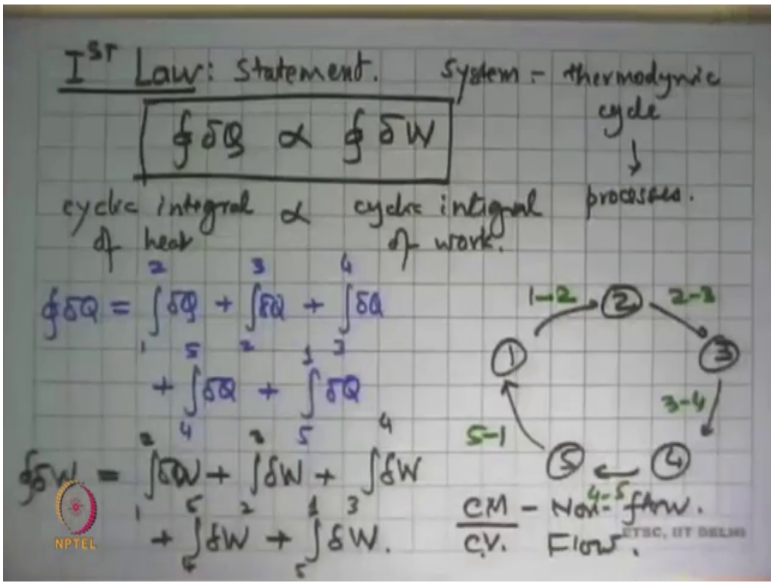
Engineering Thermodynamics
Prof. S. R. Kale
Department of Mechanical Engineering
Indian Institute of Technology, Delhi

Lecture - 13
Laws of Thermodynamics: First Laws of Thermodynamics. 1st law for Control Mass. Internal Energy. Enthalpy

(Refer Slide Time: 00:19)



I^st Law: Statement.

$$\boxed{\oint \delta Q \propto \oint \delta W}$$

cyclic integral of heat ∝ cyclic integral of work.

System – thermodynamic cycle → processes.

$$\oint \delta Q = \int_1^2 \delta Q + \int_2^3 \delta Q + \int_3^4 \delta Q + \int_4^5 \delta Q + \int_5^1 \delta Q$$

$$\oint \delta W = \int_1^2 \delta W + \int_2^3 \delta W + \int_3^4 \delta W + \int_4^5 \delta W + \int_5^1 \delta W.$$

CM – Non-flow.
C.V. Flow.

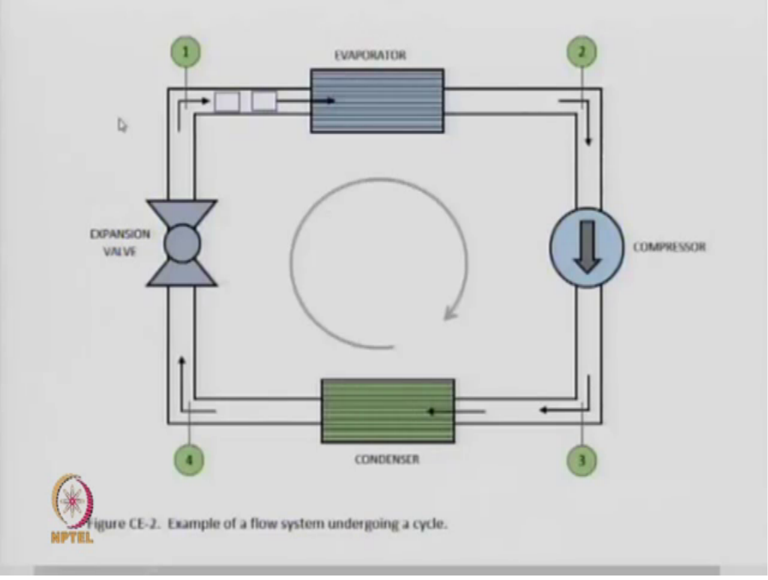
Go on to the first law. In the recycle we have only two units will use or you may still come across Fahrenheit in some instances, ok. Now, look at the first law and I first state this that for a system that undergoes a thermodynamic cycle, the cyclic integral of heat is proportional to cyclic integral of work. So, that is the statement we always start with.

So, we will invoked what is the system we have invoked what is the thermodynamics cycle which requires us to know that there are many processes, and we have invoked the concept of heat and we have invoked the concept of work all of which we learnt in the previous module that is why that module is so important. So, what this is that cyclic integral of heat is proportional to cyclic integral of work. So, quick illustration is that say a system starts with state 1, goes to state 2, goes to state 3, goes to state 4, goes to state 5 and say finally, comes back to state 1. And because its finally, come back to state 1 this has this system has undergone a thermodynamic cycle. A cycle which includes a process which is 1 to 2, 2 to 3 ,3 to 4 4 to 5, 5 to 1.

This could be a gas in a cylinder system arrangement where you keep say expanding it, relating it, contracting it, cooling it, again compressing it,. So, in anything there is option will be no restriction on what we do at this and comes back to same state. So, in this case the cyclic integral will mean that, cyclic integral of heat the symbol means that this what the cycle this will be integral of heat process 1 to 2 plus integral of heat 2 to 3 plus integral 3 to 4 plus integral 4 to 5 plus integral 5 to 1. That is the meaning of cyclic integral of heat. Any of this could also be 0 that is fine that does not that is not an issue.

And in the same way we can also write an expression for cyclic integral of work and this will be 1 to 2 delta W plus 2 to 3 delta W plus 3 to 4 delta W 4 to 5 delta W plus 5 to 1 delta W. That means, for each process we need to calculate the heat and the work. So, for this process the assurated parameters are integrals of this and I am not will just develop symbols for these in a few minutes, because this could be a single piston arrangement as I have mentioned or it could be a system where a fluid moves through different elements and comes back to its same position and that we can see on the picture with notes.

(Refer Slide Time: 04:37)



igure CE-2. Example of a flow system undergoing a cycle.

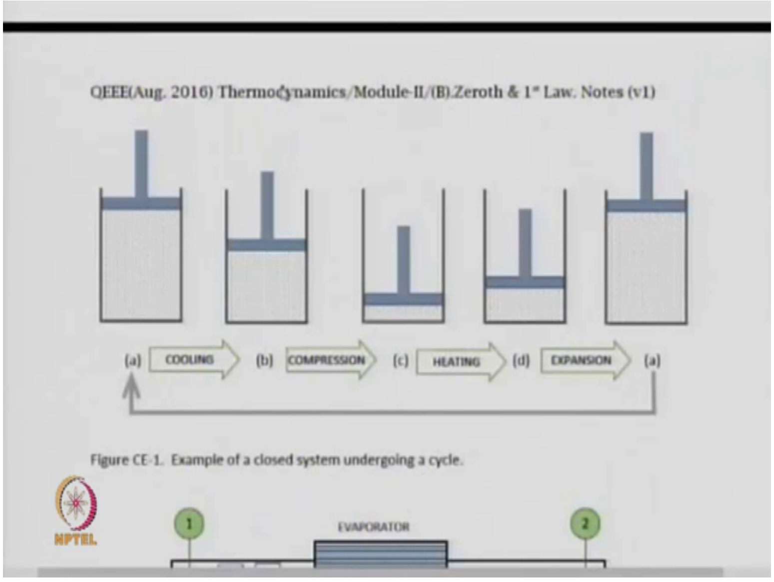
Here is the example of what happens in the refrigerator or in air conditioner. These are elements that I have denoted here and these are pipes. So, this element has gone through this pipe and slowing there you assume that there is no heat transfer, there is no work transfer. And this denotes as state 1, it goes into a device called an evaporator where process takes place where there is heat transfer, something happens to it and comes out at

2. Then this continues and flows into the compressor which is powered by the motor and here something another process happens to this, but in substance and that same element will come out over here all that every state its properties are changing and so here the state is now denoted by state 3.

Then this flows through the pipe into the condenser some process happens here which in this case heat rejection substance comes out and its now in state 4. It continues moving through this comes into the expansion wall where undergoes an expansion and after this process, it attains the same state which it was here when started the system.

So, this little element flow through this entire system and came back to the same point at the same state. The state where different when it got back then would not be a cycle. So, if it is a same state when it comes back then we say that this little element was flowing through all these and executed thermodynamic cycle.

(Refer Slide Time: 06:13)



QEEE(Aug. 2016) Thermodynamics/Module-II/(B).Zeroth & 1st Law. Notes (v1)

Figure CE-1. Example of a closed system undergoing a cycle.

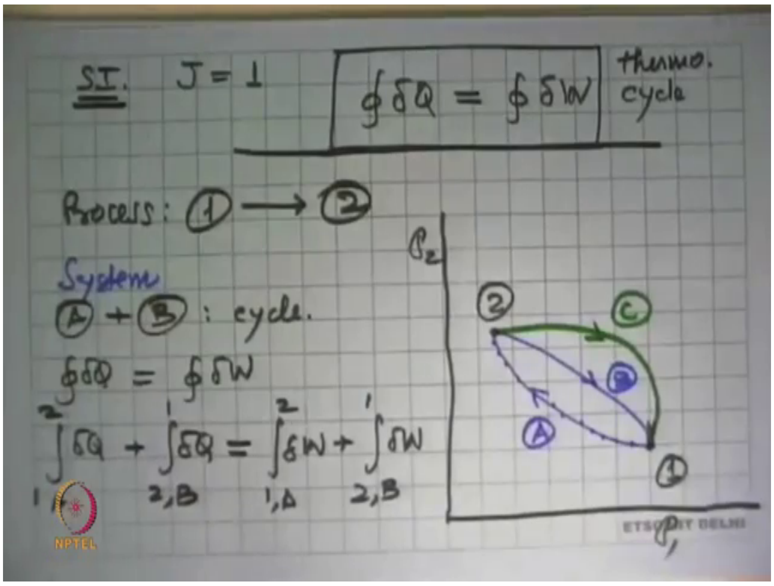
So, this is the second way by which a thermodynamic cycle can be realized and what I just prove on the sheet is a picture of this thing there was 5 process there give there were 4, we take a single piston arrangement and then we cool it. So, the piston comes down, then we put work on it and compress it and then it comes to this state c, then heated comes to state d, then you allow it to expand on against the force comes to state a which is the same as the starting state a.

So, this substance here which was locked in this which is like a control mass went through a cycle, in this case the second case that we just proved this was a flow case where the system is continuously the fluid is moving and executing different process and this is also a cycle. So, there are two ways in which a thermodynamic cycle can be achieved. So, this cycle can be done in a control mass approach or a control volume or this is a known flow process and this is a flow type of process. So, there are two ways that we can execute a thermodynamic cycle and in each case this has to be valid.

So, if you just want to apply this equation we do not know how to do things there are still so many unknowns left. So, will further work on this equation and come up with some expressions that will help us in actually getting the relationship between heat, work and what happens in the process the properties of the substance that is what we will do, ok.

The first thing we will do is we look at this situation and say what can I get rid of that proportionality and we say ok, in the SI system there is a proportionality constant which will be J which we say is one and to the first law statement becomes cyclic integral of heat is equal to cyclic integral of work and that proportionality is gone now. You have always going to use SI system.

(Refer Slide Time: 08:01)



S.I. $J = 1$

$$\boxed{\oint \delta Q = \oint \delta W}$$ thermo. cycle

Process: ① ⟶ ②

System

Ⓐ + Ⓑ : cycle.

$$\oint \delta Q = \oint \delta W$$

$$\int_{1}^{2} \delta Q + \int_{2,B}^{1} \delta Q = \int_{1,A}^{2} \delta W + \int_{2,B}^{1} \delta W$$

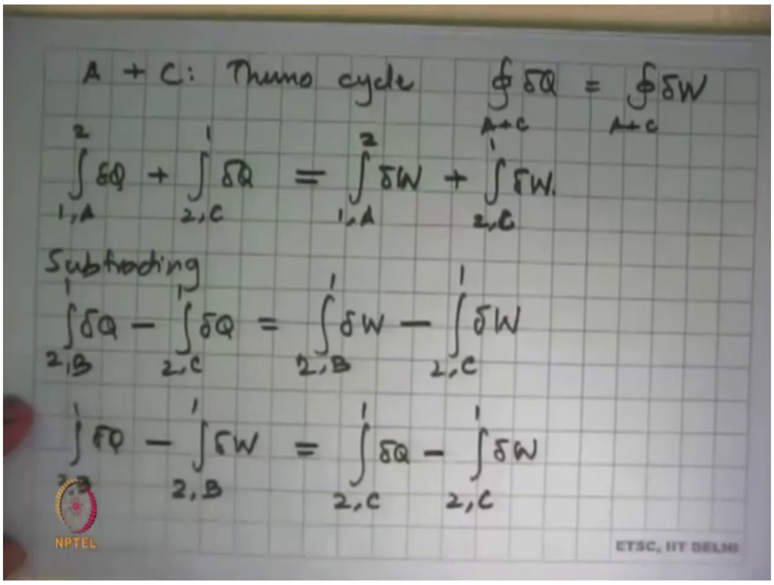
So, this is available always true, but it is always true only for a thermodynamic cycle. This we do not know what happens in a process that means, it runs from state 1 to state 2 either in a closed system or in a control volumes situation this equation cannot be directly used. So, that is what we will do next. We will work on this equation and try to come up with some expression that tells us what is expression of the first law or a process. So, this is first law for a cycle, now will look at this statement for a process and to do that they will run a small thought process and you say a I make two properties of a substance p 1 and p 2 and these are independent properties, and if I put any point on this chart, I would now properties and that would completely specify the state of the system.

So, let us say that there is state 1 over here and state 2 say over there,. And we take this system, so there is a system it could be anything it could be flow or it could be a control mass we take it from 1 to 2 following a certain path and when we say that we are following a certain path it means that at every point during the process the state of the system is known to us. And when we say since I know first law for a cycle what can I do to complete this cycle, now I only got a process 1 to 2 and say we have process can be a process that goes back and say this was another process by which it completed the cycle.

So, it excites from 1 to 2 along path A and came back 2 to 1 along path B and in doing. So, these two processes A plus B they constitute a cycle. And we can write the first law for this that cyclic integral of heat is equal to cyclic integral of work which needs on this side yeah cyclic integral of heat from 1 to 2 along path A plus cyclic integral of delta Q 2 to 1 along path B. So, this is the cyclic integral of heat. This have to be equal to cyclic integral along path A of work plus cyclic integral of work 2 to 1 along path B.

All we have done is use the expression that we got a few minutes back and now we are applying it for this cycle which is consisting of only two process, there could be more that is not very important. So, that is one expression we have. So, at least we got to the point where we are now talking of the integral of heat or integral of work for a process, but thus it has to much more than that. So, now, we say that work and bring the cycle back to state 1 by going another process a process C which means that now, A plus C constitutes a cycle.

(Refer Slide Time: 12:21)



A + C: Thermo cycle $\oint_{A+C} \delta Q = \oint_{A+C} \delta W$

$$\int_{1,A}^{2} \delta Q + \int_{2,C}^{1} \delta Q = \int_{1,A}^{2} \delta W + \int_{2,C}^{1} \delta W.$$

Subtracting

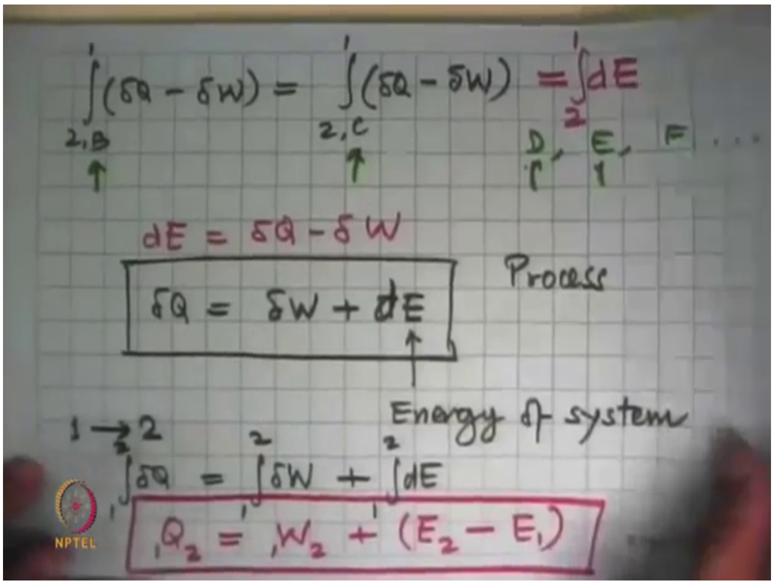
$$\int_{2,B}^{1} \delta Q - \int_{2,C}^{1} \delta Q = \int_{2,B}^{1} \delta W - \int_{2,C}^{1} \delta W$$

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

And again, we can do the same thing we did for A plus B. So, in this case it will become cyclic integral of A plus C delta Q is equal to cyclic integral of A plus C delta W earlier we did it A plus B, now we are doing it for A plus C. A and C are two processes and again like before we break up this equation and get that integral 1 to 2 along A delta Q plus integral 2 to 1 along C delta Q is equal to integral 1 to 2 along A delta W plus integral 2 to 1 along path C delta W.

So, we have now two equations the first one for A plus B the second one for A plus C. And what we do is now will subtract this two equations. And draw the matter which way is subtract let us say it is this two terms remain on the left side integral 2 to 1 along B delta Q minus integral 2 to 1 C delta Q is equal to integral 2 to 1 along B delta W minus 2 to 1 along C delta W. And now we just rearrange some terms over here and it tells us integral 2 to 1 along path B delta Q minus integral delta W 2 to 1 along path B is equal to integral 2 to 1 along path C delta Q minus integral of delta W from 2 to 1 along path C.

(Refer Slide Time: 14:59)



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

D, E, F . . .

$$dE = \delta Q - \delta W$$

$$\boxed{\delta Q = \delta W + dE}$$

Process

Energy of system

$1 \to 2$

$$\int_{1}^{2} \delta Q = \int_{1}^{2} \delta W + \int_{1}^{2} dE$$

$$\boxed{{}_1Q_2 = {}_1W_2 + (E_2 - E_1)}$$

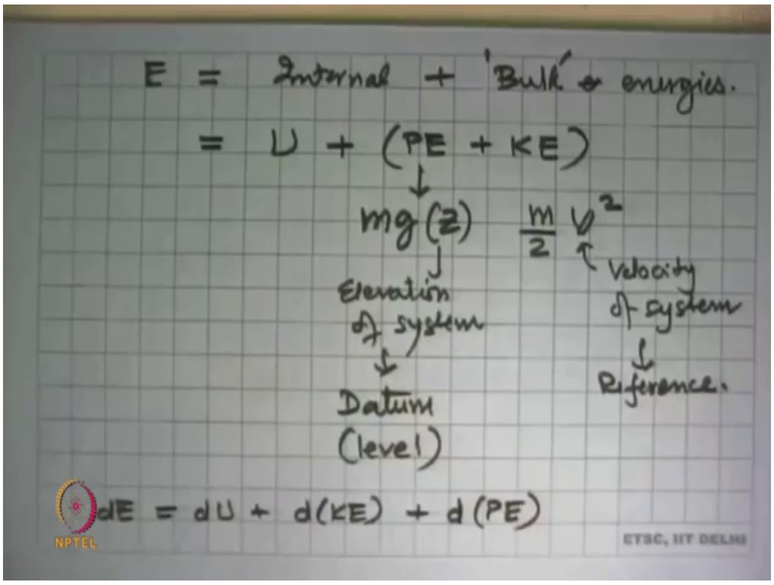
So, what it if you rearrange these now integrals limits are same and paths are the same. So, we can now write integral 2 to 1 along path B delta Q minus delta W is equal to integral 2 to 1 along path C delta Q minus delta W. Then what it tells us that is these two are equal whether you went along path B or path C or any other path D, E, F or anything like that this value of this integral will be constant, that is the thing coming out of this little arithmetic. And that is what we will call that this is the first two that does not depend on the path, so this can be put now as a exact change as integral dE.

So, we are now defining a new term dE is equal to delta Q minus delta W or the more common way that we write this expression. Delta Q is equal to delta W plus dE, and that is now valid for a process. And what it tells us heat transfer to a process that energy is equal to the sum of the work done by the system plus change in something that is we call d, now we define E as energy of the system and that is a new property that has come on.

So, we ask now what is E? Let us, before that let us complete the discussion and say well this was a elemental or a differential form of the equation what will d for a process 1 to 2. We integrate this and said delta Q 1 to 2 is equal to integral delta W 1 to 2 plus integral dE 1 to 2 and the symbols that we will use for this is Q 1 2 W 1 2 plus E 2 minus E 1. This is the first law statement for the process.

It is the most general form; in coming from that cyclic integral of heat equal to cyclic integral of work we did not make any assumptions. This is always true and any further statements of this would be of restrictive in nature that means, if this is there then this would be the case. Before we come to that let us get clarity on what we mean by energy of the system which is E, and for that we say that energy of a system is of two parts, one its internal energy and then what did I call as the bulk energy.

(Refer Slide Time: 18:35)



E = Internal + 'Bulk' energies.

$= U + (PE + KE)$

$mg(z)$ $\frac{m}{2} V^2$

Elevation of system

Datum (level)

Velocity of system

Reference.

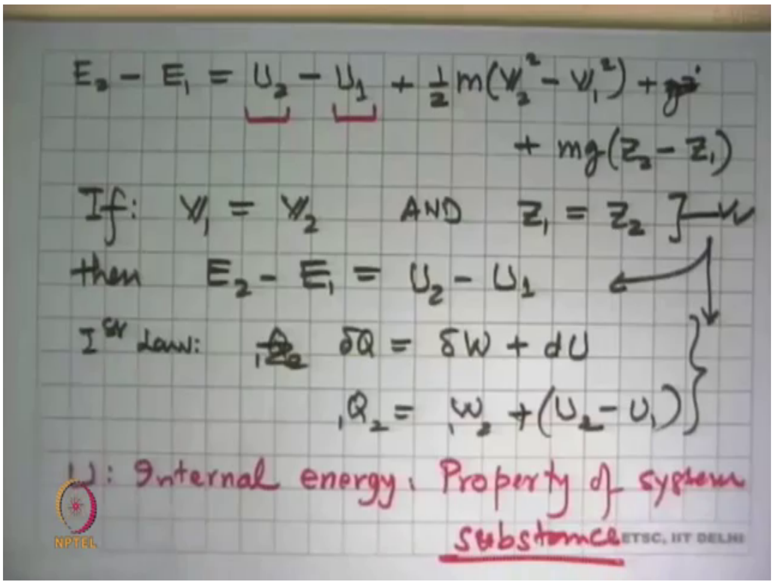
$dE = dU + d(KE) + d(PE)$

Internal energy is energy internal to the molecule which is U and by bulk we mean two types potential energy and kinetic energy. We are not going to the full derivation of this, but it given in the notes we can find that this is equal to potential energy is mass of the system mg into z and this is mass m its velocity square this V is velocity of system.

This is elevation of the system. A velocity requires a reference frame something we have learnt in school that if you have initial reference frame which means it is absolutely stationaries reference frame then you are in doing the right thing, otherwise we define certain reference frame and say on this earth this is my reference frame and relative to that it will figure out what is happening.

This requires a datum that means, some sort of a level from which we measure its elevation. So, that is the second one. And in elemental form this will become then dE is equal to dU plus d KE plus d PE. Note these are properties of the system. So, we can write them as exact differences and not the deltas. And if you want to do it as integrate it and get some numbers then that expression becomes E 2 minus E 1 is U 2 minus U 1 plus half m V 2 square minus V 1 square plus mg Z 2 minus Z.

(Refer Slide Time: 21:03)



$$E_2 - E_1 = \underbrace{U_2}_{} - \underbrace{U_1}_{} + \frac{1}{2}m(V_2^2 - V_1^2) + \cancel{gz} + mg(Z_2 - Z_1)$$

If: $V_1 = V_2$ AND $Z_1 = Z_2$ ✓

then $E_2 - E_1 = U_2 - U_1$

I^{st} law: $\cancel{{}_1\Delta_2}\ \delta Q = \delta W + dU$

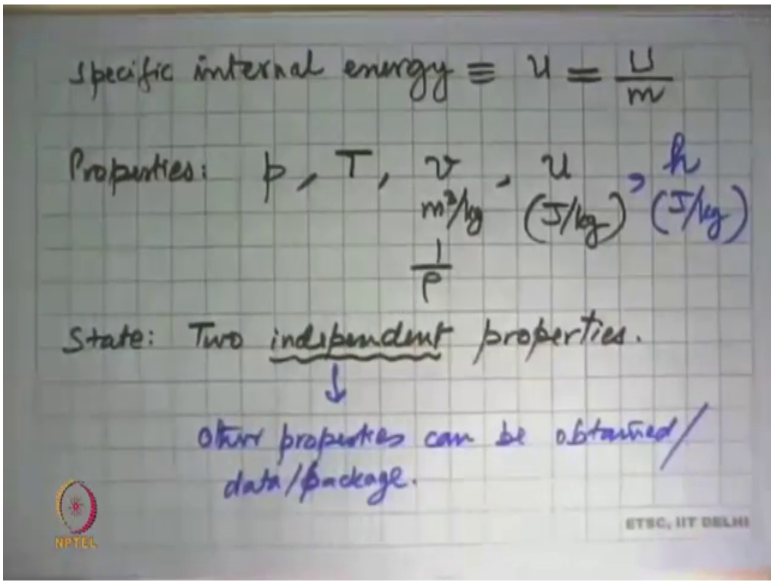
$${}_1Q_2 = {}_1W_2 + (U_2 - U_1)$$

U: Internal energy: Property of system substance

So, this is a very important step and we should be very clear that when we are writing the first law for the process the expression is that it is dE and not dU and quite often receive at the very starting point people will say this is equal to dU which we will say when is that true. For that to be true this term has to be 0, this term has to be 0 that means, if and only if V 1 is equal to V 2 that means, that velocity is in the two states are equal and the elevations remain unchanged, then E 2 minus E 1 is equal to U 2 minus U 1 and then the first law statement is in elemental form, it becomes delta Q is equal to delta W plus dU or Q 1 2 is equal to W 1 2 plus U 2 minus U 1.

So, this is restrict of condition that only if this is true then this and this they are true. If we cannot justify these then we cannot use this equation, we have to go back and work with E 2 minus E 1. But whereas, something here which is not for us that we define U 2 and U 1 for the U as energy internal to the structure of the molecule, and that is what we call internal energy and this is a property of the system when we say system we actually mean the working substance which is there in the system. And for unit mass we define that as specific internal energy as U which is u divided by the mass of the system.

(Refer Slide Time: 24:15)



Specific internal energy $\equiv u = \frac{U}{m}$

Properties: p, T, v, u, h

v: m^3/kg, $\frac{1}{\rho}$; u: (J/kg); h: (J/kg)

State: Two independent properties.

↓

other properties can be obtained/ data/package.

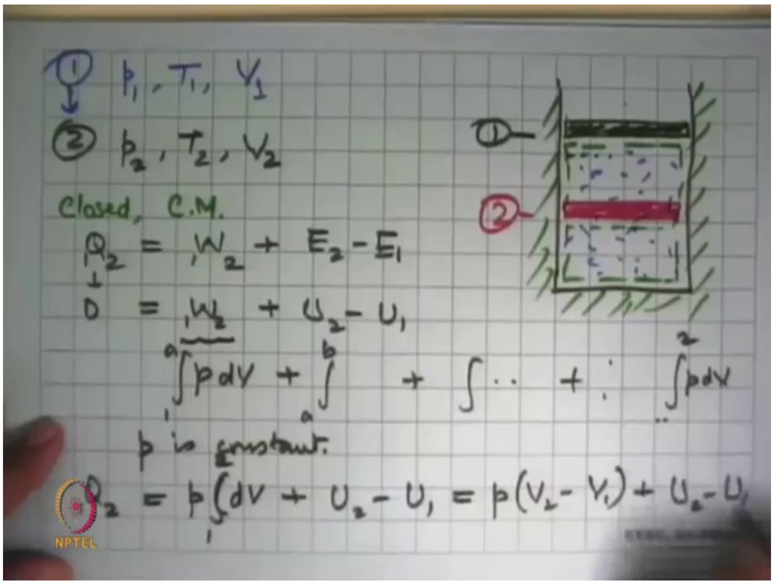
ETSC, IIT DELHI

So, that brings us to the point where we now start talking of properties of which we already knew that we have something called pressure, we also have what the units where in SI system, temperature, we got an idea for that and little scientific basis for it. We have already come across specific volume meter cube per kg which is the inverse of density kg per meter cube and now we have added a 4th to the list specific internal energy units would be like this is energy, this is mass Joules per kg.

So, if a system has 4 properties to completely specified the state how much do we need to specify. Do we under specify then we have not do not have enough information, we over specify when there is a probability that there could be contradictions. And that goes back to a basic idea that to completely specify the state we need to specify two independent properties. This word will become clear a little later in the third module. The except for some cases a though happen to be very important situations these are all independent properties.

So, if you take a system I know p and T except those few cases you can say yes I have completely specified the state which means that through this information I can get this I can get this. Or somebody says I know what is T and v, T and v is always a unique combination, the state is fully specified. We can calculate p; we can compute u and anything else. If v and u are giving then also the state is completely specified, we can go back and get p, T and everything else that we want. So, any two of these except for some cases p and T, these are all independent property from a pair of independent property the state can be completely specified, ok. So, that was the idea of internal energy and we now look at one case and see how distinct place itself out. And the example we take is a cylinder piston arrangement.

(Refer Slide Time: 27:13)



① p_1, T_1, V_1

② p_2, T_2, V_2

Closed, C.M.

$${}_1Q_2 = {}_1W_2 + E_2 - E_1$$

$$0 = \underbrace{{}_1W_2} + U_2 - U_1$$

$$\int_1^a p\,dV + \int_a^b + \int \cdots + \int_{..}^2 p\,dV$$

p is constant.

$${}_1Q_2 = p\int_1 dV + U_2 - U_1 = p(V_2 - V_1) + U_2 - U_1$$

So, we have so many substance inside this and we are working with ideal case where there is no friction between this and this and there is no leakage between this and this. These are idealization in the real world that is not the case and when one actually does the engineering of any such machine you have to flutter those things in and so that much more loses will always be there.

So, we say that this was the initial state, state 1. And state 1 the system was at p 1, T 1 and its volume was V 1. As we say that this system is insulated perfectly, perfect insulation means that there is no heat transfer taking place from this to the surroundings or from here to there also. The piston is also insulated. And this is compressed pushed down and the piston comes here, this is state 2, earlier we had here there was state 1. And now in state 2, we have p 2, T 2, and V 2, we are putting any restrictions on how it happened, how fast it happened or anything like that. And we say let us apply the first law of thermodynamics to this process the process is 1 to 2.

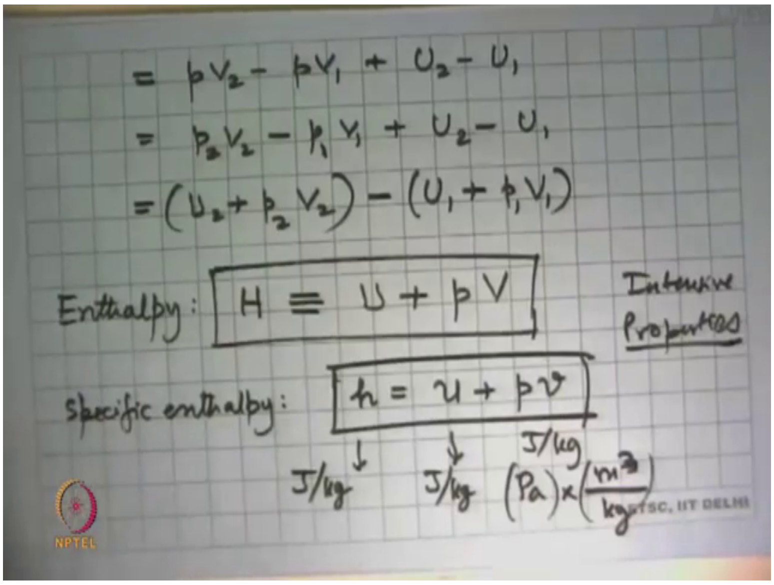
This is a closed system, if we now begin another this is our first step is to decide what is the system boundary at state 1, this was the system boundary at state 2, this is the system boundary. Whatever mass was there in state 1 is still there in state 2 and so we had justify and saying that first this is the closed system and we will apply, apply the control mass approach to this. And for this we already have the first law with us which says that Q 1 2 is equal to W 1 2 plus E 2 minus E 1.

We then look at the system and say look the c g of this gas was there now it is here, this is very very small this is hardly any change there. The system whole system was stationary it is still stationary here, so V 1 V 2 are both 0. So, we can justify say that this is equal to U 2 minus U 1 and this was perfectly insulated Q 1 2 becomes 0 and we have left with W 1 2 is equal to plus U 2 minus U 1 is equal to 0.

And in now we say how can I express the work term. So, initially this was p 1 and we say that when it was up here and it leaved a small distance down there it would be p d y and we would integrate it over the small element. And then as it going from one to the small element a, then it went from a to b we would do the same thing and we keep doing that until it finally, gets on something it reaches 2. That would be lot of small small steps that we would take to compute the work of outflow or the work inflow and by the way this is what people do in modern programs that do simulation or say an internal combustion engine that is how you want to analysis and we that need a simplification here.

We let us say that in this compression process we have done it in such a way that p is constant. And is need not even be necessary that this be insulated we can leave that in general and say ok, this is Q 1 2 and this is p constant make this will become p integral dV state 1 to 2 plus U 2 minus U 1 which will be p times V 2 minus V 1 plus U 2 minus U 1. Why we are doing this, it will become clear in the minute. The answer is we will solve that.

(Refer Slide Time: 32:21)



$$= pV_2 - pV_1 + U_2 - U_1$$

$$= p_2V_2 - p_1V_1 + U_2 - U_1$$

$$= (U_2 + p_2V_2) - (U_1 + p_1V_1)$$

Enthalpy: $\boxed{H \equiv U + pV}$

Intensive Properties

Specific enthalpy: $\boxed{h = u + pv}$

$$\underset{\text{J/kg}}{h} = \underset{\text{J/kg}}{u} + \overset{\text{J/kg}}{\underset{(\text{Pa})\times\left(\frac{m^3}{kg}\right)}{pv}}$$

So, this becomes p V 2 minus p V 1 plus U 2 minus U 1 and if p 1 and p 2 are equal we can quite generally say that this is this, minus p 1 V 1 plus U 2 minus U 1 and this gives us a term U 2 plus p 2 V 2 minus U 1 plus p 1 V 1. And what we see is the combination coming here that is what we were trying to do U plus p V, U plus p V. And this combination we define as a new property which is called the enthalpy H defined as U plus p V or in terms of specific enthalpy H is equal to U plus p V.

So, these are relations which are important by themselves and also in solving many problems as we will see in the little while H becomes far more frequent than U and so if you look for property data you would be more interested in data for H rather than data for U. The first thing is units U is Joules per kg, H will also be Joules per kg, p V should also be Joules per kg, and to get that p has to be in pascal and V has to be meter cube per kg. It is important to keep the units straight when making this calculation. We often work with kilo pascals and bar and mega pascals, but when you come to this point we have to have pascal over there

Next thing is care it to this expression through a little bit of jugglery. We assume that pressure is constant and then we substituted the initial and final pressure, but that does not matter in the end or what you have is that U, p V or all intensive properties that means, the property that depends only on the state of the system and not how it got there.

So, H is also an intensive property. If you look at this in the third module in detail, but for right now it does not matter whether the substance was in liquid phase, vapor phase, solid phase, a mixture or in a ideal gas it makes absolutely no difference this expression is always true and so the other two expression that we have written for the first law statement. They are completely independent of the application, the completely independent of the working substance and any pressure and temperature that may be there, there is no issue of having a doubt on that part.

Everything else does in solving a problem is look at special cases by removing something adding something and making that give you more easy. So, we have now defined yet another property, and if we go back to the cheat where we wrote all these properties then here we now at this list one more thing h and this is also Joules per kg.

And you like before, if you know any two of these or even these two or these two, we the state is completely specified and we can calculate the remaining properties, that is what is important. That if you have these two properties other properties can be obtained or there are data or charts or computer programs from there we can get this. And the reason for that is that all this properties are related to each other through differential equations.

In this course we do not have to go into the details of those differential equations that is the subject of an advance course in thermodynamics. But using those differential equations if we know two properties, we can do mathematical operation and get all the properties that is the idea. So, we know have that many properties to work with.