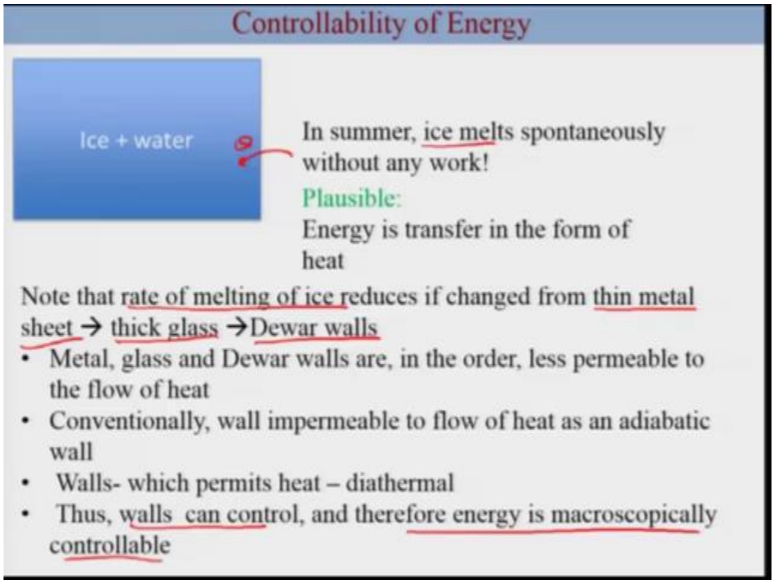
Chemical Engineering Thermodynamics
Professor Jayant K. Singh
Department of Chemical Engineering
Indian Institute of Technology, Kanpur.
Lecture 2
Measurability and Controllability of Energy

Welcome back. We were talking about controlling the energy of a system. So we will continue this discussion.

(Refer Slide Time: 0:31)



Controllability of Energy

Ice + water

In summer, ice melts spontaneously without any work!

Plausible:

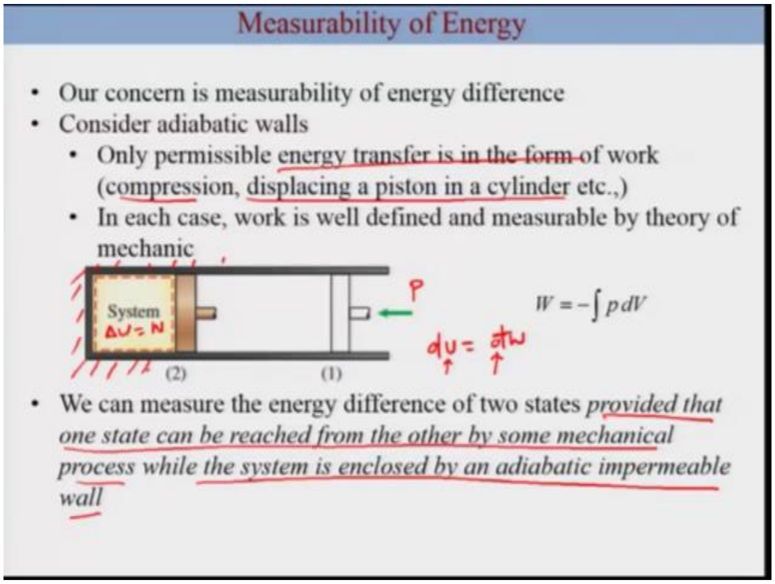
Energy is transfer in the form of heat

Note that rate of melting of ice reduces if changed from thin metal sheet → thick glass →Dewar walls

- Metal, glass and Dewar walls are, in the order, less permeable to the flow of heat
- Conventionally, wall impermeable to flow of heat as an adiabatic wall
- Walls- which permits heat – diathermal
- Thus, walls can control, and therefore energy is macroscopically controllable

So this was what we had discussed last time and we concluded that in order to control the energy walls can be modulated. In other word walls can control the energy of the system and therefore energy is microscopically controllable. Now, the next question was how do you measure the energy? .

(Refer Slide Time: 0:53)



Measurability of Energy

- Our concern is measurability of energy difference
- Consider adiabatic walls
    - Only permissible energy transfer is in the form of work (compression, displacing a piston in a cylinder etc.,)
    - In each case, work is well defined and measurable by theory of mechanic

- We can measure the energy difference of two states *provided that one state can be reached from the other by some mechanical process while the system is enclosed by an adiabatic impermeable wall*

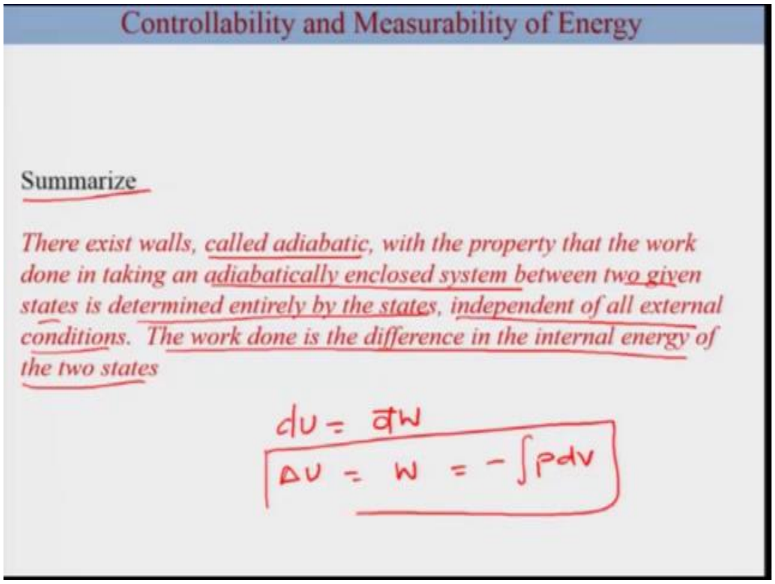
Now, what we are interested is not the absolute energy our concern is basically the measurability of energy difference. So for that we can consider an adiabatic wall. So this is basically an adiabatic wall. , and here the only permissible energy transfer is in the form of work which could be compression, displacement of piston and cylinder. So, for illustration, I am showing a piston cylinder system where the work is done very slowly on the system. So, if we have this mechanical way of doing work on an isolated system, then easily whatever being transferred whatever the change in the internal energy of the system, could be due to the work done on the system.

$$W = -\int pdV$$

$$dU = dW$$

That is something which we can easily conclude. All right. So, in other word we can write that the dU is, dW with this particular sign which indicates that the work is dependent on the path where U is basically the property which is a that is why you have exact differential. So this is basically an exact differential so we can measure the energy difference of two states provided that one state can be reached from other by some mechanical process while the system is enclose in adiabatic impermeable wall. So this is adiabatic, impermeable whatever the change in the energy that is ΔU would be due to the work done on the system.

(Refer Slide Time: 2:33)



Controllability and Measurability of Energy

Summarize

There exist walls, called adiabatic, with the property that the work done in taking an adiabatically enclosed system between two given states is determined entirely by the states, independent of all external conditions. The work done is the difference in the internal energy of the two states

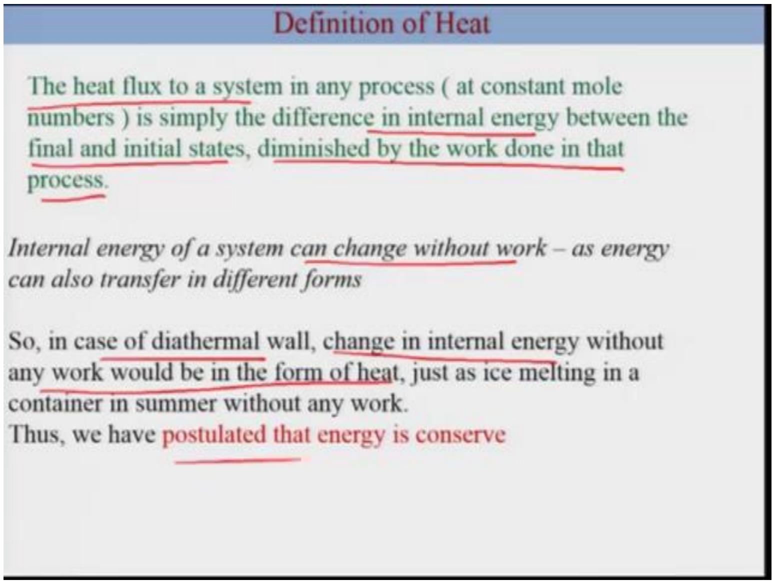
$dU = \text{đ}W$

$\boxed{\Delta U = W = -\int p dV}$

So that is why we can summarize there exists walls call adiabatic with the property that the work done in taking and adiabatically enclosed system between two given state is determined entirely by the state independent of all external conditions. The work done is the difference in the internal energy of the two states as I said. So, in the, with respect to the previous example this will be this particular expression.

$$\Delta U = W = -\int pdV$$

(Refer Slide Time: 3:14)



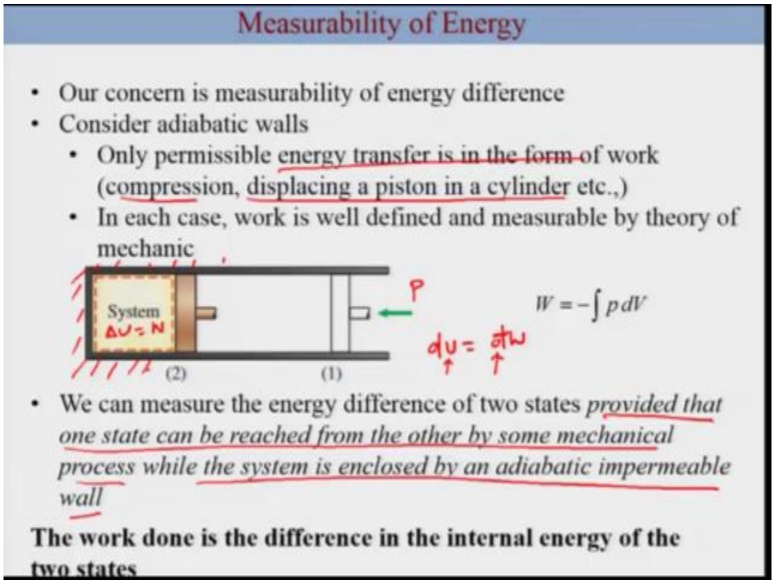
Definition of Heat

The heat flux to a system in any process (at constant mole numbers) is simply the difference in internal energy between the final and initial states, diminished by the work done in that process.

Internal energy of a system can change without work – as energy can also transfer in different forms

So, in case of diathermal wall, change in internal energy without any work would be in the form of heat, just as ice melting in a container in summer without any work.

Thus, we have postulated that energy is conserve



Measurability of Energy

- Our concern is measurability of energy difference
- Consider adiabatic walls
  - Only permissible energy transfer is in the form of work (compression, displacing a piston in a cylinder etc.,)
  - In each case, work is well defined and measurable by theory of mechanic

$$W = -\int p\,dV$$

- We can measure the energy difference of two states *provided that one state can be reached from the other by some mechanical process while the system is enclosed by an adiabatic impermeable wall*

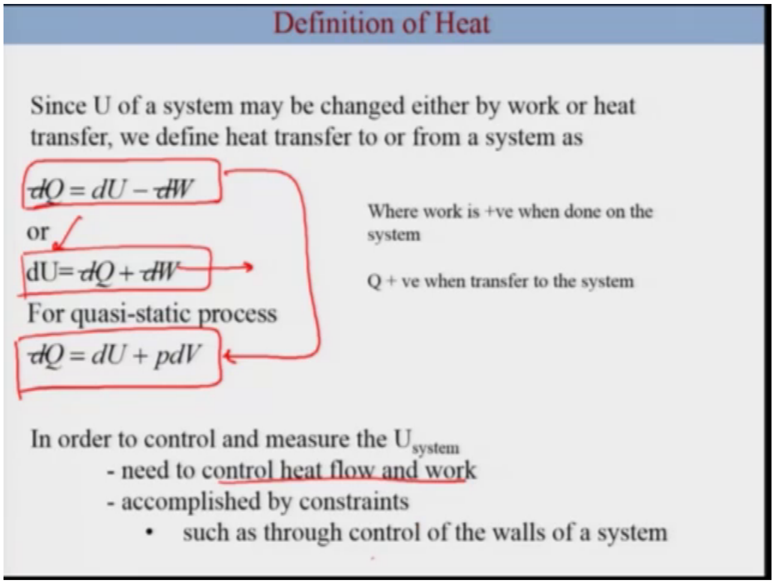
The work done is the difference in the internal energy of the two states

Now, let us talk about heat because the description which we have been given earlier in this particular discussion here was that we were using adiabatically impermeable system or impermeable walls, which essentially means that there was no heat transfer. In such case, but then if we have also discussed that ice can melt in summer, you know, so ice in a water can easily melt in summer without doing any work indicates that the heat flux can be calculated. if you can have a diathermal wall.

And essentially if you can measure the internal energy then the changes in the internal energy will be directly related to the heat transfer of the system. In such case where you have do not where you do not have any work associated with it. So this is a, what we define as a heat, the heat flux to a system in any process particularly when you have a the number of moles are not changing is simply the difference in the internal energy between final and initial state diminished by the work done in that process.

So, if there is no work essentially the change in the internal energy is nothing but the heat but if there is a work then some part of that change of the internal energy is due to the work done on the system. So, internal energy of a system can change without work also, in such case the change is associated with the heat transfer. So, in the case of a diathermal wall change in the internal energy without any work could be in the form of heat as I already mentioned just as ice melting in a container in summer without any work. So this is, this directly comes from this energy conservation concepts.

(Refer Slide Time: 5:03)



Definition of Heat

Since U of a system may be changed either by work or heat transfer, we define heat transfer to or from a system as

$$\boxed{\text{đ}Q = dU - \text{đ}W}$$

or

$$\boxed{dU = \text{đ}Q + \text{đ}W}$$

For quasi-static process

$$\boxed{\text{đ}Q = dU + pdV}$$

Where work is +ve when done on the system

Q + ve when transfer to the system

In order to control and measure the U_{system}
- need to control heat flow and work
- accomplished by constraints
    - such as through control of the walls of a system

Now, with this particular background we can now emphasize the expression of the basic changes in the energy with respect to the heat and as well as the work in the form of this expression, which we often call first law of thermodynamics. So, this is says that particularly, the definition is the dQ, the heat transferred to the system is

$$dQ = dU - dW$$

$or, \qquad dU = dQ + dW$

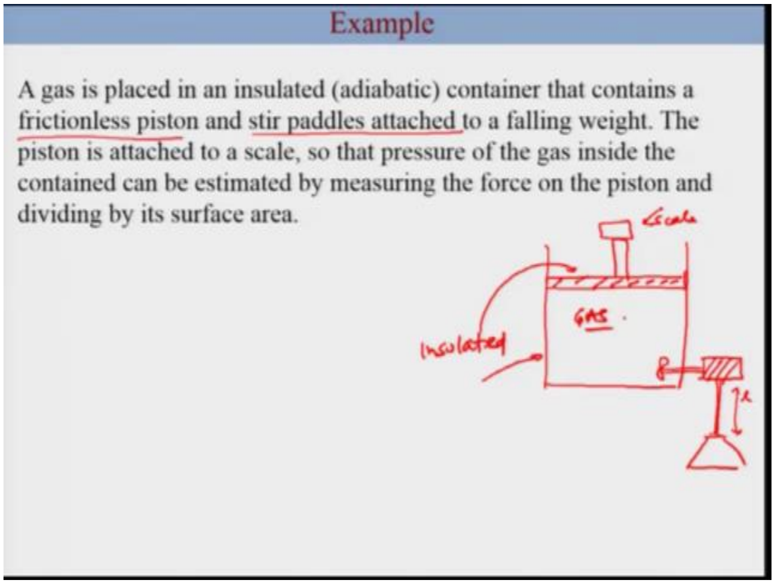
For a quasi-static process where the work here is only the contribution due to the change in the boundary of the system in such case you have,

$$dW = -pdV$$

$$dQ = dU + pdV$$

So, the convention is that in both the cases we are considering that the heat and work is positive if heat is supplied to the system or work is done on the system. So from this aspect if you want to control the internal energy of the system, we need to control the heat flow in the work which can be accomplished by constraint that is to the walls of a system.

(Refer Slide Time: 6:35)



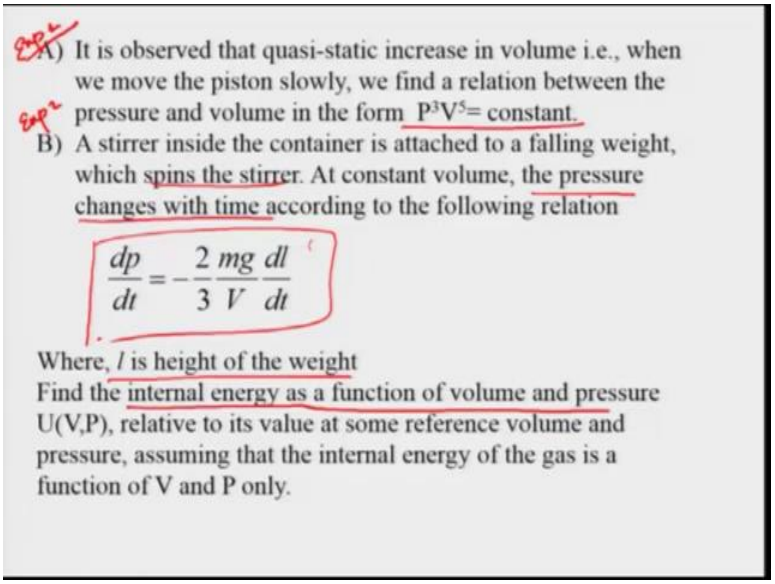
Example

A gas is placed in an insulated (adiabatic) container that contains a frictionless piston and stir paddles attached to a falling weight. The piston is attached to a scale, so that pressure of the gas inside the contained can be estimated by measuring the force on the piston and dividing by its surface area.

So with this overall discussions the concept of controlling in the measurability of the energy and as well as the definitions of the work and and the heat we can apply this concept now to simple example, so this is an example of a gas which is placed in an insulated adiabatic container, that contains a piston, a frictionless piston and a stirrer that is attached to a falling weight. So, this could be visualized in this form. So that is you have a container and let us say your piston.

And this is some kind of a scale is there which can be measured you can measure the forces on the piston and through the scale, and this is all insulated. So, basically this is wall insulated. Now, you have a stirrer here which is attached to a weight. So this maybe strings, so essentially the change in the height here which could be here let us say L the change in the height would corresponds to some kind of work done on the system. So this is the gas here, so this is our system.

(Refer Slide Time: 8:16)



Exp^{1} A) It is observed that quasi-static increase in volume i.e., when we move the piston slowly, we find a relation between the pressure and volume in the form P^3V^5= constant.

Exp^{2} B) A stirrer inside the container is attached to a falling weight, which spins the stirrer. At constant volume, the pressure changes with time according to the following relation

$$\boxed{\frac{dp}{dt}=-\frac{2}{3}\frac{mg}{V}\frac{dl}{dt}}$$

Where, l is height of the weight

Find the internal energy as a function of volume and pressure U(V,P), relative to its value at some reference volume and pressure, assuming that the internal energy of the gas is a function of V and P only.

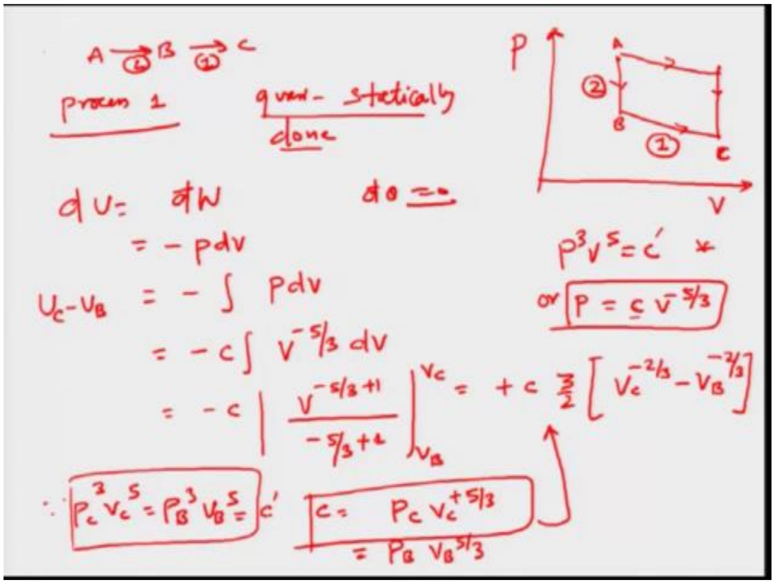
So with this particular system, there are two observations which we have that if you do quasi-static increase in the volume, so this could be considered the experiment one and this could be done experiment two. It was observed that if you do a quasi-static increase in the volume that is when you move the piston slowly we find that a relation between the pressure and the volume is in the form.

$$P^3V^5 = constant$$

$$\frac{dp}{dt} = -\frac{2}{3}\frac{mg}{V}\frac{dl}{dt}$$

In the second experiment if you spins the stir which means this process is at a constant volume the pressure of the gas of the system changes with time according to the following relation where L is the height of the weight. Now, the question is find the internal energy as a function of volume and pressure related to its value at some reference volume and pressure assuming that the internal energy of the gas is a function of only volume and pressure.

(Refer Slide Time: 9:25)



$A \xrightarrow{②} B \xrightarrow{①} C$

process 1   quasi-statically done

$dU = đW$ $đQ = 0$

$= -p\,dV$

$U_C - U_B = -\int p\,dV$

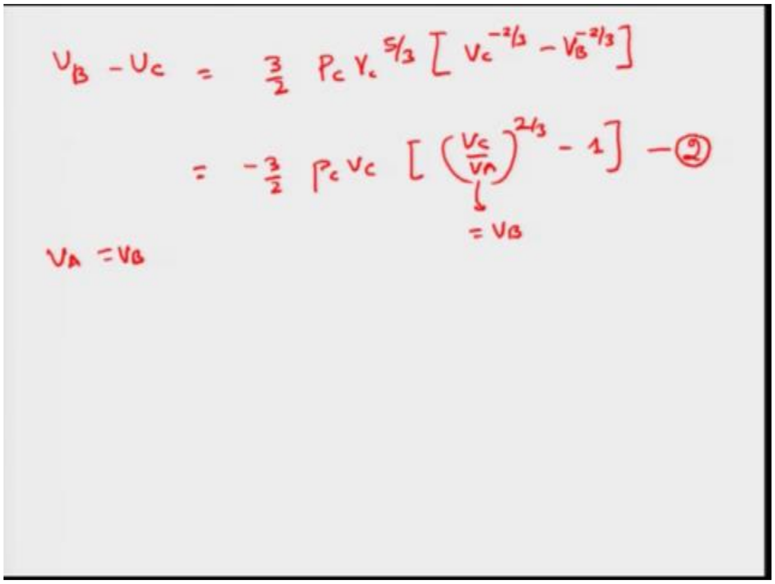
$= -c\int V^{-5/3}\,dV$

$= -c \left| \frac{V^{-5/3+1}}{-5/3+1} \right|_{V_B}^{V_C} = +c\,\frac{3}{2}\left[V_C^{-2/3} - V_B^{-2/3}\right]$

$p^3 V^5 = c'$ *

or $\boxed{P = c\,V^{-5/3}}$

$\therefore \boxed{P_C^3 V_C^5 = P_B^3 V_B^5 = c'}$ $\boxed{c = P_C V_C^{+5/3}}$ $= P_B V_B^{5/3}$



$U_B - U_C = \frac{3}{2} P_C V_C^{5/3}\left[V_C^{-2/3} - V_B^{-2/3}\right]$

$= -\frac{3}{2} P_C V_C \left[\left(\frac{V_C}{\underbrace{V_A}_{=V_B}}\right)^{2/3} - 1\right]$ — ②

$V_A = V_B$

Now, these are the two experiments. So essentially we can start considering with so a process diagram here. So this is P and this is V and let us assume that initial point is A, and final point is C. Now, this can be done using these two particular experiments, look at in the first experiment, pressure and the volume both changes and in the second experiment the volume is constant. So, let us do this at a constant volume and so this is the first experiment, second experiment we can say this is B and you can also do in this way.

So this can be also done so you can also follow this from A to B, you can do also the first tech first experiment followed by second experiment. So, the question is basically to find out the internal energy as a function of volume and pressure for such a gas. Alright, so what we can do is we can start we consider the two experiment in this way. We will do the second experiment first followed by the first experiment that means the path is going to be A to B, B to C. So, this is our first process. This is our second process. So, for A to B that is process one. This is second process. We would assume that this is a quasi-statically done.

That means extremely slow process. So in such case considering that, so let me correct myself here. So we will be first doing first working on. So, let me say this is a process one. This is a process two, so this is let us say process one and two and so first let me find out the process one change in the internal energy along this path for this particular process. So this is going to be, the reason is that your dQ is zero because it is insulated adiabatic if you look at it is all insulated.

So, there is no heat transferred to the system. So, let me just write down this expression here.

$$U_c - U_B = -\int PdV$$

$$P = cV^{-\frac{5}{3}}$$

So, this you can get it from this expression, so you plug in C here.

$$c = P_c V_c^{\frac{5}{3}} = P_B V_B^{\frac{5}{3}}$$

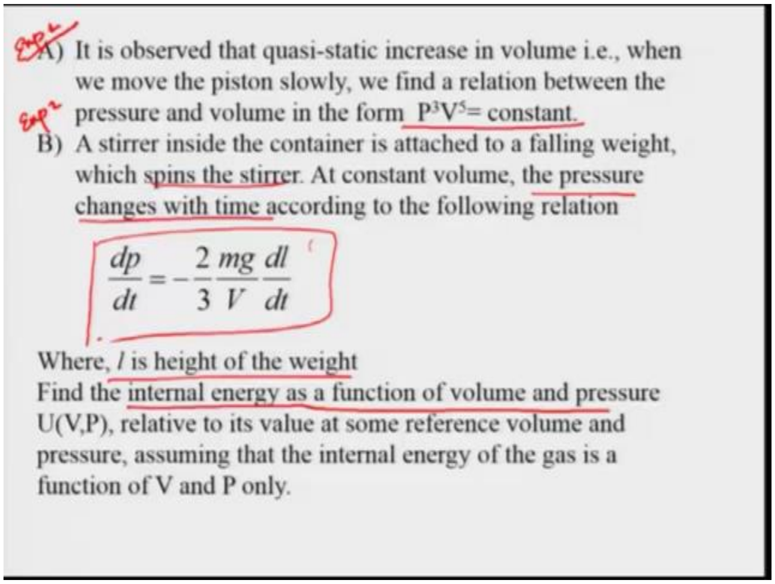
$$U_c - U_B = \frac{3}{2} P_c V_c \left[\left(\frac{V_c}{V_A}\right)^{\frac{2}{3}} - 1 \right]$$

You can further simplify. So, this is let us say this is equation two.

So the other thing is that now we also know that,

$$V_A = V_B$$

(Refer Slide Time: 15:16)



Exp 1 A) It is observed that quasi-static increase in volume i.e., when we move the piston slowly, we find a relation between the pressure and volume in the form P^3V^5= constant.

Exp 2 B) A stirrer inside the container is attached to a falling weight, which spins the stirrer. At constant volume, the pressure changes with time according to the following relation

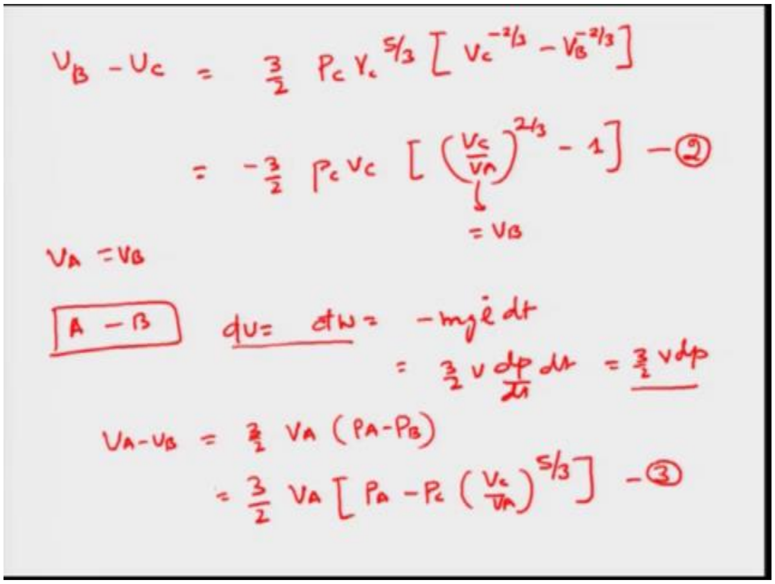
$$\boxed{\frac{dp}{dt} = -\frac{2}{3}\frac{mg}{V}\frac{dl}{dt}}$$

Where, *l* is height of the weight

Find the internal energy as a function of volume and pressure U(V,P), relative to its value at some reference volume and pressure, assuming that the internal energy of the gas is a function of V and P only.

Now, let us look at the case where this experiment two where the work is done on the system where we are using the stirrer to do the work?

(Refer Slide Time: 15:21)



$$U_B - U_C = \frac{3}{2} P_C V_C^{5/3}\left[V_C^{-2/3} - V_B^{-2/3}\right]$$

$$= -\frac{3}{2} P_C V_C \left[\Big(\frac{V_C}{\underset{\substack{\downarrow \\ = V_B}}{V_A}}\Big)^{2/3} - 1\right] \quad -②$$

$$V_A = V_B$$

$$\boxed{A - B} \qquad \underline{dU = dW} = -mg\dot{l}\,dt$$

$$= \frac{3}{2} V \frac{dp}{dt} dt = \underline{\frac{3}{2} V dp}$$

$$U_A - U_B = \frac{3}{2} V_A (P_A - P_B)$$

$$= \frac{3}{2} V_A \left[P_A - P_C \Big(\frac{V_C}{V_A}\Big)^{5/3}\right] \quad -③$$

So in such case, so the path is basically this case A B.

So, where we have dU is equal to the work,

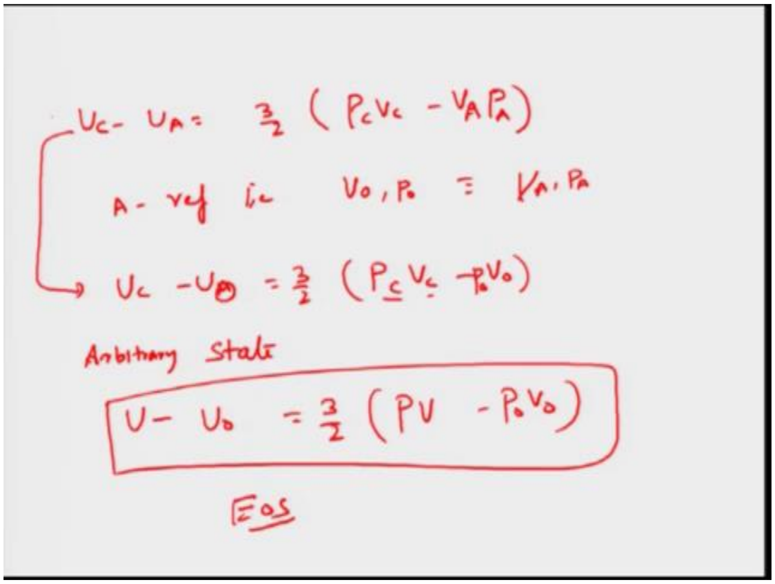
$$dU = -mg\dot{l}dt = \frac{3}{2}Vdp$$

So here with this expression we can find out that,

$$U_A - U_B = \frac{3}{2}V_A\left[P_A - P_C\left(\frac{V_C}{V_A}\right)^{\frac{5}{3}}\right]$$

So this will give us the following expression.

(Refer Slide Time: 16:56)



$U_C - U_A = \frac{3}{2}(P_C V_C - V_A P_A)$

A - ref i.e $V_0, P_0 \equiv V_A, P_A$

$U_C - U_0 = \frac{3}{2}(P_C V_C - P_0 V_0)$

Arbitrary State

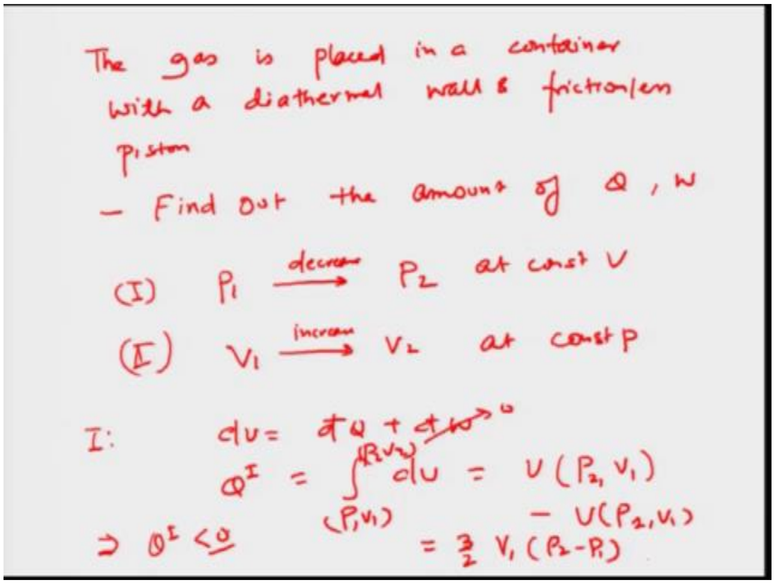
$\boxed{U - U_0 = \frac{3}{2}(PV - P_0 V_0)}$

EoS

$$U - U_0 = \frac{3}{2}(PV - P_0V_0)$$

Now, this is nothing but an equation of state, if you look at it to this equation the state connects the internal energy with pressure and the volume another example, which is a classic example of equation of state is ideal gas equation of state. So, this is what we have derived now, you can use this equation of state to find out a couple of more things.

(Refer Slide Time: 18:36)



The gas is placed in a container with a diathermal wall & frictionless piston

- Find out the amount of Q , W

(I) $P_1 \xrightarrow{\text{decrease}} P_2$ at const V

(II) $V_1 \xrightarrow{\text{increase}} V_2$ at const P

I: $dU = đQ + \cancel{đW} \to 0$

$Q^I = \int_{(P_1 V_1)}^{(P_2 V_1)} dU = U(P_2, V_1) - U(P_1, V_1)$

$= \frac{3}{2} V_1 (P_2 - P_1)$

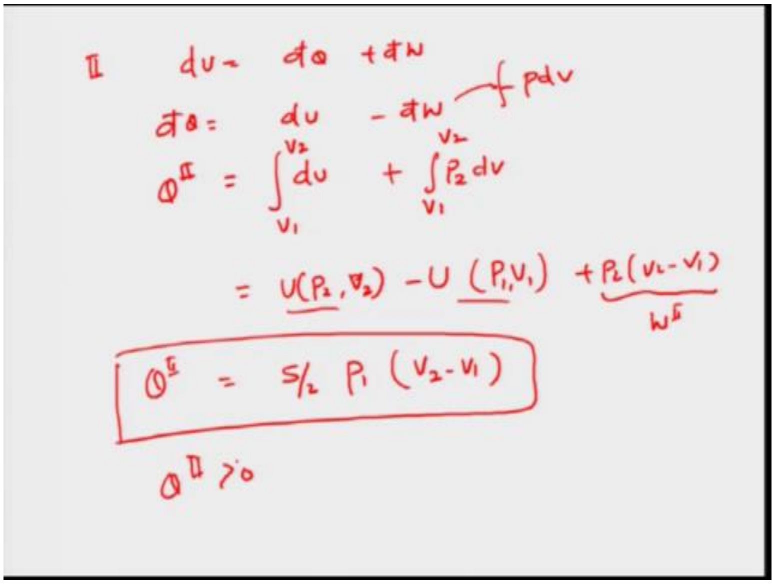
$\Rightarrow \underline{Q^I < 0}$

So, for example, I am not going to derive anything, but let us assume that you have a gas which follows this equation of state, and if the gas is placed in a container with the diathermal wall and frictionless piston. Find out the amount of heat and work necessary for two step process. So, in the first step, the first step is where the pressure produces at constant volume and in the second process second step volume increases at constant pressure.

So you can you make use of this equation of state which we just arrived in order to solve this, for a further case of first one since it is a constant volume.

$$Q^1 = \int_{P_1 V_1}^{P_2 V_2} dU = \frac{3}{2} V_1 (P_2 - P_1)$$

(Refer Slide Time: 21:10)



$$\text{II} \quad dU = \text{đ}Q + \text{đ}W$$

$$\text{đ}Q = dU - \text{đ}W \quad -\int p\,dV$$

$$Q^{\text{II}} = \int_{V_1}^{V_2} dU + \int_{V_1}^{V_2} P_2\,dV$$

$$= \underline{U(P_2},V_2) - U\,\underline{(P_1},V_1) + \underbrace{P_2(V_2 - V_1)}_{W^{\text{II}}}$$

$$\boxed{Q^{\text{II}} = \tfrac{5}{2} P_1 (V_2 - V_1)}$$

$$Q^{\text{II}} > 0$$

I will conclude by simply doing this exercise for the process two which is the case where the volume increases from V1 to V2 at constant pressure again, you can write down this expression? Volume is not constant anymore so you are going to integrate dU and this is pdV.

$$Q^2 = \frac{5}{2}P_1(V_2 - V_1)$$

So in this case again, the V2 is more. So, in this case the V 2 is more than V 1 and hence Q 2 is positive. So, this is basically what I wanted to cover. So, what we have gone through is definition of the heat and work, controllability and measurability of energy and making use of the first basic postulate in order to do a simple analysis deriving the equation of state for a gas and taking the equation of state to solve few example problems. So, we will talk more in details more elaboration of the postulate to lay the foundation of the basic thermodynamic theories. So have a good day. We will see you tomorrow.