Chemical Principles 2

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Work and Heat Part 01

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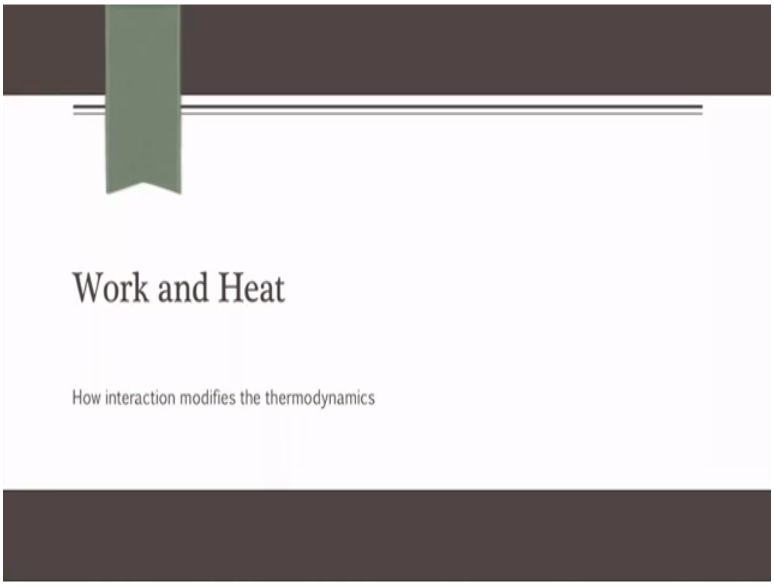

Welcome to the next lecture. So today we are going to talk about work and heat.

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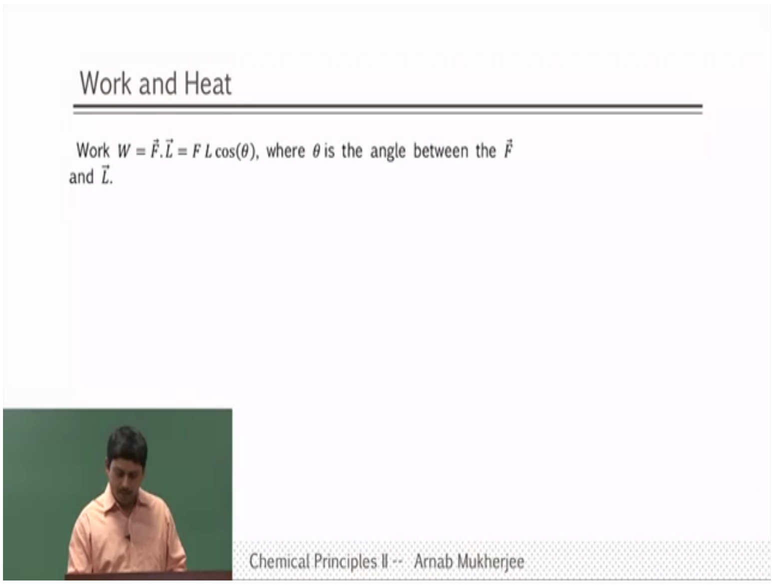

First of all we will discuss what is work.

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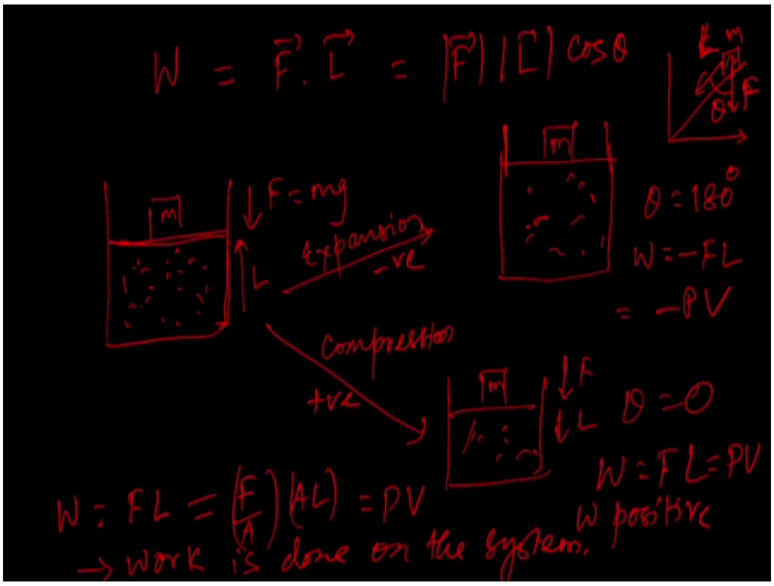

So we all know that work is, so you know what is work? Work is force into displacement, right force is a vector, displacement is a vector, and we can write work as the dot product of force and displacement. So now if I write that expand that it will be modulus of the force, modulus of the displacement and Cos theta which means that we have done several times these kind of problems where there is a mass m and then the force is pulling in this direction, force is pulling in this direction (sorry) and the displacement is in this direction L and the work done will be depending on the angle theta, right we have done that kind of problems you know mass in a slanted direction and all.

However, in the type of thermo dynamical work that we are going to consider here typically we will consider a box full of gas molecules and a mass m sitting on top of that. Now when a mass m is sitting on top of a piston so this is the piston, then the force that is acting on the gas is on this direction and that force is typically mg mass multiplied by the gravitational attraction g.

Now there can be two different situations one is compression, another is expansion. So in case of expansion the length let us say the area is fixed for a fixed area the length of the or the height of the gas molecules is going to increase, right let us say I draw that. So now since that happens which indicates that the displacement is in the opposite direction of the force, what is the theta there when there is expansion? Theta is no, in the expansion case, theta is 180 degree, right.

So since theta is 180 degree your work done will be minus F, when I am not giving any vector sign which means that I am just taking the modulus F into L, right which is in that case now let us say, okay leave it here. For compression however, what is happening is in case of compression your force is acting on that direction and your displacement is also along that direction, so theta is 0 degree, so work is just FL.

So you see in case of compression the work is positive I will say positive, in case of expansion work is negative you just note down that we will come back to that. Now since we are writing work as F into L, F by A into A into L, I am just dividing and multiplying with A, F by A we know to be pressure, AL will be the volume surface area into length will be the volume, so you see work done is basically for gas system is nothing but PV.

But in case of expansion it will be minus PV and in case of compression it is plus PV and that is a very important point that is often confusing in you know thermo dynamic classes that when one takes work to be positive and when the work is to be negative, but we have to consider by convention that we always consider work is done on the system, so we have to see what is the work done on the system, okay that is what we always take as a convention.

So conventionally therefore when we do a compression then in case of compression there is a positive work done on the system and in case of expansion it is a negative work done on the system. So you see that in case of expansion the gas molecule is doing the work, system is doing the work, so system is doing a positive work. Therefore, oppositely conversely work done on the system is negative, have you got that this particular part?

So because the gas molecule is expanding so gas molecules is pushing the piston up, pushing the mass up so it is doing the work, it is doing a positive work. Therefore, the work done on the system is negative. Similarly if you see the compression, now here we are doing work the mass is doing work on the gas and it is a positive one. So if you we have to always take conventionally work done on the system because if you do that you will see that whenever the work done on the system is positive, the internal energy of the system will increase. So therefore we will always equate internal energy to work done by talking work done on the system.

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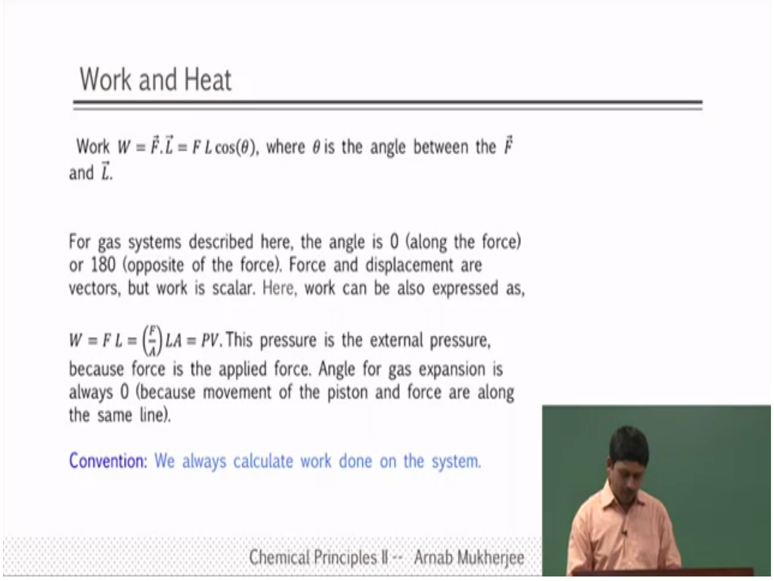

So let us see, yes so we have talked about that we always calculate work done on the system, okay.

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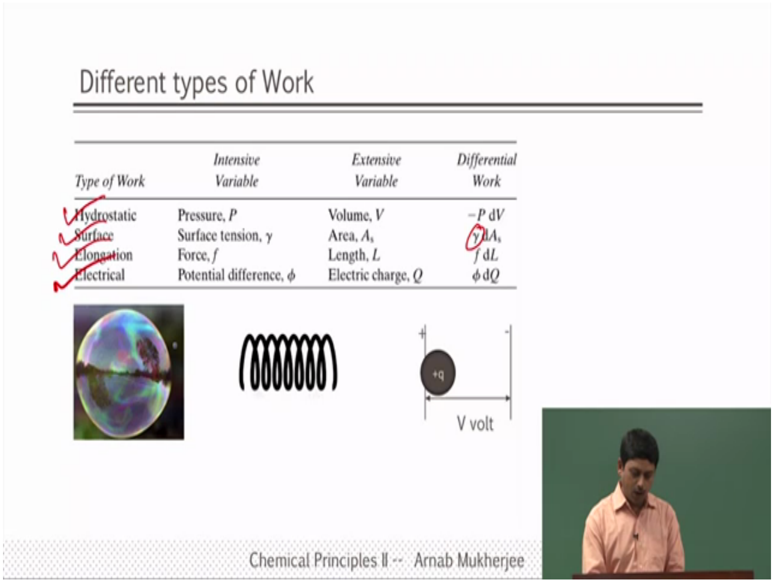

Now this is a PV work however, there can be other kinds of work also. So PV work is like hydrostatic work and then there are other kinds of work also so let us say if in case of a bubble when the you know bubble you know becomes bigger and bigger so it is actually working against the surface area because there is a surface tension associated with that, so as the surface area increases it requires more and more work.

Elongation so when we have let us say we take a rubber band of length L and we try to extend it, so that is the work that is done and that the force multiplied by the length which we discussed will be a kind of work or elongation work and another work is electrical work where you know the charge is carried over electric potential and that will give rise to some kind of work. So there are different kinds of work, but we will consider mainly PV kind of work in this particular course.

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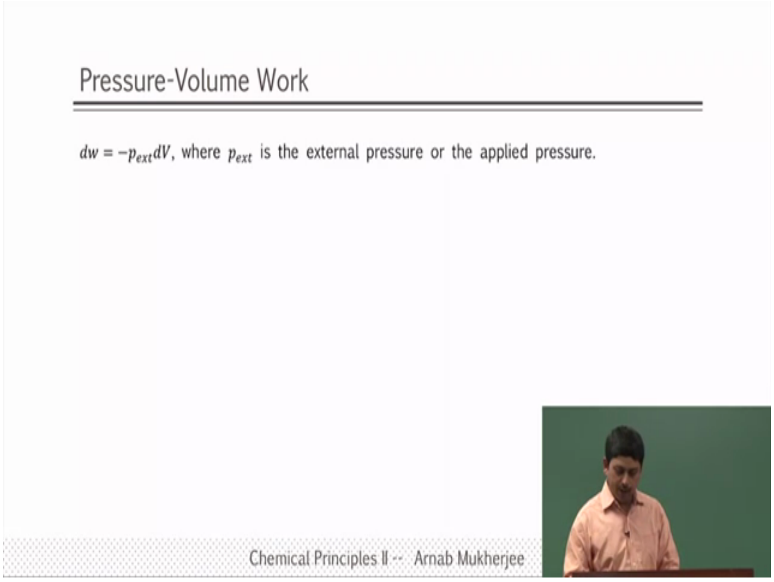

So for very small amount of changes when the work is done on the system, so what will be the sign then?

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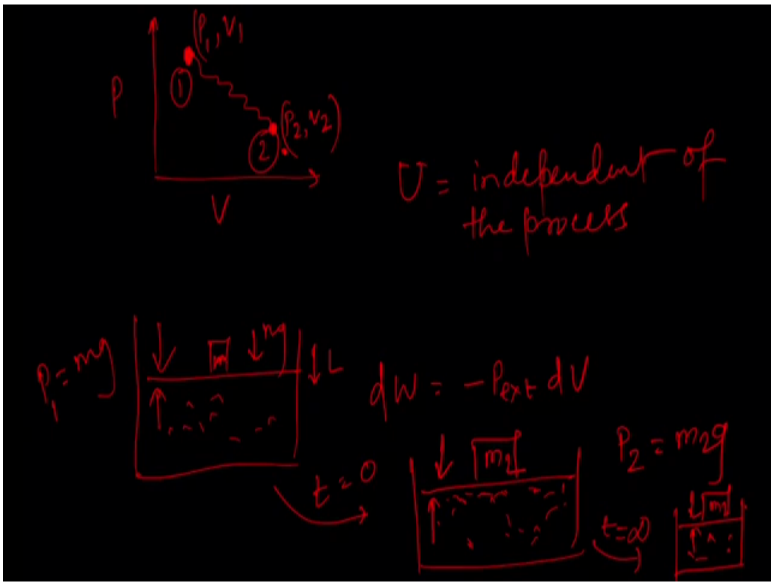

So let us say we have a mass m, right mg. So you see that if we have by convention if you take work done on the system always and that to be positive, then we can write that as dW as minus P external dV. So it is how much the external mass is doing the work on the gas, work done on the system means how much the mass is doing the work on the gas, right. So it is the pressure exerted by the mass which means the external pressure that is under consideration. So right now when the system is in equilibrium your internal pressure and external pressure are equal, they are balanced.

However, let us say that point we can consider as here, so let us say it a PV diagram and initial pressure is P 1, volume is V 1, when there is a mass m sitting there. Now let us say suddenly we are going to change the system to m 2, so whenever we change the system to m 2, so here the pressure was mg let us say that was P 1 equal to mg and here the pressure is m 2 g, what is going to happen?

Now let us say when we change at t equal to 0, we just replace m by m 2, suddenly there is an imbalance between the internal pressure and external pressure at t equal to 0, internal pressure is still mg, but external pressure is now m 2 g. So what will happen now the system will start to go to an equilibrium. Now initially so that the pressure here the gas molecules here will try to adjust and there will be lot of turmoil, so this is called typically the non-equilibrium situation which thermo dynamics does not care.

What thermo dynamics cares is that, if we wait long enough let us say we call it that t equal to infinity but we do not need practically an infinite time, we wait long enough then what is going to happen is the internal pressure is now going to be in equilibrium with the external pressure, okay and it will adapt correspondingly a different volume let us call that as P 2 and V 2.

What happened in between this and this we do not know, we only know the initial point and the final point remember always that thermo dynamics does not tell you what happens in between, thermo dynamics only tells you one equilibrium point to another equilibrium point only and also it does not care about the time that it takes to go that equilibrium point, it may take 10 seconds or a million years, ultimately what we are going to see is that one equilibrium point to the next equilibrium point so that is why we do not know what is there in between.

But given the information of P 1, V 1 and P 2, V 2 we can calculate certain properties, first property is that that internal energy U that is independent of how we do that, independent of the process which means that given this initial and final point we will know that what is the change or difference between the internal energy of the initial point and final point. However, do you think that the work done will be same every time when you go from state 1 to state 2, okay let us do that through some example, okay.

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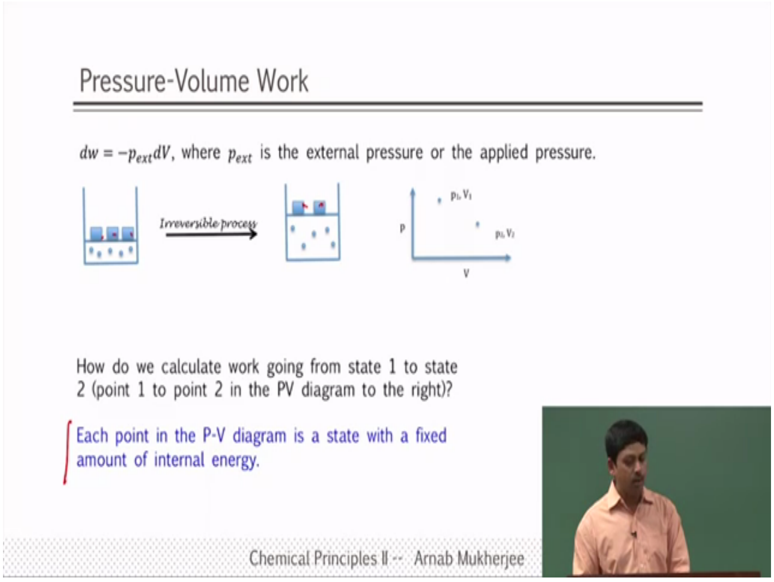

So let us see (yes) so this is what we talked about, so here there was 3 masses which suddenly change to 2 and then we got different states, okay. Now how do we calculate the work going from state 1 to state 2, how do we calculate that? And each point in the PV diagram so each point in the PV diagram is a state, right the state is defined by these two points for one component system one molar one component system if we specify two variables that is enough to specify the system because which means that if we know PV we know the t automatically for n equal to 1, 1 molar.

So since we know that we will specify the system with (P 1) no with two values P and V and we will get the internal energy for that, but however, work done will strictly depend on how we do that.

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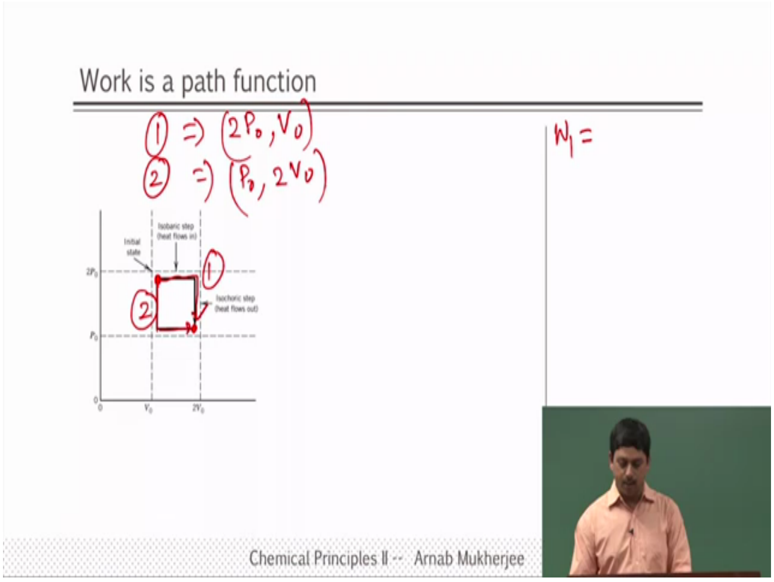

So for example let us take this particular problem in which our initial point let us say is this one where the pressure is 2P 0, it is not exactly 2P 0 but let us call it 2P 0 and then and volume is V 0, so our initial state 1 is characterized by 2P 0 pressure and V 0 volume, our final point is here which is characterized by P 0 pressure and 2V 0 volume it will be just up you know opposite volume will increase because pressure is decreasing.

Now in order to go from state 1 to state 2 either we can take this route or we can take this route, let us call that route number 1 or path number 1 and let us call that path number 2 and let us calculate the work done for path number 1. So work done, now how do we define work done?

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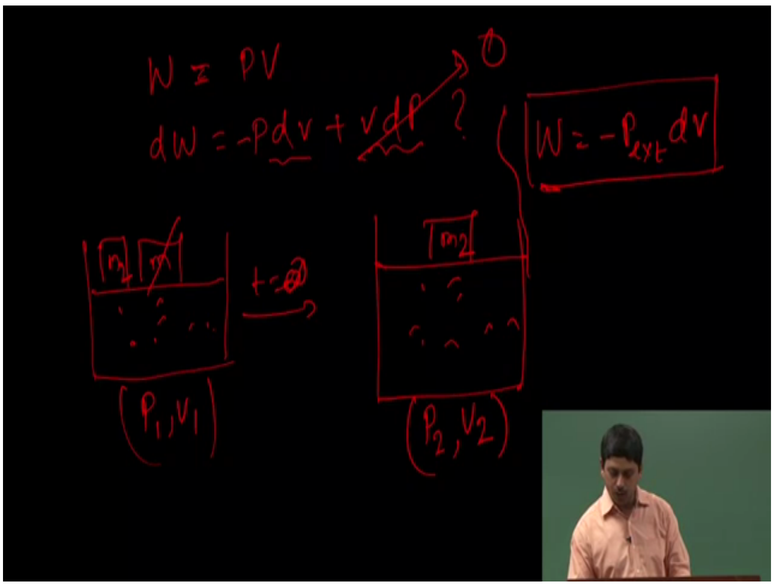

So remember we already we discussed that work done is basically PV, now if I do dW which means should it be Pdv plus vdP, do you think it should be like that? Except there is a one problem here the problem is that you see when I say vdP that means I am allowing the pressure to change, but imagine what was the situation? The situation was that I had mass m with the gas and I suddenly change it at t equal to 0, t equal to 0 means I can replace it, I can cut it and put mass m 2, okay and then I wait sometime let us say t equal to infinity and then I get a different system where my m 2 is there and my volume has changed, so this is my P 1 V 1 and this is my P 2 V 2.

Now did the pressure changed? Because see our system that we talked about was m 2 in the beginning at t equal to 0 and m 2 at the end that did not changed, what changed was only the volume because based on the external pressure the volume got adjusted. Therefore, the dP is 0, okay and since we are always talking about work done against the external pressure we have this minus Pdv because you see if the volume increases it is a positive quantity, then work done on the system will be negative and expansion is a negative one, if volume decreases dv will be negative term and negative negative will be positive, so compression will give you a positive work.

So the formula for work done is minus Pdv, okay. Now since we know that work done is minus Pdv but external dv that is also another important point because the system is now adjusting with the external pressure so either you can think of the system or the external pressure ding the work whatever you can think of ultimately this is the formula that we are going to use always P external dV.

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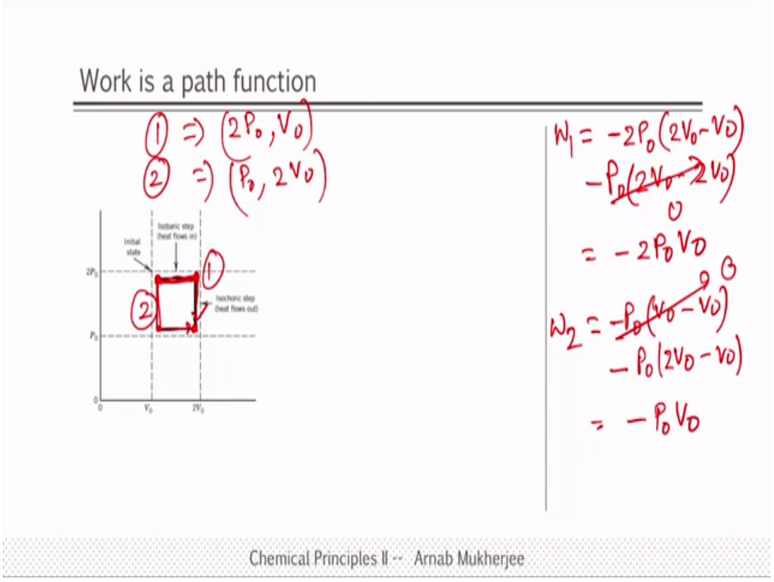

Now let us see for the route number 1, so it goes (from 2P 0) at 2P 0 because pressure is remaining constant, but volume changes from V 0 to 2V 0, right so what is the work done in that state in first step can you tell me? P external is minus 2P 0 into 2V 0 minus V 0, right. In the next step you see the external pressure you know can you tell me how much is the external pressure in the next step?

Step means from here to here, in this step, what is the external pressure? Imagine that finally it is equilibrating to that pressure whatever the external pressure you did at t equal to 0 at the t equal to infinity also that pressure is remaining. So you have to always consider the final pressure that you are going to see in the system. So in the next step what is the pressure that you are going to take? P not, correct minus P not but volume did not changed, so 2V 0 minus 2V 0, which means that is 0, so this is 0 and the first one is giving you minus 2P 0 V 0 that is the work done in the route number 1.

What is the work done in route number 2? First step, first step is final pressure is P 0, right so minus P 0 into volume did not changed and that was V 0 minus V 0 and the second step external pressure is P 0, right and volume changed from V 0 to 2V 0, so this gives you 0, it gives you minus P 0 V 0. So you see in two different routes by two different routes or two different paths going from same point, same fixed point to another fixed point you are getting different work done, okay so.

Student is questioning: Why have been taken to final pressure?

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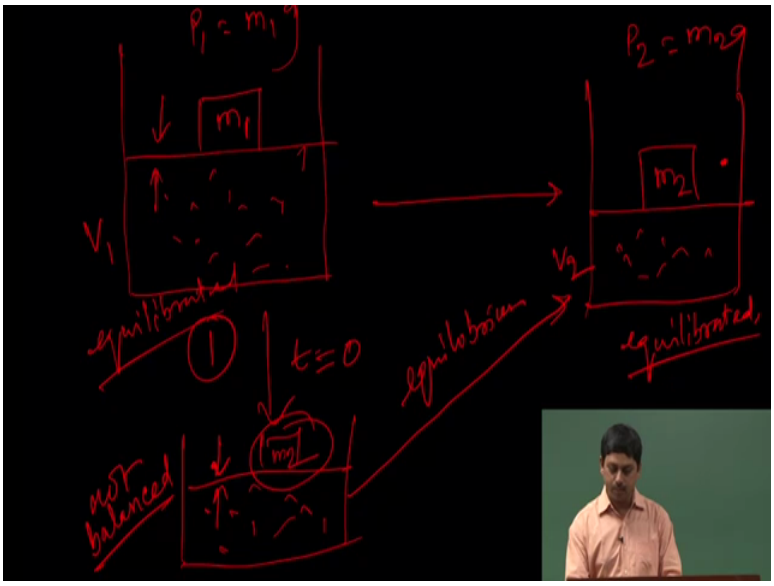

Yes, so as I explained to you that let us say, so the question is that why you are taking final pressure? I will explain that once more, let us say I start with a mass m and that system we call that as state 1, okay and I am going to a state where the mass is let us say m 2, here the volume was V 1, here the volume is V 2, okay I can (())(18:53) mass m 1, m 1 V 1, m 2 V 2, okay. (So m) So that means our P 1 is m 1 g and our P 2 is m 2 g, okay. So now how did we do this particular operation? Although this is an equilibrated system, correct this is also an equilibrated system, so these are two equilibrated systems.

But when we try to do that at t equal to 0, we have changed the mass from m 1 to m 2 at t equal to 0 and then allowed the system to go equilibrium. So that means the system did worked against this external pressure because at this external pressure there was no work, system was perfectly balanced the internal pressure and the external pressure was perfectly balanced.

In this case however, the internal pressure and external pressure is not balanced and that so either work was done. So that means the system the gas molecule expanded against m 2 g and came here and see this is our final pressure, so that is why we are taking the final pressure for the calculation, is it clear?

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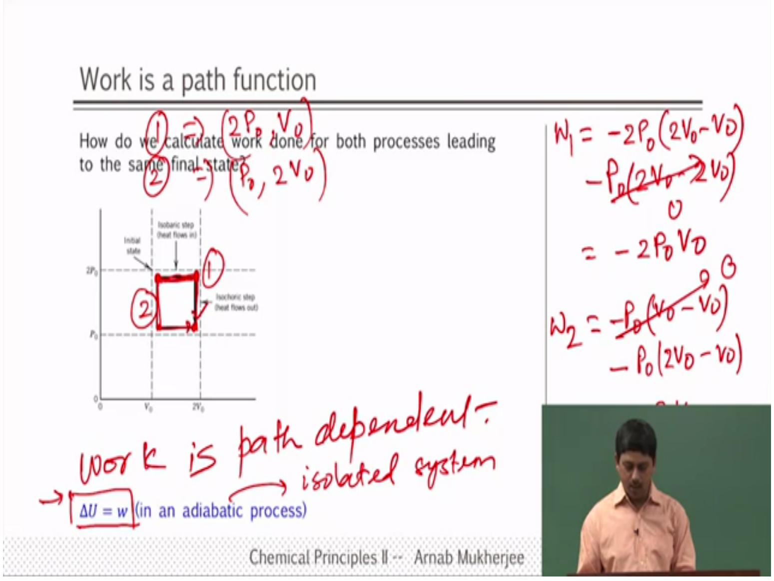

So that means what we say is that we say that work is path dependent. Now how does the system will do the work? The system will do the work because in order to do the work you know how it has to go from one step to another step, right. So let us say if you do not supply anything any heat or anything, so when it is expanding your internal energy has to decrease, right because the particles are separating from each other that is why we talked about real gases and all, right.

You saw that when the particles are going apart from each other, your energies were increasing, right so interactions were decreasing. So and when there is getting compressed then the other thing were happening, right. So in an adiabatic process or you can say that in case of isolated system when there is no heat input or output is allowed then the system is using its internal energy to do the work and we can write that delta U that means change in the internal energy is equal to the work done on the system, not by the system.

If you do work on the system then your internal energy will increase, right you compress the gas your system internal energy will increase, you expand the gas internal energy will decrease. So that is why work done on the system, so whenever we write work that means it is inherently assumed that it is work done on the system and that will increase the internal energy of the system.

So because we are not supplying any other thing, so when a process happens it has to happen through some energy, it has to spend something, so that is what it spends so that is the first part.