Course on Phase Equilibrium Thermodynamics
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Lecture 03
First Law of Thermodynamics

Well good day to all of you, so in the last 2 classes I have already completed the introduction and by this time you know that what is a phase? Of course I had completed to rather I forgotten to mention what a phase is? A phase is that portion of matter which is uniform throughout in physical structure and chemical composition or in other words it is a homogeneous piece of matter. So therefore any system that we select that may comprise of single phase or that may comprise of more than one phases, okay.

Now when we have a system comprising of more than one phases then naturally within that particular system the 2 phases are going to interact they both the phases they settle down to an equilibrium state. And in thermodynamics what are you going to study particularly? We are going to study the properties or the relationships between properties of the 2 phases of any particular system and when the system has a whole interacts with the surroundings by virtue of either heat or work, how the states of the 2 phases they change? How they are connected? And what are the relationships governing phase equilibrium when 2 or more phases are in equilibrium within any particular system?

Now before we go to 2 phase systems, the first thing which you are going to deal with is the simplest thing we are going to deal with homogeneous systems or single phase systems. We are going to find out the relationships between the properties of the different single phase or homogeneous systems and the relationships of these properties with the energy interactions which the system has with the surroundings. We are going to take up close systems first and then we are going to deal with open systems or rather we are going to extend the analysis for open systems at one and an isolated systems at the other end.

So therefore after we study the energy interactions, next we need to know that whether any process is possible in a system or not or whether there are some processes which are possible some processes which occur spontaneously to bring about the change in a system and some processes they are not possible and we need to expend energy for them or rather to make them happen.

Or in other words we shall be discussing in brief about the feasibility of the different processes which a system may undergo. And after that once we have understood more or less the heat work or rather the energy interactions between a system and surroundings for the time being, if initially we are going to take single phase systems we understand what are the feasible processes in the system, then the next thing which we do is before going into the details of phase equilibrium we are going to deal with single component 2 phase systems and then we go for 2 components or multi-component multiphase systems.

So gradually we proceed and as we proceed the complexity increases and as I have already mentioned in my introductory lecture that since many of you will be interested in petroleum refineries etc, so I will be touching upon some portions of hydrocarbon thermodynamics the remaining can be clarified from the book of Edmister or any other book which you find is rudiment.

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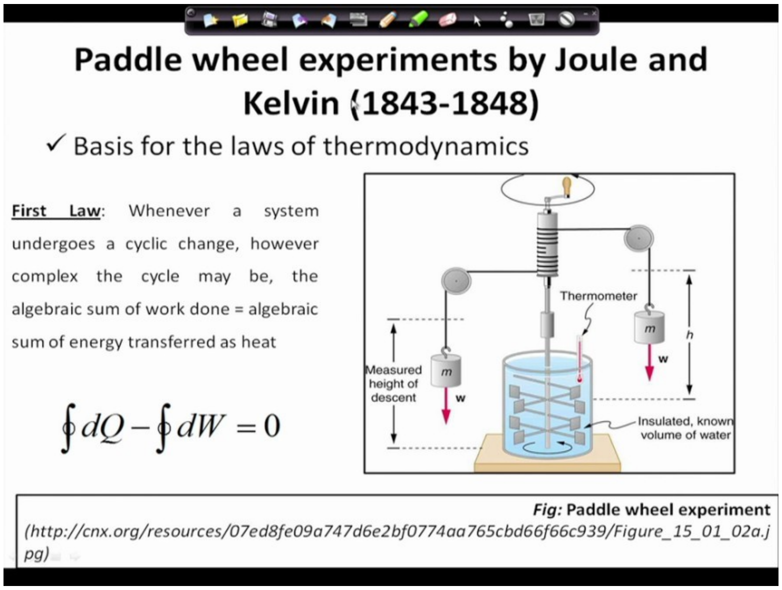

Paddle wheel experiments by Joule and Kelvin (1843-1848)

✓ Basis for the laws of thermodynamics

First Law: Whenever a system undergoes a cyclic change, however complex the cycle may be, the algebraic sum of work done = algebraic sum of energy transferred as heat

$$\oint dQ - \oint dW = 0$$

Fig: **Paddle wheel experiment**
(http://cnx.org/resources/07ed8fe09a747d6e2bf0774aa765cbd66f66c939/Figure_15_01_02a.jpg)

Now the entire we the paradigm of thermodynamics it is governed by primarily the 2 laws along with zeroth law and third law of thermodynamics which is also there. Now these 2 laws they had originated from a series of experiments which had been performed by Joule and Kelvin between 1843 to 1848 they are known as the famous paddle wheel experiments what did they do? The experiments were very simple at that time they were quite crude but they came up with some very important observations which formed the basis of the 2 important laws of thermodynamics. What was the experiment that they did?

The experiment was they had contained water in a insulated vessel and in that particular vessel it was connected with a paddle wheel and this particular paddle wheel it was rotated by the lowering of the mass which was attached to the pulley arrangement on the top. So therefore what these 2 scientists they had tried to do? They had rotated this particular paddlewheel with quite sufficient speed and they had heated the water contained in the vessel, okay.

And how much amount of work was done or how much amount of heat was rather how much amount of work was done on this particular water that could be manifested only by a change of state of the system from an initial temperature T1 to a final temperature T2 which was noted by means of the thermometer. Now after the paddle wheel they also use other types of devices to perform work on this same volume of water kept in an insulated rigid container.

They found out that no matter whatever device they used in order to perform this amount of work it was found that the amount of work performed was proportional to the amount of temperature increased. For each case the temperature increased they have maintained the temperature increase as constant and they found out that for each case the amount of work performed it was proportional to the temperature increase which occurred.

And after each experiment after the temperature increased what they did? They broke the insulation and immersed this volume of water inside the water bath to bring it back to the original temperature and that they could find out what was the heat given up to the amount of water contained in the water bath. Now this particular experiment which they did they found 2 very important observations which formed the basis of the first law and the second law of thermodynamics.

The first thing as I have already mentioned they found out that the amount of work done was proportional to the temperature increase in each case, no matter how the work was performed and they observed that whenever the system it undergoed the cyclic change, what was the cyclic change? When the initial and final states of the system are the same mind it, cyclic changes can be reversible they can be irreversible it is important to remember that a reversible cyclic changes both the system and the surroundings come back to their original state and for a irreversible cyclic change it is the system which is brought back to its original state the surroundings does not come.

When they performed a series of irreversible experiments because as we have already discussed it is not possible to obtain reversible processes or reversible cyclic processes in practice. So what did they find? They found out that whenever a system was undergoing a cyclic change however complex the cycle maybe it was found that the cyclic integral of dQ was always proportional to the cyclic integral of dW where the constant of proportionality was 1 in SI units.

As a result of which the first law can be mathematically expressed as given as this particular expression. Now from this particular expression they found out some very important observations which led to the law of conservation of energy as we all know. It is important is to remember that first law does not directly give you the law of conservation of energy it is a consequence of first law. In this particular experiment they also had another very important observation, they found out that when they were performing of work the temperature was increasing and then when after the temperature increased they broke down the insulation and immersed this particular volume of water in a water bath when it gave up heat and came back to its original state.

The same experiment was performed as I have already mentioned by different ways of work the same process was followed and the people found out that it was possible for going from state 1 to state 2 during that experiments that is they could heat up by performing work for all the experiments but the reverse process could not be performed, they could not use the heat content of this particular system in order to lower this particular weight.

So this was another very important observation they found out or in other words they could not first use the heat in order to perform work although the law of conservation of energy was obeyed in the process. So therefore these are the 2 observations first thing was that as it is shown by this mathematical statement from where we are going to see shortly we arrived at the law of conservation of energy and the second observation was while doing work and increasing the temperature of the system is the feasible one the reverse process could not be performed.

And if we have to use heat transfer in order to perform some amount of work they found out that some amount of heat has to be lost to a surrounding at lower temperature and only the remaining amount of heat some amount of useful work can be performed. Thus while the entire amount of work can be converted to heat the entire amount of heat cannot be converted to work as a result of which now we know that heat is a lower grade of energy as compared to mechanical energies.

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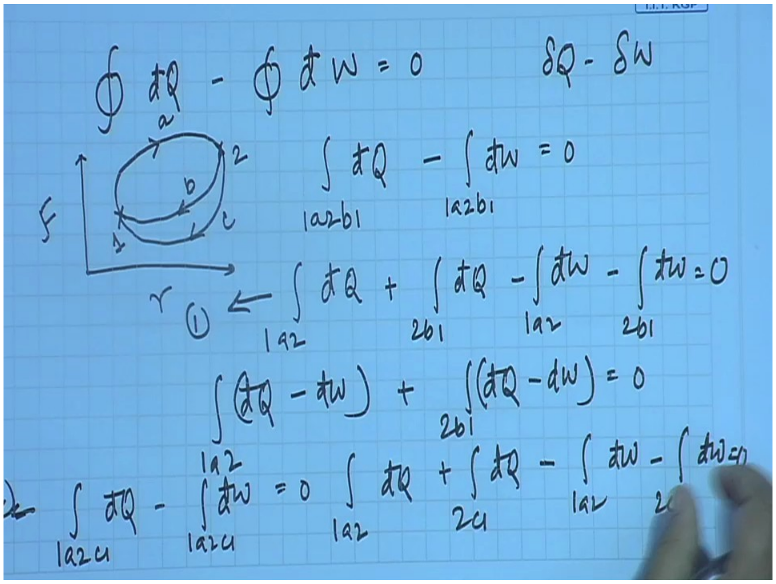

$$\oint \text{đ}Q - \oint \text{đ}W = 0 \qquad \delta Q - \delta W$$

$$\int_{1a2b1} \text{đ}Q - \int_{1a2b1} \text{đ}W = 0$$

① $\leftarrow \int_{1a2} \text{đ}Q + \int_{2b1} \text{đ}Q - \int_{1a2} \text{đ}W - \int_{2b1} \text{đ}W = 0$

$$\int_{1a2} (\text{đ}Q - \text{đ}W) + \int_{2b1} (\text{đ}Q - dW) = 0$$

$\int_{1a2c1} \text{đ}Q - \int_{1a2c1} \text{đ}W = 0 \qquad \int_{1a2} \text{đ}Q + \int_{2c1} \text{đ}Q - \int_{1a2} \text{đ}W - \int_{2} \text{đ}W = 0$

So these were the 2 observations based on which the 2 laws of thermodynamics were formulated. Let us now see the formulation of the first law of thermodynamics, as I have told you it gives you the equation as dQ. Well, I will just mention that it is not the, these here are not cut so therefore they do not show an exact differential this is a typographical error which has happened but you please remember during your studies it’s very important that you show the inexact differentials by either this thing or you can also write it down as Delta Q minus Delta W. In the class I will be cutting the Ds to denote inexact differentials.

So therefore from this particular process suppose again I distance all of these suppose I assume reversible processes and I plot the reversible processes not on a PV plot but on a generalize F-r plot where F is a generalized thermodynamic driving force, r is generalized displacement. Now here suppose my initial state was 1 from this initial state I go to the state 2 by a reversible process which can be plotted reversible process 1a2 which can be shown by a solid line here and I come back from here by another reversible process 2b1. Now my entire process 1a2b1 is a reversible cyclic process.

So for this entire process I can write down that integral of 1a2b1 dQ minus integral 1a2b1 dW this is equal to 0, so therefore I can also break it down and write it down as dQ 1a2 plus integral dQ 2b1 minus integral dW 1a2 minus integral dW 2b1 this is equal to 0. I can rearrange it and write it down as integral dQ minus dW 1a2 plus integral dQ minus dW 2b1 this is equal to 0, I can write it down in this particular way.

Now instead of 2b1, I can also come back by another process and again a reversible process by a different path which is 2c1. So for this particular 1a2c1 for this particular cyclic integral also I can write it down as 1a2c1dQ minus integral dW1a2c1 this is equal to 0. In the same way I can break it down and I can write it down as integral 1a2dQ plus integral 2c1dQ minus integral 1a2dW minus integral 2c1dW that is equal to 0. Now if I subtract equation 2 from equation 1 what am I going to get? I will just write down the equations once more for your convenience and then I perform the subtraction.

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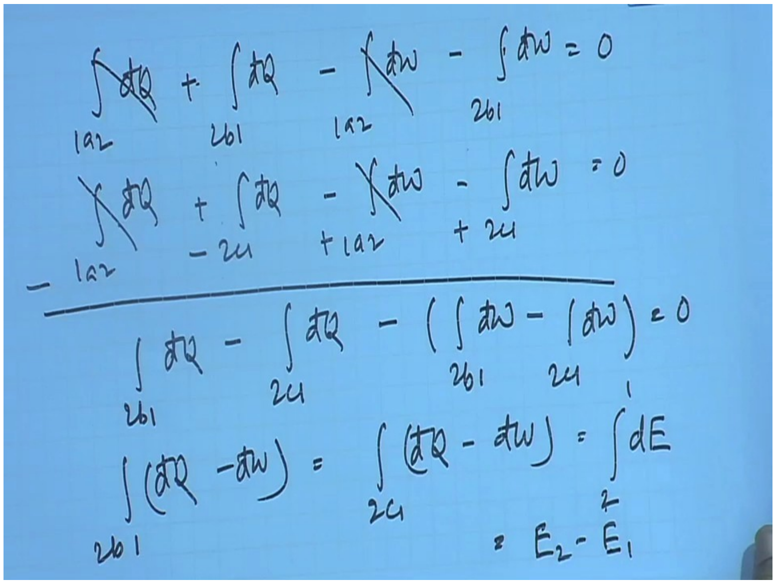

$$\cancel{\int_{1a2} dQ} + \int_{2b1} dQ - \cancel{\int_{1a2} dW} - \int_{2b1} dW = 0$$

$$-\ \underset{1a2}{\cancel{\int dQ}} + \underset{-\,2c1}{\int dQ} - \underset{+\,1a2}{\cancel{\int dW}} - \underset{+\,2c1}{\int dW} = 0$$

$$\int_{2b1} dQ - \int_{2c1} dQ - \left(\int_{2b1} dW - \int_{2c1} dW \right) = 0$$

$$\int_{2b1} (dQ - dW) = \int_{2c1} (dQ - dW) = \int_{2}^{1} dE$$

$$= E_2 - E_1$$

First equation is 1a2 plus dQ 2b1 minus dW1a2 minus integral dW 2b1 equals to 0 and the second equation is dQ1a2 plus dQ2c1 again dW 1a2 dW 2c1 equals to 0. Now if I subtract one from the other what do I get? I find that these dQs and these dWs they cancel out and what do I get? I get integral dQ2b1 minus integral dQ2c1 minus integral dW2b1 minus integral dW2c1 this whole thing equal to 0 or in other words can I write it down as integral dQ minus dW 2b1 this is equal to integral dQ minus dW 2c1 can I write it down in this particular way? And moment I have written it down in this particular way can you tell me what does it imply?

It implies that dQ it depends upon the path dW depends upon the path but the difference between dQ and dW that is equal for both the paths 2b1 and 2c1. When the initial state and the final state initial state is 2 in both cases the final state is 1 in both cases when the initial and final states are the same then the difference between 2 dQ and dW this particular quantity remains the same, what does it mean?

It means that dQ although dQ is a path function dW is a path function the difference between the two must be a state function and that should depend upon the initial state and the final state. And this particular difference the difference between dQ and dW this is stored as internal energy or as energy of the system and this energy of the system it depends upon the initial state and the final state it does not matter whether we are coming from the initial 2 the final state via path c or via path b the difference is the same this is nothing but E2 minus E1, right?

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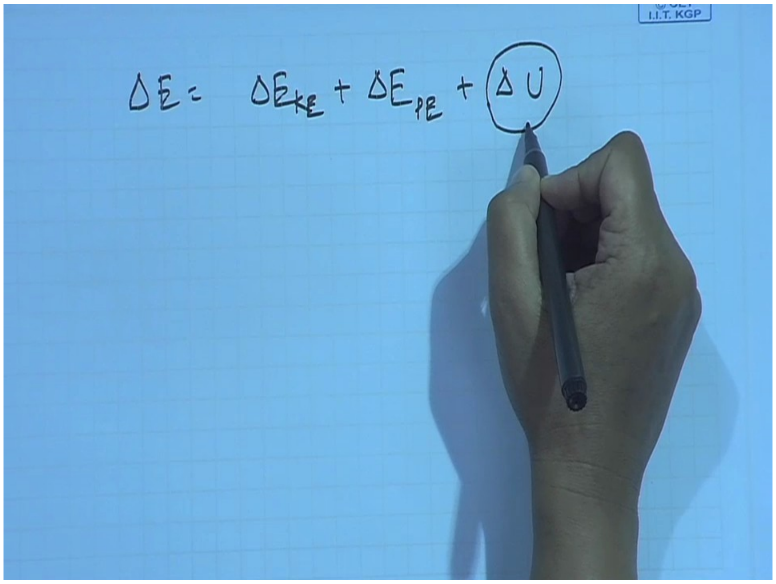

So therefore from here what do we get? We get rather the first thing which we get is that the difference between these 2 is equal to the energy stored in the system and this particular energy stored this Delta E this is a property of the system, this Delta E this comprises of the Kinetic energy of the system, the potential energy of the system and also the internal energy of the system plus and this internal energy comprises of the energy of the ultimate particles which comprises of of a the different motions of the molecules etc etc.

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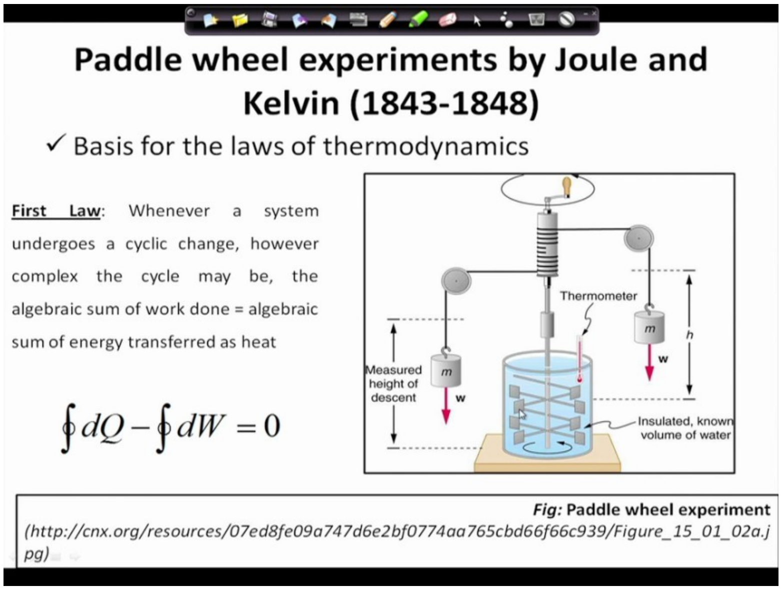

Paddle wheel experiments by Joule and Kelvin (1843-1848)

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Fig: **Paddle wheel experiment**
(http://cnx.org/resources/07ed8fe09a747d6e2bf0774aa765cbd66f66c939/Figure_15_01_02a.jpg)

And this is the internal energy which was manifested by the increase in temperature in this paddle wheel experiment. Usually in thermodynamics we deal with we deal with stationary systems which do not have much displacement.

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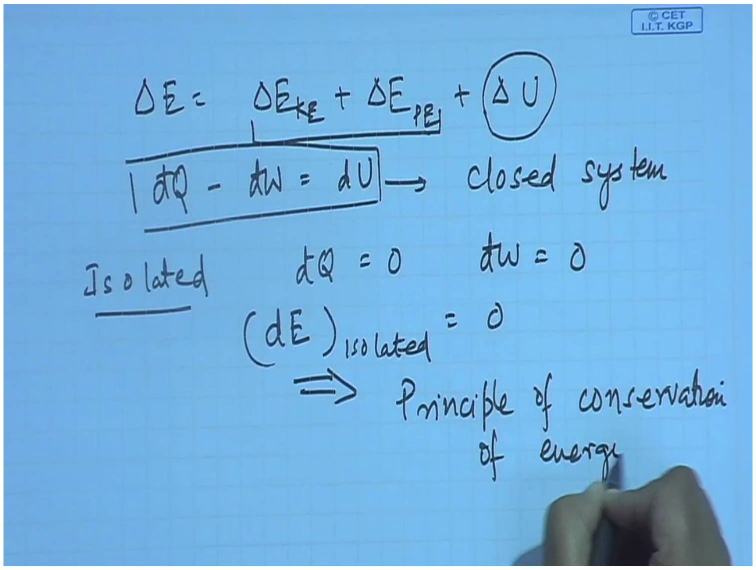

$$\Delta E = \underbrace{\Delta E_{KE} + \Delta E_{PE}} + \Delta U$$

$$\boxed{dQ - dW = dU} \longrightarrow \text{closed system}$$

Isolated $dQ = 0$ $dW = 0$

$$(dE)_{isolated} = 0$$

$\Rightarrow$ Principle of conservation of energy

So therefore usually these 2 terms are 0 and therefore Delta E reduces to Delta U. And therefore from here we get that for a closed system dQ minus dW equals to dU this occurs for a closed system. So therefore for a closed system we can always say that the net energy change in the system is equal to the net energy transfer across the system boundary.

Now what happens for an isolated system, for an isolated system we know that it does not allow any sort of work either or rather any sort of interaction between the system and the surroundings so therefore for an isolated system what do we get? dQ equals to 0, dW equals to 0 which naturally brings you to the dE for an isolated system equal to 0 which is nothing but the principle of conservation of energy.

So therefore we find that from the first Law what do we get? We find that for closed systems the net energy change of the system is equal to the net energy interaction between the system and the surroundings and energy is conserved for an isolated system. Within an isolated system suppose there are differences in driving force between 2 parts of the system then definitely the 2 parts will interact but the total energy of the system remains constant which is known as the principle of conservation of energy and this particular principle of conservation of energy it includes all types of energy including the Kinetic energy or the mechanical energy the internal energy and so on and so forth.

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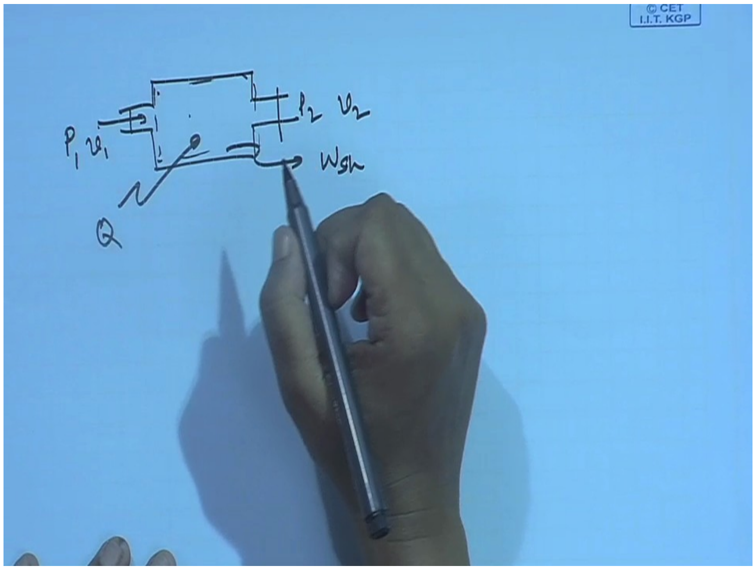

Now from here what do we get for an open system, for an open system what do we have let us see? Suppose we and let me remind you for most of the things that we work out a chemical reactor, a nozzle, a pump, a compressor most of these they deal with open systems. Now for open system suppose I take up an open system in this particular manner it is just a black box because it can be anything. So therefore I take it up as a black box.

So say for example it can be a reactor it can be anything so from here we find that at pressure P1 some amount of volume is entering here the pressure is P2 and some amount of volume V2 goes out here we find that shaft work possibly this particular device it performs some amount of shaft work may or may not perform, some amount of heat enters in this particular system and then we find that here some additional work is required other than the shaft work to push this volume of fluid inside and this work is done on the system. So therefore it is negative work and some amount of work the system does to push out some volume of liquid or some volume of this system out through it.

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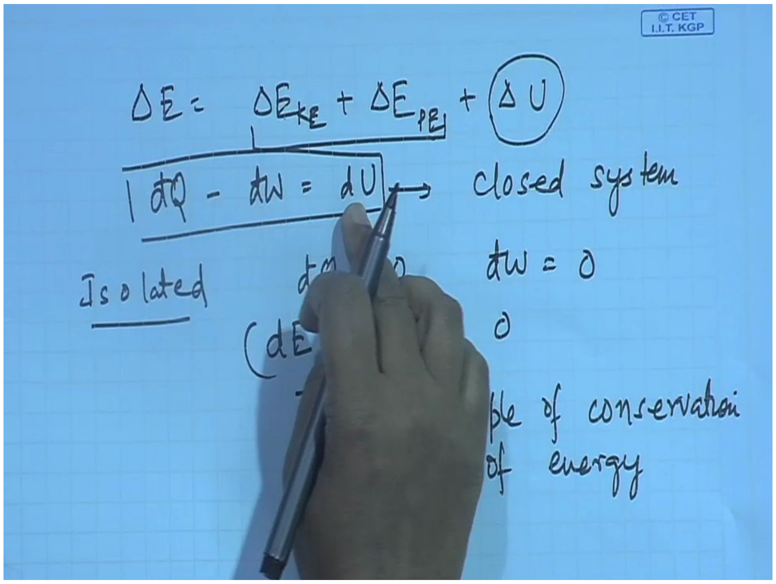

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$\Delta E = \underbrace{\Delta E_{KE} + \Delta E_{PE}}\ + \boxed{\Delta U}$

$\boxed{dQ - dW = dU} \rightarrow$ closed system

Isolated

$dW = 0$

0

$(dE$

ple of conservation of energy

So therefore this was my reactor and what do I do? In order to use the first Law for closed systems I need to keep the mass of the system constant.

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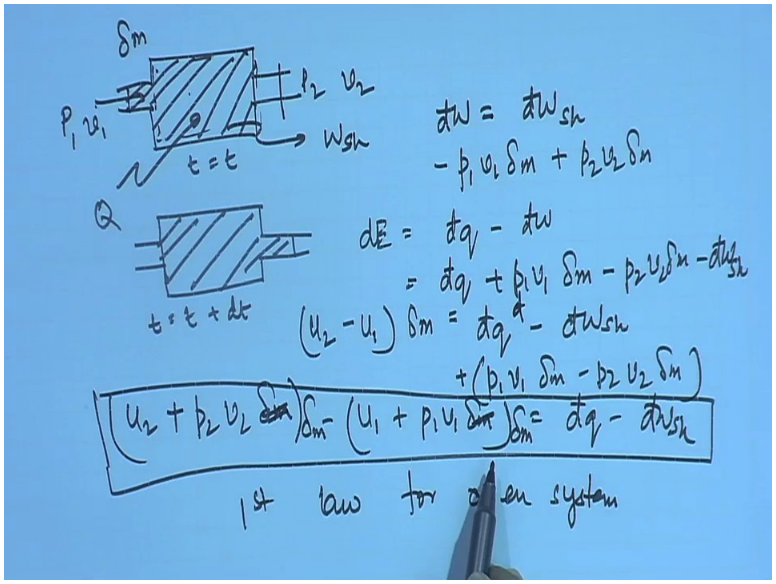

$$\text{đ}W = \text{đ}W_{sh} - p_1 v_1 \delta m + p_2 v_2 \delta m$$

$$dE = \text{đ}q - \text{đ}W$$
$$= \text{đ}q + p_1 v_1 \delta m - p_2 v_2 \delta m - \text{đ}W_{sh}$$

$$(u_2 - u_1)\,\delta m = \text{đ}q - \text{đ}W_{sh} + (p_1 v_1 \delta m - p_2 v_2 \delta m)$$

$$\boxed{(u_2 + p_2 v_2 \cancel{\delta m})\,\delta m - (u_1 + p_1 v_1 \cancel{\delta m})\,\delta m = \text{đ}q - \text{đ}W_{sh}}$$

1st law for open system

So therefore I devise my system such that its mass remains constant while some particular fluid it keeps on flowing through it and the device interacts with the surrounding by virtue of work and heat. So what do we do? We assume that the system comprises of the amount of mass which is contained in this particular control volume and the amount of mass which is going to enter in this control volume during time dt. So therefore at time t this is my system, this whole thing is my system. And at time t plus dt I assume that my system has some amount of mass has gone out through this, so now my system changes into this particular configuration.

So what do I find? I find that my system comprises of a fixed mass of gas which is enclosed by a flexible boundary and I break my entire process into small timescales dt during this time scale dt say some amount of mass Delta m is entering the system some amount of mass Delta m is going out of the system. So therefore at time t my particular system comprises of the entire mass here plus the Delta m mass which is going to enter here and at time t plus dt my system comprises of the time the mass which has already and the mass which has gone out during this time t plus dt.

Now in this particular case what is my dW? dW definitely will comprise of the shaft work and along with that it is going to comprise of the work which was done on the fluid so that it can enter and the work which the system did on the fluid such that it can go out. So therefore the total work in this case comprises of the shaft work and the work which was done on the system in pushing this fluid plus the work done by this system in pushing out the fluid.

So therefore in this particular case my dE equals to dQ minus dW where this particular dW can be written down as minus P2V2 Delta m minus dW shaft, right? So therefore for stationary systems where there is no potential energy change also for those particular cases E can be written down as U. So therefore in this particular case I get U2 minus U1 into Delta m this is nothing but equal to dQ minus dW shaft plus P1V1 Delta m minus P2V2 Delta m or in other words if I bring it here to this side I get U2 plus P2V2 Delta m minus U1 plus P1V1 Delta m this is equal to dQ minus dW shaft. This is my first Law for open systems.

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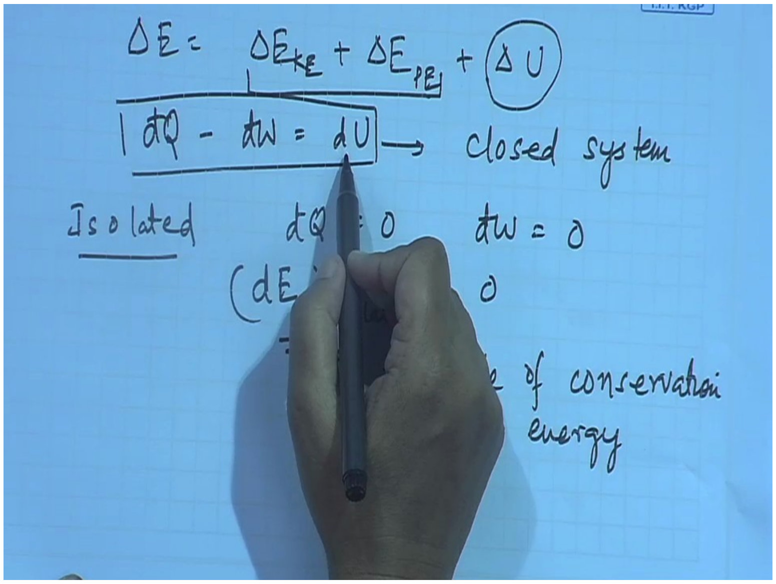

I am sorry this Delta m should have been here this Delta m, sorry for making this mistake or in other words what I get is, I get that what this particular for open systems what I get that while in closed systems my dQ minus dW was equal to dU.

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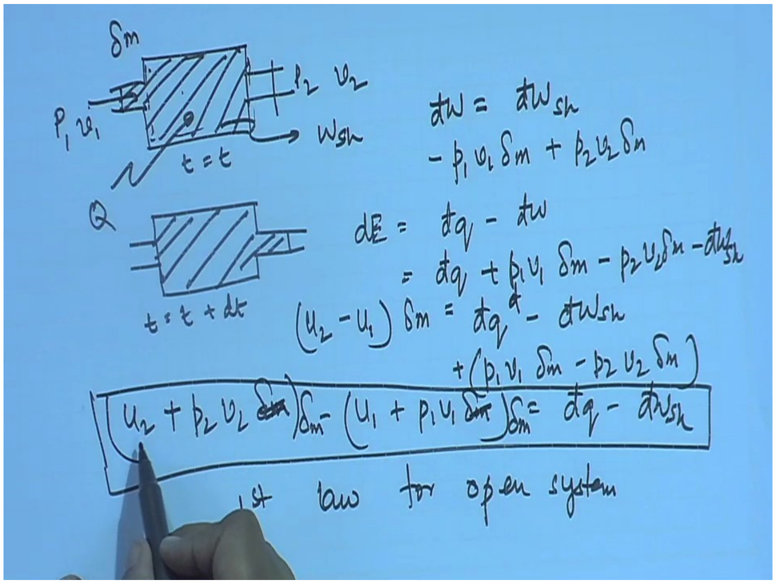

$$\text{đ}W = \text{đ}W_{sh} - p_1 v_1 \delta m + p_2 v_2 \delta m$$

$$dE = \text{đ}q - \text{đ}w$$

$$= \text{đ}q + p_1 v_1 \delta m - p_2 v_2 \delta m - \text{đ}W_{sh}$$

$$(u_2 - u_1)\,\delta m = \text{đ}q - \text{đ}W_{sh} + (p_1 v_1 \delta m - p_2 v_2 \delta m)$$

$$\boxed{(u_2 + p_2 v_2 \cancel{\delta m})\,\delta m - (u_1 + p_1 v_1 \cancel{\delta m})\,\delta m = \text{đ}q - \text{đ}W_{sh}}$$

1st law for open system

In this case I find that dQ minus dW shaft this is equal to some particular term which also has which is a property of the system and has the units of energy that is U2 plus P2V2 here U1 plus PIV1 and as possibly you are aware of this fact that U plus PV is nothing but the we have defined it with another particular property group which is known as the Enthalpy of the system.

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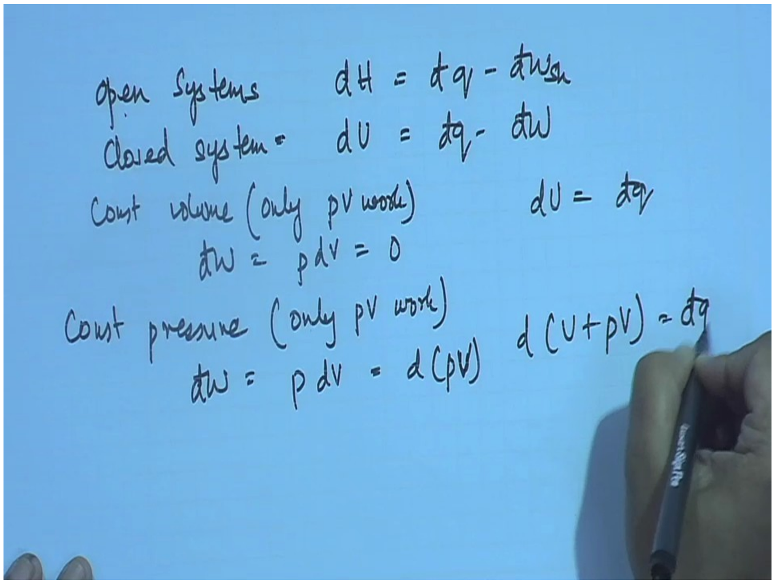

open systems $dH = \text{đ}q - \text{đ}W_{sh}$

Closed system: $dU = \text{đ}q - \text{đ}W$

Const volume (only pV work) $dU = \text{đ}q$

$\text{đ}W = p\,dV = 0$

Const pressure (only pV work) $d(U + pV) = \text{đ}q$

$\text{đ}W = p\,dV = d(pV)$

So therefore for open systems we can write it down as dH which equal to dq minus dW shaft. For closed systems we had dU was equal to dq minus dW. Now suppose we take a close system at constant volume, what happens? And suppose we assume that the only work which can be performed is PV work or in other words dW equals to PdV. So in this case for constant volume work done is equal to 0 and dU equals to dq.

Suppose I take up a constant pressure process and or other a Isobaric process again assume only PV work is done. So in this case dW equals to PdV which is nothing but equal to d pV as well isn’t it? So therefore for this particular case what do I find? We find for this particular case d of u plus PV equals to dq.

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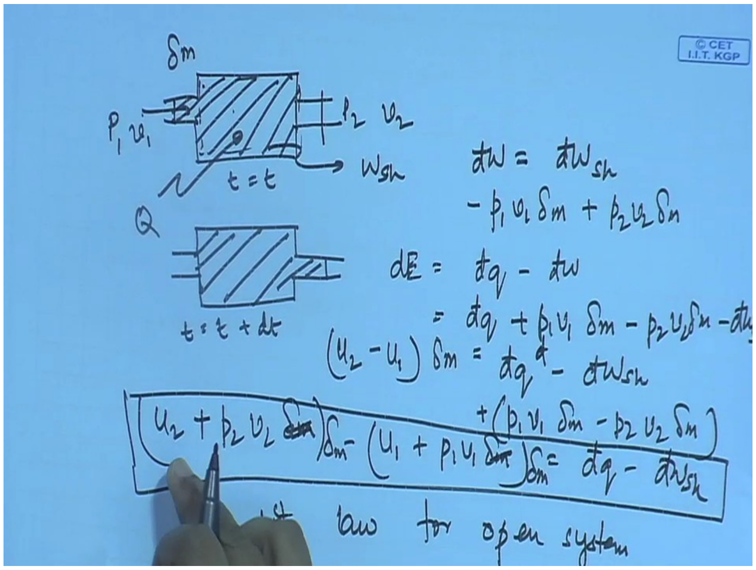

$$\bar{d}W = \bar{d}W_{sh} - p_1 v_1 \delta m + p_2 v_2 \delta m$$

$$dE = \bar{d}q - \bar{d}w$$

$$= \bar{d}q + p_1 v_1 \delta m - p_2 v_2 \delta m - \bar{d}w$$

$$(u_2 - u_1)\,\delta m = \bar{d}q - \bar{d}W_{sh} + (p_1 v_1 \delta m - p_2 v_2 \delta m)$$

$$\boxed{(u_2 + p_2 v_2 \cancel{\delta m})\,\delta m - (u_1 + p_1 v_1 \cancel{\delta m})\,\delta m = \bar{d}q - \bar{d}W_{sh}}$$

st law for open system

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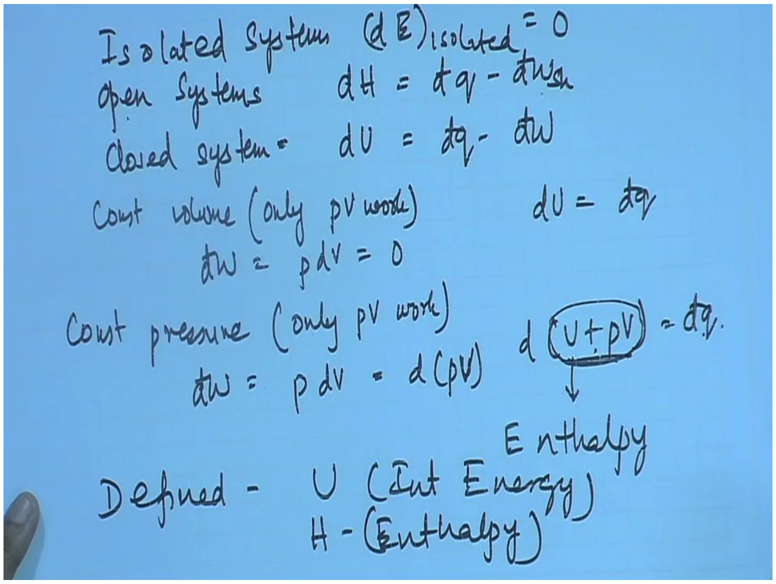

Isolated System $(dE)_{\text{isolated}} = 0$

open Systems $dH = \text{đ}q - \text{đ}W_{sh}$

Closed system: $dU = \text{đ}q - \text{đ}W$

Const volume (only pV work) $dU = \text{đ}q$

$\text{đ}W = p\,dV = 0$

Const pressure (only pV work) $d\,\underbrace{(U+pV)}_{\text{Enthalpy}} = \text{đ}q.$

$\text{đ}W = p\,dV = d(pV)$

Defined - U (Int Energy)

H - (Enthalpy)

The same u plus PV which I had got in for a close system, I find that we have come across the same u plus pV for an Isobaric close system as well. So we find that this particular term u plus pV which also has a property of energy, so this we encounter very frequently so instead of writing u plus pV every time we thought of defining it as one particular term and we define this particular term as the Enthalpy of the system.

So therefore from the first Law what did we do? We found out that the first Law deduces the law of conservation of energy for an isolated system and it gave the law as dU equals to dq minus dW for a closed system and particularly since as we know that we are primarily very frequently we encounter isobaric processes or isobaric processes this reduces to dq equals to dH and also for open systems we find that law reduces to dq minus dW shaft equals to dH. So at the end of the first Law we have defined 2 new properties one is the internal energy of the system and the other is the enthalpy of the system.

Next class I would like to elaborate a little more on the enthalpy of the system and I would like also to talk about how much amount of temperature rise we can obtain by some particular heat interaction between the system and the surroundings or I would like to discuss a little more about the heat capacities and the specific heat capacities of the systems before I close the first Law and go for the second law of thermodynamics, thank you very much.