Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 04
Introduction - part 1

Hello everyone in the last lecture we discussed the properties of real gases in today's lecture we will start the laws of thermodynamics. Now before we discuss what is thermodynamics what we study in thermodynamics? We will first define few terminology that will be frequently used.

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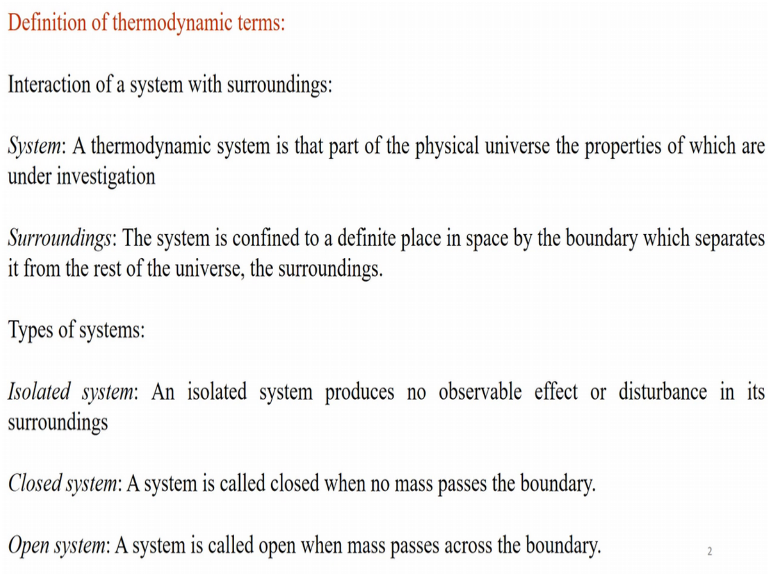

Now, we will first discuss definition of thermodynamic terms and as we told in the very beginning the thermodynamics tells us about the interaction of a macroscopic system with it is surrounding. Now what do you mean by a system and surrounding. Now a system is defined as part of that physical universe the properties of which we are investigating. What does it mean suppose we are discussing the expansion of a gas and the gas is put in a container.

Now that gas is the system here and then what will be the surrounding the surrounding will be the immediate environment that the gas has, actually it is not only the immediate environment it is the rest of the universe because it is said that the system is confined to a definite place in space by a boundary which separates it from the universe which is called as surroundings.

But usually the effects will be observed in it is immediate environment, which is just outside the boundary. Now this presence of the boundary is very crucial because the boundary is the thing that defines the separation between the system and the surrounding

Now, depending on the nature of the boundary we can have different types of systems for example, open system closed system and isolated system a system is keep called an isolated system if it produces no observable effect or disturbance in it is surrounding.

Now, what will be a perfect example of an isolated system there is no such perfect example, but we can think that suppose there is a gas in a container which is thermally insulated. So, there will be no heat exchange with the surrounding and of course, since it is in a container there will be no mass exchange also with the surrounding. So, we can say that that system is an example of an isolated system.

Now, think about it the universe as a whole is an isolated system because there is no surrounding of the universe by surrounding we mean the part of the universe, which is not a part of the system. So, the rest of the universe is sounding. So, universe as a whole is also an isolated system.

Now, what is a closed system a closed system is when the system does not exchange any mass with the surrounding we just give you an example of the system at the very beginning that consider a gas in a container. So, this gas if we confine it in a container no gas molecule will come out outside and also no new gas molecules from the environment will enter that container. So, that system that system of gas molecules inside the container can be thought of as a closed system.

Now, remember that for a closed system the system can exchange heat with the surrounding, which means the wall has to be now thermally conducting if the wall is insulated then the system is an isolated system now what about open system a system is called an open system when mass passes across the boundary.

Now, think about a living body like our body we breathe we take oxygen we can hell oxygen and we breathe out carbon dioxide which means we are constantly exchanging mass with the surrounding. So, any living system is an example of open system

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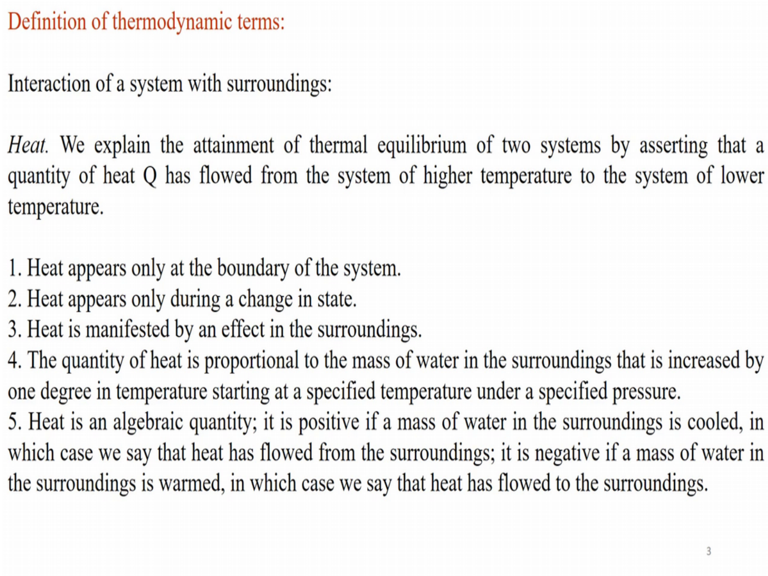

Now, let us define some other terms what is very important in thermodynamics as we discussed is the interaction of macroscopic system with it is surrounding and during this interaction there is flow of heat into the system or into the surrounding. Now heat is defined as follows we explain the attainment of a thermal equilibrium of 2 systems by asserting that the quantity of heat, which we denote usually as capital Q from the system of higher temperature to the system of lower temperature.

So, there is no such definition that how much heat a system has heat has only meaning when a transformation happens we will discuss it in detail immediately. Now here are some properties of heat; heat appears only at the boundary of the system. What does that mean; that means, in any process or any process that involves a change of the state of the system heat will either flow into the system from the surrounding or to the surrounding from the system. So, the heat flows across the boundary and that is what we are going to quantify.

Secondly heat appears only during the change in state that is what we already discussed and; that means, when a system is in thermal equilibrium we cannot say that how much heat it has that is a meaningless question only when the system does a transition then only we can ask a question how much heat is absorbed or how much heat is released.

Thirdly heat is manifested by an affecting surrounding. So, remember that there is a system and there is a surrounding and we are going to do some experiments on the system. Now we have to see the effects of these changes which we are performing on the system; however, these changes are observed in the surrounding due to the change in the system there will be an effect in the surrounding. For example, if we do a process in which the heat is absorbed by the system, then the temperature of the surrounding should go down and that is the meaning what we what we say here that heat is manifested by an effect in the surrounding.

Number 4 is the quantity of heat is proportional to the mass of water in the surroundings that is increased by 1 degree in temperature starting at a specific temperature under a specified pressure. Now this thing you have studied how much heat you need to raise the temperature of water, why water because the specific of water is maximum and for a finite change in temperature we need a sufficient amount of energy which is heat in this case to raise the temperature for water. So, that is just an operational concept how we will measure heat.

Number 5 which is most important is that heat is an algebraic quantity; means if in a process or in a series of process we first say that heat is released by the system and eventually heat is absorbed by the system. We can take the difference and ask the question how much net heat it is absorbed or released into the system, which means we can add or subtract the amount of heat released or absorbed so; that means, mathematically heat is an algebraic quantity.

Now, we will follow a convention here it is positive if the mass of water in the surrounding is cooled, which means surrounding getting cooled means the temperature of the surrounding is falling down which means heat has flown from the surrounding into the system and that would take as a positive quantity, which means in which case we say that the heat has flowed from the surroundings and the opposite thing is if the heat is flown from the system into the surrounding. So, the mass of the water will be warmed up. So, the temperature of the water will arise in which case we say that the heat flow or the associated change in heat has a negative sign.

So, this is a convention again which will be followed throughout this course now just like heat we also can define another quantity of energy, which is work usually in thermodynamics will constantly be discussing how heat is converted into work or work is converted into heat because that is the main purpose if you want to create or develop a heat engine

Now, let us define what do we mean by work in this case we will make an analogy with mechanical work we are going to describe each term in very detail with examples very soon.

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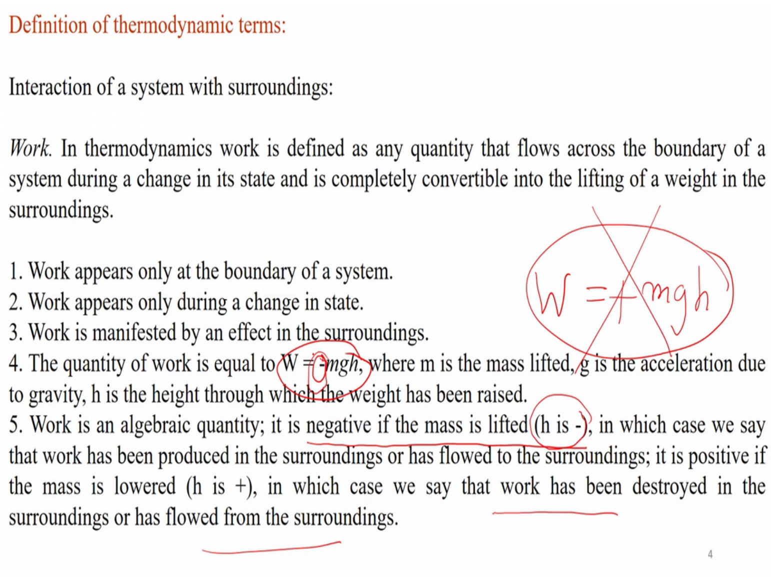

Now, in thermodynamics work is defined as any quantity; by quantity I mean here that any energy quantity that flows across the boundary of a system during a change in it is state and it is completely convertible into the lifting of a weight into the surrounding.

Now, we will give an example where the lifting of the weight will be connected to the expansion or compression of a gas and the associated heat flow. Now lifting of a weight means actually it is a mechanical work. So, we will draw an analogy between the mechanical work and thermodynamics as before we pointed out some properties of heat here we are pointing out some properties of work that we have to keep in mind.

Now, remember work is also a form of energy just like heat. So, work also appears only at the boundary of the system and the logic is just like we provided for heat. Similarly work appears only during a change in state there is no meaning if I ask the question how much work a system has, the system performs work only when it transforms a change in state. Similarly just like heat work is also manifested by an effect in the surrounding in this case we will show that the masses in the surrounding are lifted up or down if work is performed or work is destroyed. The quantity of work is equal to W is equal to minus mgh, where m is the mass lifted g is the acceleration due to gravity and h is the height through which the weight or the mass has been raised.

Now, notice this minus sign which is very very important here in many older textbook you will see a definition of the work is W is mgh. So, we will not use this definition in this course we will use the more modern definition where the work is defined as negative of mgh. We will discuss why we are taking this negative sign in detail just like heat work is also an algebraic quantity, you can ask this question if for a series of processes work is performed by the system and then in the next process work is done on the system how much network has been spent on the system or how much network the system has performed.

So, mathematically saying work is an algebraic quantity we will consider it as negative if the mass is lifted this is very very important which means the height is in this case should be negative because the height we are lifting, but we will take it as a negative quantity we will come back to it in which case the work has been produced in the surrounding or has flown into the surrounding. We will take it positive if the surrounding performs and work on the system which means masses will be lowered in the surrounding.

Now, remember that again this is a convention just like for heat we took conventions earlier for the convention of the heat remember that when heat is flown into the system we took it as a positive quantity. So, keeping and analogy with that than the in the newer convention we are saying when the work is done by the surrounding on the system will take it as a positive quantity and in order to do that we have introduced this minus sign here which will be clear in a moment.

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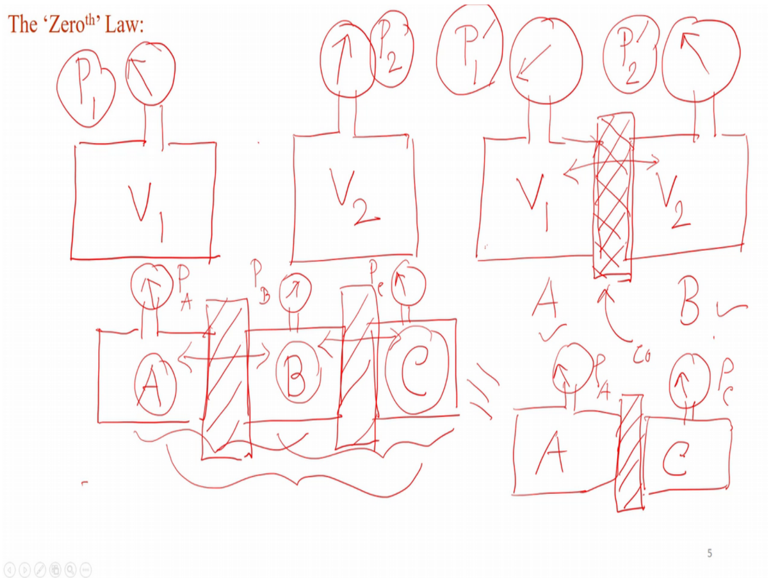

Now, let us first discuss the Zeroth law of thermodynamics now this sounds little bit odd what is a Zeroth law the reason being when thermodynamics was developed in the mostly the 18th century and 19th century people; first realized the law of conservation of energy and subsequently the directionality of a process, which they termed as first law of thermodynamics and second law of thermodynamics which we will eventually cover.

Now, later on scientists realized that a more fundamental law exists that is the law of thermal equilibrium and since already they have termed the law of conservation in of energy as the first law of thermodynamics they called the more fundamental law as which is basically the law of thermal equilibrium as the Zeroth law. Now let us try to understand very conceptually what is the Zeroth law let us consider a system.

Now, in this case will be frequently using this system, which is a gaseous system in a container. Now suppose we have a container and in this container there is a gas and the volume of the gas is V 1 and attached with this container is a pressure gauge which denotes the pressure supposed initially the pressure is P 1. And now what we do is we bring in another system of say volume V 2 which as before is connected to a pressure gauge and suppose the pressure reading for that is P 2.

Now, what happens if we now imagine initially these 2 systems which we call as system A n and say system B are far away from each other. So, they are not in contact now suppose let us bring them in contact and what happens since the container volume is fixed the volume of the gases will also be fixed they will not change and now consider a wall between them that is thermally conducting wall.

So, if it is thermally conducting heat will flow or heat can flow across this boundary because it is thermally conducting and as a result the pressure will show some change in the reading in these 2 systems, which we call as P 1 prime and P 2 prime. So, P 1 prime and P 2 prime are the final pressure of these 2 systems.

Now, consider that we begin with A 3 system where the first system as before we denote as A and then the second system as B and the third system as C. Now in the earlier case when we touch these 2 system or make a contact through this of these 2 systems through this conducting wall and as I said that heat can flow freely across the boundary, which means now the system A and B are in thermal equilibrium and since they are now in thermal equilibrium in order to maintain the thermal equilibrium, the pressure has changed for system 1 or system a from P 1 to P 1 prime and for system B 2 from P 2 to P 2 prime.

Now, suppose a similar condition where system A and B are connected through a conducting wall, similarly system B and C are also connected through a conducting wall and we are also measuring the pressure for these systems, which are showing some reading say P A P B and P C. Now what is the situation here A and B are in thermal equilibrium which means it can flow across the boundary it must flow that. So, that is why we chose a conducting boundary since B and C are also in thermal equilibrium it should flow also across the second boundary.

The Zeroth law says if A system if 2 systems say A and C are in thermal equilibrium with another system B the 2 systems should also be thermally in thermal equilibrium with each other, what does it mean conceptually is that this is equivalent to drawing that this system A and this system C are also in thermal equilibrium although they are not directly connected through an thermally conducting wall.

So, here we get the actual. So, let us see the actual statement of the Zeroth law of thermodynamics.

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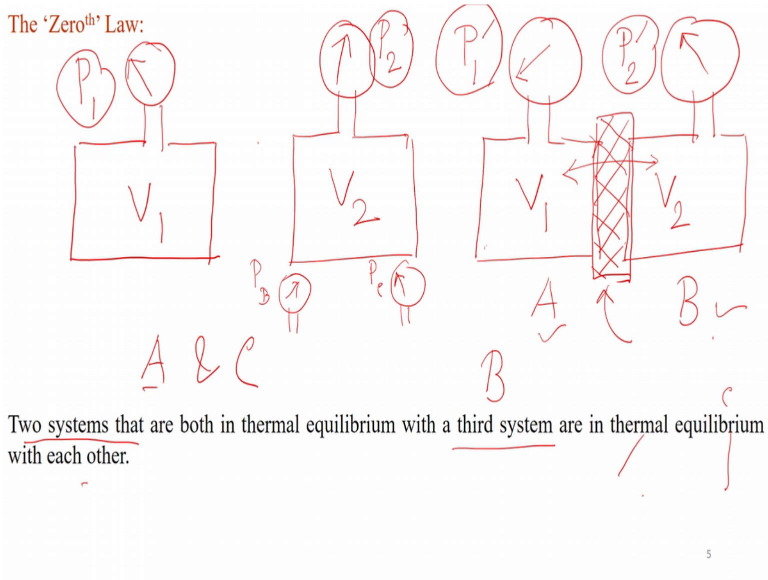

So, the Zeroth law says 2 systems that are both in thermal equilibrium these 2 systems which chose remember as A and C the 2 systems, which are in which are both in thermal equilibrium with a third system which is chose as B are in thermal equilibrium with each other which means A and C are also in thermal equilibrium.

Now, you have already learnt the ideal gas equation. So, if you think that this gas behaves ideally initially what we did that in the initial example was that this I had 2 systems A and B remember as drawn here.

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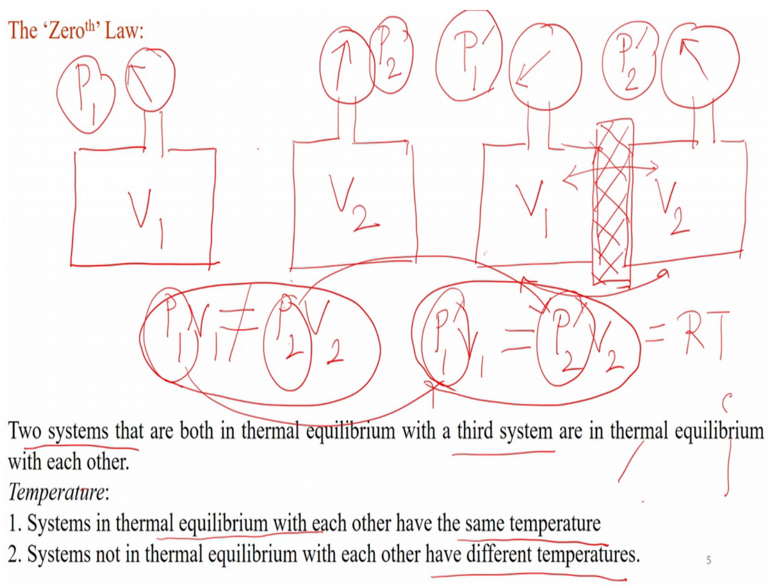

And then I had a pressure P 1 for the first system and P 2 for the second system and you know that since the volumes are not changing in the final state I had P 1 prime and the same volume for the system A and for system B, I had P 2 prime and the same following since the following did not change.

Now, since P V equal to R T and since R is a constant what we meant by that is P 1 V 1 initially cannot be equal to P 2 V 2, because if they are equal the temperature of the system a and system B must have been equal. Then the systems are already in thermal equilibrium and there should not be any change in the pressure. So, initially our choice was P 1 V 1 was not equal to P 2 V 2. And that is why when they when we kept or when we brought them into thermal contact, we found a situation that the pressure of each of the system changed, which means under thermal equilibrium since for they have the same temperature which is suppose T. So, P prime P 1 prime P 1 is equal to R T also P 2 prime P 2 is equal to R T. So, we have add at a condition which is this.

So, in order to do that the pressure of system A and the pressure of system B has changed from P 1 to P 1 prime and from P 2 to P 2 prime. So, this shows just conceptually that if the systems are in thermal equilibrium the temperature must be the same for those systems. So, we have some operational definition for temperature the system in thermal equilibrium with each other have the same temperature and systems, which are not in thermal equilibrium have different temperature. In this example which we had shown initially the systems had different temperatures that is why A P 1 V 1 was not equal to P 2 V 2 and moment we brought them in thermal contact through a conducting wall heat flew across the boundary and then the flow of heat brought the temperature of the 2 systems equal and now the systems are in thermal equilibrium.

So, this is a conceptual X explanation based on a thought experiment that we just did. So, again the Zeroth law says that if the 2 systems are both in thermal equilibrium with a third system, then the 2 systems must be in thermal equilibrium with each other.

Now, let us move on and start the concept of work. So, far what we have discussed is the concept of heat flow and the associated temperature. So, the heat flow has a meaning only when there is a concept of difference in temperature if the temperatures were equal for 2 systems there would not be any heat flow.

Now, let us consider the how we will quantify work in this case as I said we will be talking about the pressure volume work.

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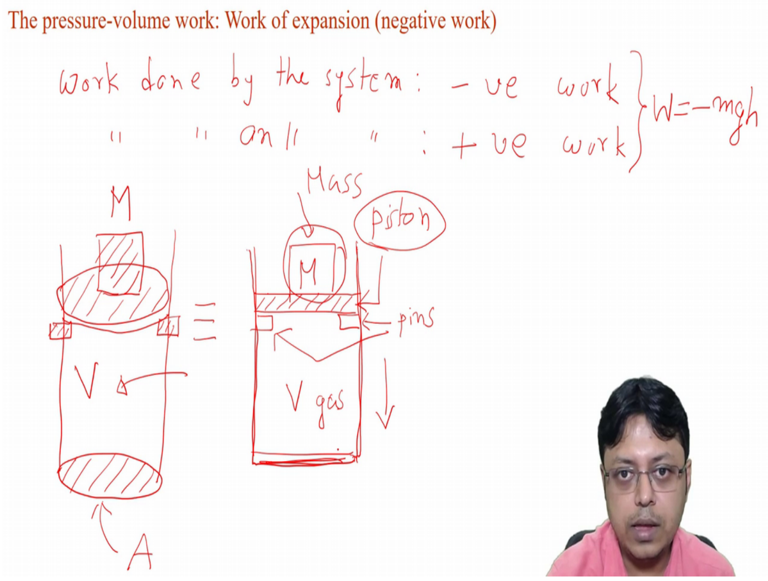

Now again remember that the convention is if the work is done by the system, then we will call it as a negative work and if work is done on the system by the surroundings then we will call it as a positive work and for that we asserted that the definition of the world in the definition of the work we have to insert a negative sign.

Now, think about again a system or a hypothetical system which is a gas in a container in this case think about the container as a cylinder. So, this is a gas inside this container which has a certain volume and this is the cross sectional area of the base of the cylinder, which we call as say A for area and what we have done is that we have put a mass on a piston which is lying at the top of the cylinder and of course, this mass is not falling because we have put say some pin here which you can remove. So, this will be our hypothetical system which is a gasp confined in a cylinder.

Now, frequently we will be drawing it as a simple drawing where we will not show that area. So, this is the piston and A mass is kept on the piston and there are 2 pins which hold this piston and the gas has certain following. So, this is our system. So, rest of the universe which is outside this system is called surrounding. Now this piston will also assume has no mass meaning all the effect of the mass is coming from this mass. So, this is a very idealized situation. Secondly, when the piston moves up or down if we remove those pins for example, and if the mass is not creating a higher pressure than the gas then of course, the piston will move down we will discuss all those things and during the movement will also assume that there is no friction of the piston with the wall of this container.

So, the piston is actually massless and the motion of the piston is frictionless. So, there is no dissipation of energy due to the movement of the piston alone and also there is no forces are created on the gas due to the weight of the piston because the piston is massless.

Now, let us try to consider how will you quantify work.

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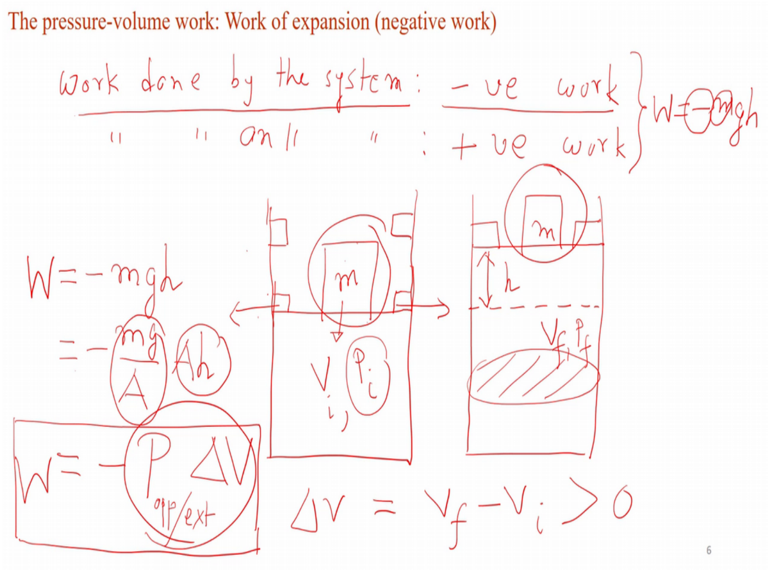

Now think about it suppose initially suppose this is our system and this is the piston and then we have kept a mass on it and suppose the pins are connected like this in this case the pressure inside this pressure of this gas, which we denote as say P i i is for initial pressure and the associated falling mass V i the pressure is enough to raise this mass which we denoted as M, we have been using the mass as small m. So, let us just write it as small m instead of capital M.

Now, suppose we laid this pins away and assume that there was another pin which was lying here. So, what will happen the gas since the pressure was higher enough to hold this mass. So, the gas will now expand because the mass alone cannot hold this piston and which means the gas will now expand and come to a situation where the piston will now touch these pins. So, the mass is now here. So, as you see the mass has been now lifted in the surrounding which means the gas has done some work, we have to show that this is a negative work and we have to also quantify what do you mean by the work.

Now, let us look at the change in the height of the piston as you can see that the gas has expanded and the piston has moved by an height which we call as H. So, in this case the work done in our convention will be minus mg into h. Now you can divide it by the area of the cylinder and again multiplied by the area of the cylinder. Now remember if I do that what is this quantity what is mg mg is nothing, but mass time's escalation. So, mg represents the force acting on the gas through the piston. So, force by area is nothing, but the pressure. So, mg by A is the pressure in this case this is nothing, but the opposing pressure or external pressure. So, instead of writing it as P will write it as P opposing or sometimes we will write it as P ext which means it is an external pressure, this is not a pressure of the system or pressure of the gas this is the pressure created by this mass on the system.

Now, what we have in the second term is A times h what is a remember that A is basically the cross sectional area of the piston and what is h h is change in height. So, area time's length is nothing, but volume in this case it is the change in height. So, area time's height or h change in height is nothing, but the change in volume.

So, what we got is an expression for the work done as minus B opposing or minus B external into delta V where P opposing or P external is the external pressure that was acting on the system during the expansion or compression will also talk about compression means; during the change the acting pressure that is denoted as P opposing or P external and delta v is the associated volume change.

Now, suppose the final volume will denote as V f and the final pressure as P f in this case of course, P f is greater than V i, because the gas has expanded. So, delta V is nothing, but P f minus V i which is greater than 0 which means the work done here is negative, this is in accord with our convention that if the work done work is done by the system we will take it as negative that is why we had to introduce this negative sign now this is clear why we took the negative sign in the expression for work.

Now, we will discuss what will be the amount of work for the case of compression again it is a pressure following work remembers that. So, let us try to draw it.

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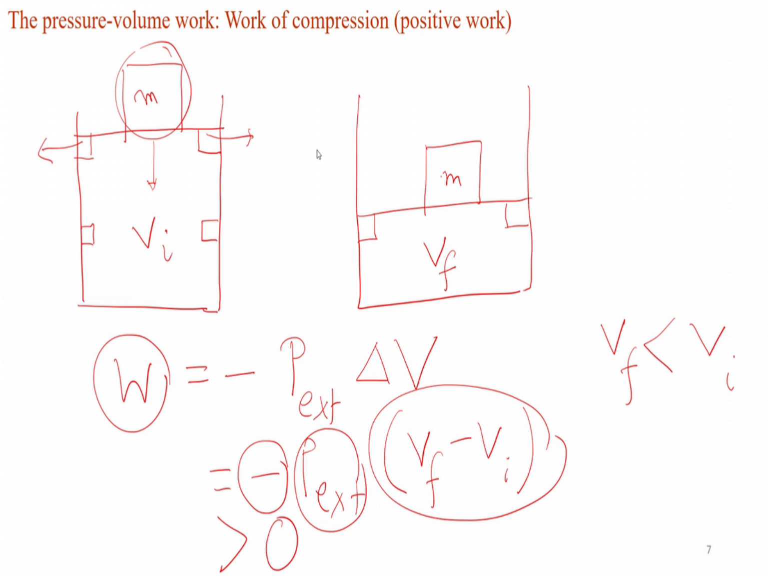

So, in the case of compression we have a opposite situation. So, initially suppose the volume was vi according to our convention and then it was the piston was held by 2 pins and there was a mass now of course, this mass is creating more pressure that is why if we remove the spins the mass will fall and let us put 2 more pins so, that the piston will fall up to a certain height.

So, if we suddenly remove these 2 pins what will happen is that the mass will fall up to here shrinking the gas. So, the volumes of the gas will reduced and as before let us just calculate I was using small n notation for the mass. So, as before the work done will be minus P external into delta V now in this case what is delta V delta V is change in volume which is V final minus V initial, but note that here V final is less than V initial which means that this work must be positive because this is a negative quantity and we have a negative sign external pressure cannot be negative it is always a positive quantity. So, now, the work is done on the system by the surrounding and this is consistent with our definition that we will take this work as a positive work. So, that is the importance of this negative sign.