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Course
on
Laws of Thermodynamics

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Lecture 07: First Law of Thermodynamics
for Closed Systems (Part I)

Today's agenda will be to discuss about the first law of thermodynamics for a control mass system.

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1st Law of Thermodynamics

1st Law for a cyclic process

$$\oint \delta Q = \oint \delta W$$
$$\oint \delta Q = \oint \delta W$$
$$\oint \delta Q = \oint \delta W \rightarrow \Delta I$$

$\int_{2B}^{1B} \delta W$ ①

$W + \int_{2C}^{1C} \delta W$ ②

$\int_{2B}^{1B} \delta Q - \delta W = \int_{2C}^{1C} (\delta Q - \delta W)$

So the first law of thermodynamics as it is classical inspection long back when people were arguing about the inter convertibility of heat and work see this is a classical philosophical way of looking into thermodynamics so the one quest in thermodynamics as always been that how to convert heat to work that means convert thermal energy into a form of energy that could be utilized to do work.

So to do that people came across various process and people where conceptualizing various process so one such type of process is a cyclic process, so the first law of a cyclic process was the first version of the first law that was classically introduced but we will see later on that the first law although introduced through the concepts of heat and work is conceptually nothing but a description or depiction of conservation of energy in it is generalized from.

So here in the conservation of for the conservation of energy we are considering heat and work as two interaction mechanism between the system and the surrounding but eventually it is not just heat and work but other forms of energy transfer also that we are taking into account while discussing about the first law general, well as for the classical state when we will be concerning mainly with energy transfer associated with heat and work.

So for a cyclic process the first law states that the cyclic integral of heat is proportional to the cyclic \propto work that means in the in a cyclic process whatever is the work done whatever is the heat transfer that is proportional to the work done, so if we think of something which is very simple instead of discussing the classical Joule's experiment which you have done which we have gone through in the even in the high school level.

Let us think of a simple experiment without any instrument, so you just rub your palms so if you rub your palms you will see that what you are doing is your doing some work and if the other way around this work is being converted into something which we will learn latter on as the intermolecular form of energy and that eventually we will heat up the your palms.

So there is a relationship between heat and work that we understand and in a cyclic process whatever is the work done and whatever is the heat transfer they are proportionate to each other or in other words it is called as the cyclic integral of heat is proportional to the cyclic integral of work, if you reduce this proportionality to a equality then you can write this J is called as mechanical equivalent heat which was introduced in those days.

Because the heat and the work units where different just to patch up the difference in units between of heat and work, so for example the heat unit was classically calorie and the work unit was Joule on the other hand in the SI system you have the heat and work units both are same units that is both are Joule and therefore these mechanically equivalent of heat in that case is worm.

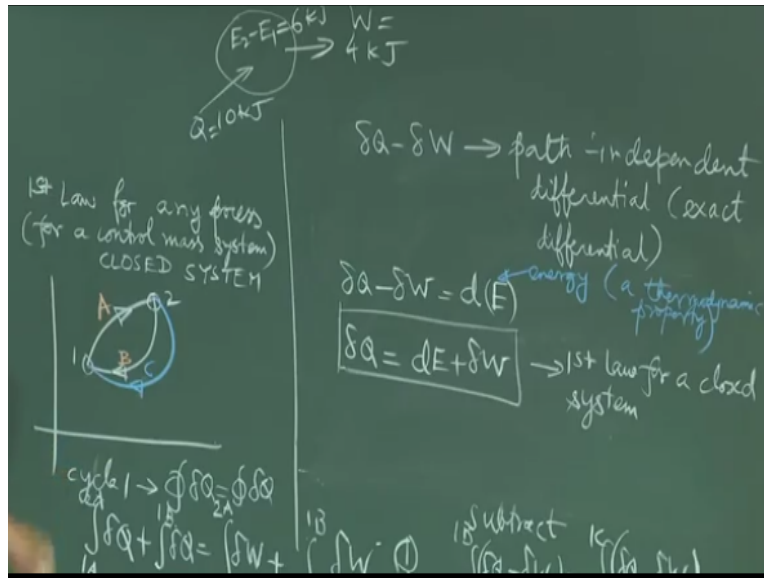
So this J is nothing but a unit converter from 1 unit to the other but if the both the heat and work are experienced in the same unit then it is cyclic integral of heat is = cyclic integral of work in the SI system the next we will discuss first law of any process for a control mass system or close system so in some books it will be written as control mass system in some little bit older books it is written as close system but they essentially mean the same that is the system, boundary across with there is no mass flow so now let us try to plot a process diagram I am not committing whether it is PV TV whatever some process diagram while we have one cycle made of two process what is the cyclic process or cyclic process is such that.

You start with an initial state after going through a sequence of thermodynamic process you come back to the same state then you say that, a thermodynamics cycle is completed so for the cycle one the individual process are A and B, let us consider another cycle where we have covers the path 12 / a but the written from 2 to 1 you have by path C therefore we can say that for cycle one if we apply the first law cyclic \int of heat is equal cyclic integral of work that means \int of δQ from 1 to 2 / path A + \int of δQ from 2 to 1 / path B = \int of Δ similarly.

For cycle two 1A to 2A δQ + from 2 to 1 it will be path C okay, so now what we can see from here is something as follows if you subtract these two 1 from the other you will see that we subtract cyclic \int of $\delta Q - \delta W$, from 2B to 1B = cyclic \int of $\delta Q - \delta W$ from 2C to 1C okay so what we can see here is something very interesting δQ is a path depend function the δW is also a path depended but $\delta Q - \delta W$ \int of the at that is not path depended because if you are fixing up the states one and two the difference between δQ and δW the \int of that does not change from path B to C and these are any.

Arbitrary paths that mean we can say that \int of $\delta Q - \delta W$ is the path in depended function that means it is a point function so we can say that $\delta Q - \delta w$.

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This is a path independent differential or exact differential. So we can write $\delta Q - \delta w = d$ of something, d of a thermodynamic property, why? Because if you have two differentials or if you have a differential such that the differential is operating on an operator where the change in that particular parameter.

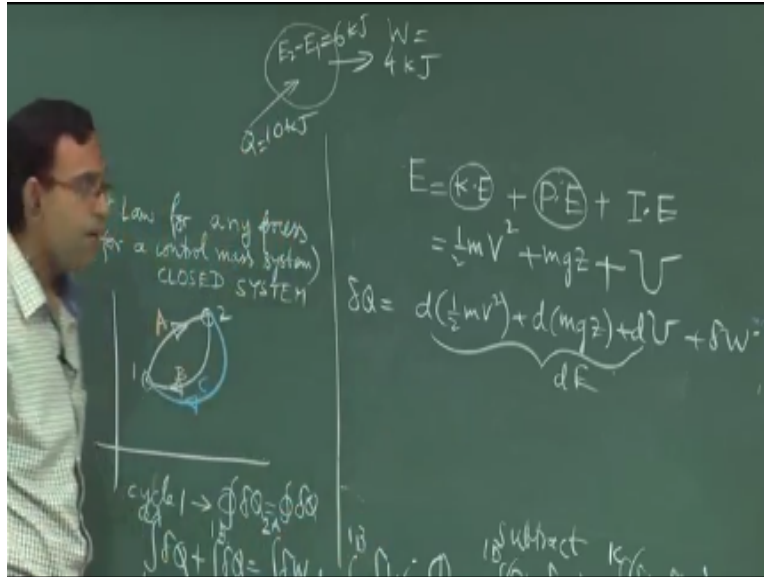
That does not depend on the path so $\delta Q - \delta W$ its difference when integrated whether it is through B or path B it is just dependent on the n states 1 and 2 we can write that as the exact differential of a thermodynamic property that is the definition of a thermodynamic property that the change in property a property is such a parameter where its change does not depend on the path but it only depends on the n states.

So this E is called as the energy of the system this is a thermodynamic property, so we can write $\delta Q = dE + \delta W$ this is the first law for a close system. Undergoing any process it need not be cyclic process so certain things that we have to understand very carefully, so first of all what is the physical interpretation of this let us say you transfer 10 kilo joule of heat towards this step so let us say this is a system.

You transfer 10 kilo joule of heat and the system utilizes four kilo joule of heat to do some one so it uses it keeps up out of these 4 kilo joule of heat to do what, then the balance will increase the energy of the system by an amount $10 - 4 = 6$ kilo joules, so if you transfer some heat to a system if a part of that is utilize to do what, the remaining part of the heat will be utilized to increase the energy of the system. So this is grossly a statement of energy balance which follows from

intuition. The next question is, that when we say energy what kind of energy we are talking about?

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So when we say energy we say we normally discuss about kinetic energy + potential energy these are mechanical forms of energy + thermal energy which we call as internal energy, so if you say what is the definition of internal energy in terms of classical or macroscopic thermodynamics it is a bit tricky or it is a bit on a very conservative side it is trying to address the situation without referring to what are the physical implications of these.

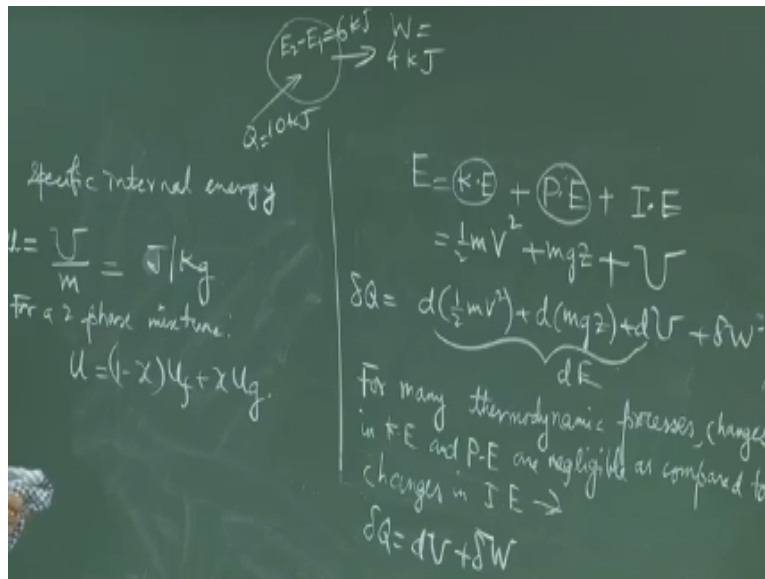
What it is saying, it is saying that any form of energy rather than kinetic or potential energy is internal energy, this is the classical way of looking into it but eventually the internal energy from microscopic view point will be dependent on the atomic structure chemical bonding and all these things and it will include the vibration translational and rotational degrees of freedom of the atomic or molecular entities.

But the gross manifestation of the mechanical energy will be the kinetic energy and the potential energy so from a macroscopic view point again the internal energy will not get into the details of the definition but what we can say is that it is just the form of energy which is other than kinetic energy and potential energy, so it will include visual everything other than kinetic and potential energy many other things that we have possibly not listed when I was talking about the atomic

and inter atomic interactions. So kinetic energy typically is $\frac{1}{2}mv^2$ potential energy is mgz and internal we symbolize as U .

So $\delta Q = d(\frac{1}{2}mv^2) + d(mgz) + d(U) + \delta W$ so this is essentially dE , now there are many thermodynamic processes for which the kinetic and potential energy changes are negligible has compared to the changes in thermal energy. So we can say that.

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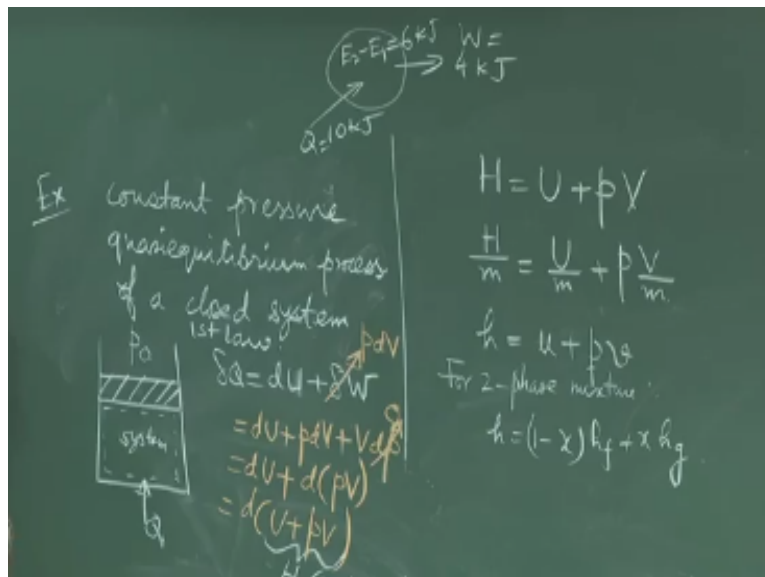
For many thermodynamic processes changes in kinetic energy and potential energy are negligible as compared to changes in internal energy, so for such a scenario we can write $\delta Q = dU + \delta W$ so this is the form of the first law which you are familiar with from your school level, only one important difference is that in the school level possibly you would have written dQ and dW but we have to understand that because these are dependent on thermodynamic path and not point functions, it is customized to write these as δQ and δW instead of dQ and dW .

And when you write these $\delta Q = dU + \delta W$ the assumption is that kinetic energy and potential changes are negligible this is not something which is very obvious because some people would do not go through the derivations we will normally take this as the exact form of the first law no, ideally there should also come an additional term which will include the changes in kinetic energy and potential energy. Again by these we are emphasizing that we are not talking about any process where kinetic energy and potential energy themselves are negligible; we are considering that their changes are negligible.

These energies may be important but their changes are not that important as compared to the changes in the thermal form of energy that is what we are talking about here. So through this we have introduced to a new property which is called as internal energy this internal energy data is given in the table as other properties like specific volume you will have specific internal energy, so specific internal energy.

There is a u this is U/m okay, so this is expressed in the unit of J/kg and for a two phase mixture, so the rule of mixture is same as that of the rule of mixtures for the specific volume. Now we have learnt the first law we will then try to use the first law for an example which is the constant pressure quasi equilibrium process.

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Quasi equilibrium process undergone by a close system of a close system of a close system constant pressure quasi equilibrium process of a close system, let us say that you have the piston set in that arrangement and then heat is transferred slowly to the system so that this system expands during the process it is expand slowly the pressure will remain the same why? See the internal pressure for equilibrium will be same as that of the resistance pressure.

So what is the resistance pressure? The resistance pressure is the atmospheric pressure plus mass of the piston in to g divided by a , so if this weight of the piston does not change and the atmosphere equation does not change there is no reason to believe that the internal pressure will

also not change okay. So what we can conclude from here is that this is the model case where under constant pressure the system volume will expand due to heating.

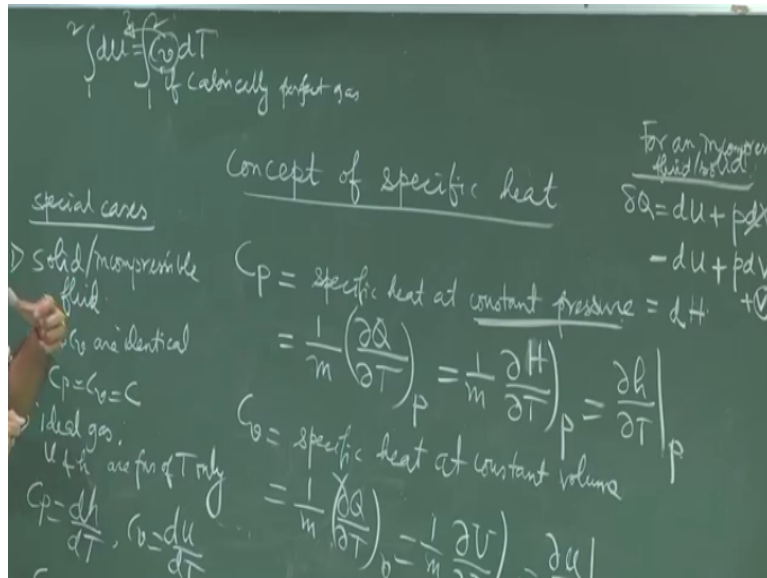
So we can write here assuming negligible changes in kinetic energy and potential energy this form of the first law again very important assumption neglecting changes in kinetic energy and potential energy. Because it is a quasi equilibrium process we can write this as pdv , so this we can write $du + pdv$ then we can also add vdp why? Because these are as good as adding 0 because it is a constant pressure process. So dp is 0 therefore vdp is as good as adding 0, so this is $du + pdv + vdp$ is $d(pv)$.

So we can write this as $d(u + pv)$ so we have got a new combination of properties where if u which is a property p is property and v is a property this combination of property is also a property and this is called enthalpy. So h or enthalpy by definition is $u + pv$ so we have introduced this through this example of a constant pressure process but the enthalpy is defined for any state no matter whether the state is arrived through a constant pressure process or not it is just defined as a combination of properties.

So you can write the corresponding specific properties small $h = u + pv$ so in the thermodynamic tables you will find that sometimes h is tabulated sometimes it is not tabulated but you can calculate it by $u + pv$. So either way if it is not tabulated you can calculate using this sometimes for helping your calculation this is already tabulated, and for a two phase mixture again this is the rule of mixture that is given.

Next we will try to learn the concept of specific heat of matter and these definitions we will try to learn in the light of the understanding of the first law that we have just discussed so far.

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When we say concept of specific heat, there is a definition which is C_p which is specific heat at constant pressure so what is this so specific means per unit mass the rate of heat transfer required for each degree for change in temperature so what we can say from here is that specific heat will mean that heat transfer required to change the temperature of unit mass by one degree.

The heat transfers will depend on the process so specific heat at constant pressure means this process is being executed at constant pressure and we have seen already that for a constant pressure process if we have designed constant pressure cross equilibrium process this is nothing but so H by aim is small $\partial h / \partial T$ at constant pressure.

Similarly C_v is specific heat at constant volume so at constant volume see ∂Q is equal to D_u plus ∂W which is $p dv$ for cross equilibrium process of a simple compressible substance so for constant volume process the what done is 0 so ∂Q is equal to D_u so $1/M$ special cases number one is solid or incompressible fluid so if we have a solid have a incompressible fluid there is no distinction between C_p and C_v why see for a incompressible fluid this is 0 or even you can add for a incompressible fluid the specific volume is small so for designable D_p this vdv is also 0.

There how for an incompressible fluid on a solid you can write du at dh is at same only for incompressible fluid or solid because all this like $dv = 0$ or vdv is small all this we can conclude only for incompressible fluid or solid so for therefore in this case C_p and C_v are identical so we can say C_p is equal to see which is also known as specific heat capacity next for an ideal gas u and h are functions of t only, so this is very important.

Normally for substances this u and h will be a function of two independent properties but for an ideal gas it can be shown that the internal energy and enthalpy are functions of temperature only and nothing else. Therefore we can write C_p now is dh/dt because h is the function of t only, not a question of keeping pressure constant, volume constant this does not matter because h is the function of T only.

So and then $C_v = du/dt$, so C_p we can now write in this way $C_p - C_v = d/t$ of $h-u$, so $h-u$ is Pv dt of Pv and for an ideal gas $Pv = RT$, so this is d/t of so this is R . So the formula $C_p - C_v = R$, this you can apply for ideal gases. So for an ideal gas the change in the enthalpy or change in the internal energy, so for example if you are writing du this is $C_v dT$ so the change in the internal energy, you can write by using this formula. Now a very important situation is the situation is when C_p and C_v are constant, for those ideal gases where C_p and C_v constant these are called calorically perfect gas.

So there is a different between perfect gas and ideal gas. Ideal gas it obeys the ideal gas equation of state but the perfect gas is something where the C_p and C_v are not functions of temperature but are constant these are called as calorically perfect gas. So these you can take out of the integral if it is calorically perfect gas, if it is not calorically perfect gas you cannot take it out of the integral, so you can take it out of the integral it is simply $C_v \times T_2 - T_1$ where the C_v is some constant C_v , similarly for C_p .

So what are the factors on which C_p and C_v depends, these depend on whether it is mono atomic or die atomic or poly atomic gas. For mono atomic gas you have, because of the restricted degree of freedom you will have the depends of C_p C_v with the temperature not very important. For di atomic gas like hydrogen, oxygen all these for di atomic gas you will find that the depends C_p C_v with temperature is more that C_p C_v will more strongly depend on temperature. However for poly atomic gas where the number of atoms in the molecule is even more you will find that the C_p C_v variation with temperature is even more because of the added degrees of freedom.

Therefore we can say that we can say that there are many situations where either because of large number of the degrees of freedom or because of large temperature range over C_p C_v it may not be possible to treat C_p C_v as constant, in that situation we will have to use this C_p C_v as function and integrate these two top get the changes in properties like internal energy and enthalpy. To

summarize we have discussed about the first law of system, undergoing a cyclic, undergoing any process.

We have introduced the concepts of internal energy and enthalpy and we have discussed about the specific heats the concept of specific heat at constant pressure at constant volume and we have discussed about the special case of ideal gas. Thank you very much, in the next session we will be discussing or working out some example problems, illustrating the use first law thermodynamics for a close system.