment
- ☐ Adibatic changes

"Calorie"

$\oint đW = -\oint đQ$

$\oint (đW - đQ) = 0$

$\oint dU = 0$

$PV^{\gamma} = \text{const.}$

So, we first started with the mechanical equivalence of work and heat art equivalence between work and heat where we showed that if we want to raise the temperature of the system it is not necessary that we have to supply heat we can also do some work in the surrounding and the work can be destroyed to produce it and that was experimental shown by joule where he used the falling of a mass to rotate a paddle system immersed in a liquid that increased the temperature of the liquid water and hence Joule concluded that the old concept that when heat is exchanged there is something called caloric which actually gets transferred between 2 bodies.

He rejected that caloric hypothesis and he said just by doing mechanical work you can also heat up a system the second thing is that the concept of energy we discussed where we discussed for any cyclic process the work done should be equivalent to the heat withdrawn, but in that case we saw that for any cyclic process the system comes back to his initial state. So, what destroyed in the surrounding increases the temperature in the surrounding and since by convention we took that heat flowing from the surrounding into the system is positive since in this case heat was increased in the surrounding we took a negative sign and that difference we found that is always 0 for any cyclic process which means actually we can define a quantity which is a noun state function because for any cyclic process that quantity is 0.

And we call it called it as internal energy or energy we just described or discussed why it is better to call it as an internal energy not the energy and then we talked about changes at constant volume which was carried out by joule in an experiment and he found that for gases del U del V T is 0 which is not actually 0 for real gases for ideal gases it is 0 and we just get a molecular picture for why it is 0.

And then we also considered the changes at constant pressure they are we considered the concept of enthalpy and just like Joules experiment there was another experiment Joule Thomson experiment where we discussed the magnitude or how to quantify the quantity del H del P T and we saw that it can be connected to something known as Joule Thomson coefficient.

And then we discussed the adiabatic changes and we discussed that for compared to any isothermal change the adiabatic changes will be much steeper because for adiabatic change the pressure following relations are P V to the power gamma is equal to constant where gamma is always greater than one we took some examples and we showed that why gamma is greater than.

Thank you.