Course on Phase Equilibrium Thermodynamics
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Lecture 02
Introduction (contd.)

A very good day to all of you, so we have come to the second class of phase equilibrium thermodynamics, in the last class I had given you a very brief introduction regarding systems, surroundings, boundaries and equilibrium state of a system etc. Now when does a system deviate from equilibrium? As I told you in the last class under normal circumstances if any particular system is left to itself it will not deviate from the equilibrium state because it is most comfortable when it is in the equilibrium state there are no driving forces and there is no incentive there is no need for the system to change.

A system changes only when it interacts with the surroundings by virtue of some sort of an energy interaction or a mass interaction and when it is interacting it undergoes a process by virtue of this particular process, it shifts from one particular equilibrium state it continues this particular path till it reaches a second equilibrium state again when there are no unbalanced forces and it has no tendency or there is no tendency of the system to deviate from the second equilibrium state unless again it is forced to do so.

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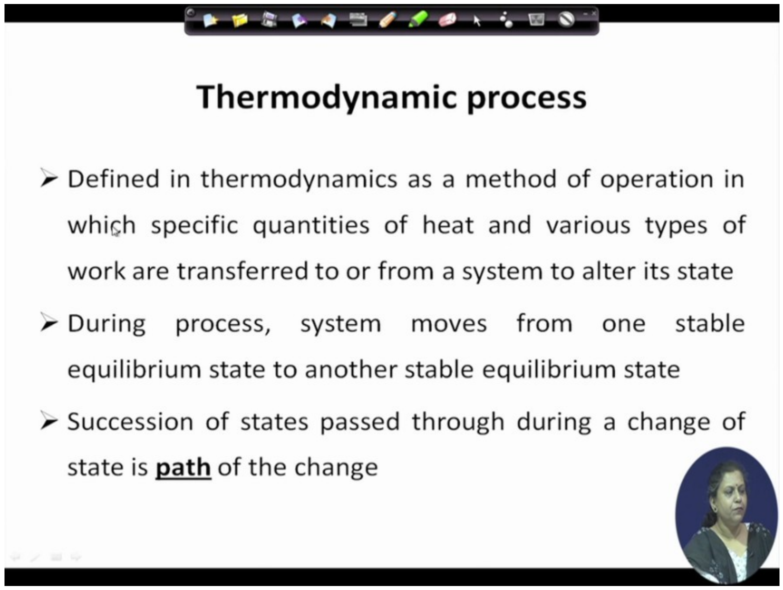

So therefore the process which a system undergoes it is defined as a method of operation in which specific quantities of heat and rather it is better now we do not discuss about heat, work etc in which a system interacts with the surrounding by virtue of some sort of energy interaction as well as may be there can be some mass interaction also and during the process the system moves from one equilibrium stable state to another equilibrium state and the succession of states which the system passes during this particular change that is known as the path of the process.

Now let me tell you that usually whenever we undergo any particular process it is quite fast, right? And it is very difficult for a system to remain in equilibrium during all the states it is undergoing when it is going from one equilibrium state to another equilibrium state. An idealized situation is a situation where a system while undergoing a process passes through a succession of equilibrium states but this is an idealization and often we assume that a system is actually passing through a succession of equilibrium states during the process and we call such a process a reversible process.

Now let me remind you again a reversible process is an idealization it is never possible to, we can try to attain a reversible process but it is never possible to realize a reversible process in practice, most processes are irreversible. If so why are we so interested about reversible processes? We always try to rather simulate or model or rather analyze any particular process assuming it to be reversible and then we find that or rather we incorporate an efficiency factor to come to the actual energy interactions in the irreversible process, why so?

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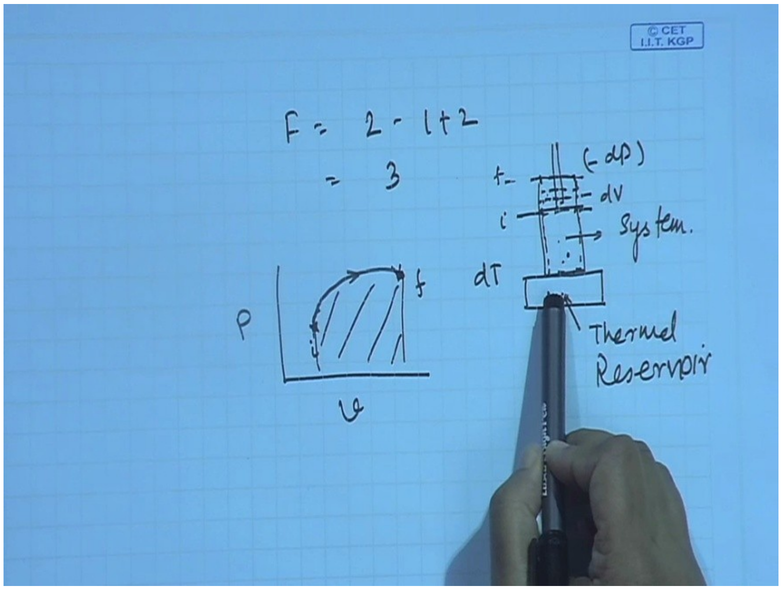

Why are reversible processes which can never be realized in practice so very important? The reason is very simple, see suppose we take some particular amount of gas in a pistol cylinder arrangement a very conventional system which will be dealing now and again in our course of thermodynamics, again possibly due to the history of thermodynamics originating from heat engines and heat cycles. So say for this particular system in this case the gas which is contained in this particular cylinder this is my system, right?

And what I do? We need this system it is in contact with the thermal reservoir at a higher temperature, fine? So under this condition what happens? Some amount of energy flows from this particular reservoir into the system, when some amount of energy flows suppose we can maintain the condition such that, as the energy flows we do not allow temperature rise of the system on the contrary the system keeps on expanding in volume and the piston keeps on going up very slowly such that with entry of heat by an infinitesimal amount which occurs when there is a dT difference of temperature between the thermal reservoir and the system then the heat flow from the reservoir to the system occurs very slowly.

And under that condition the system, it expands under a very slow rate and we find that with time the system gradually increases in volume by dV amount and its pressure reduces by minus dP amount, right? So therefore we can assume that at each and every state the system was in an equilibrium state. What does it imply? It implies that at each and every instant of time the system had one particular pressure value, one particular volume value, the volume value went on increasing very slowly, the pressure value went on decreasing very slowly, it is true but for each particular state for each particular state the system was undergoing from its initial position of the piston here to say the final position of the piston here, the each and every state which the system was undergoing it could be characterized by a unique set of properties or in other words the system was in an equilibrium state at each and every position.

So therefore if we can plot the state of the system see on a PV plot maybe this is my initial state and say this is my final state, so I know in this particular case it was I can actually plot the path of the process. So therefore in this particular case when I can actually trace the path of the process as we shall see after sometime it is very easy for us to identify the energy interactions which the system had with the surroundings during its entire path.

It is given by the area under the curve that will be and you also know possibly and I will just discuss shortly. This area under the curve gives the energy interaction between the system and the surroundings, so therefore in order to calculate the energy interaction it is very important to trace the path of the process. The path of the process can be traced only for a reversible process.

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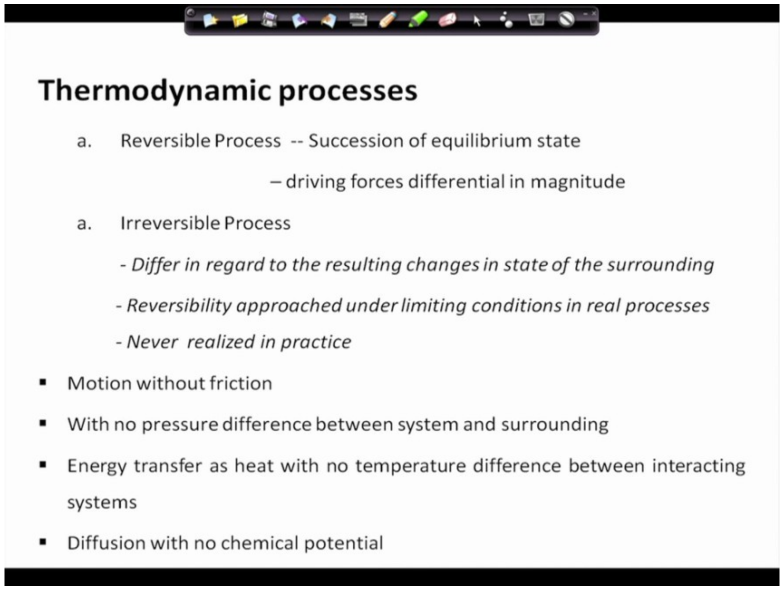

So therefore a reversible process although an idealization it is very important we try to simulate or we try to idealize each particular process as a reversible process where it comprises of a succession of equilibrium states with driving forces between the system and the surroundings being differential in magnitude and this occurs for some too idealized situations like motion without a friction, no pressure difference between system and surrounding and infinitesimal similar pressure difference between systems and surroundings.

Energy being transferred just like the piston cylinder arrangement which I have shown. Energy is being transferred with almost no temperature difference between the interacting systems and so on and so forth. Now well, there is one thing which I would like to mention, right? Now what is the basic difference between a reversible and an irreversible process? When I ask this question in the class the answer which I get is that on reversing the process the system comes back to its original state but this is not the correct answer.

It can always happen even in a cyclic process also that when we reverse the process the system comes back to its original system the important part is that a difference between reversible and irreversible processes are with the changes in the state of the surroundings. For an irreversible process even when we reverse the process the system might come back to its original state but the surrounding is not going to come back and for a reversible process both the system as well as the surrounding comes back to its original state.

Now well, the most important part of my introductory lecture, why just as I have said a system if left to itself it remains in an equilibrium state. It changes from 1 equilibrium state to another through a Series of steps which comprise a processes etc. And the process occurs only when there is some energy interaction between the system and the surrounding. Now this word energy you have been hearing about this word since your school days and possibly in your physics book you have learned whenever I asked in the class what is energy? The answer which I received almost every year is energy is the capacity to do work then the next question is what is work?

So therefore these terms are very common you have been using them since your childhood energy, work, process, system all these words are very common in fact the entire concept of thermodynamics, it is based on common everyday experiences we are dealing with very common words which you use in your everyday but sadly that does not make the study of thermodynamics easier, on the other hand it is always almost the contrary thing.

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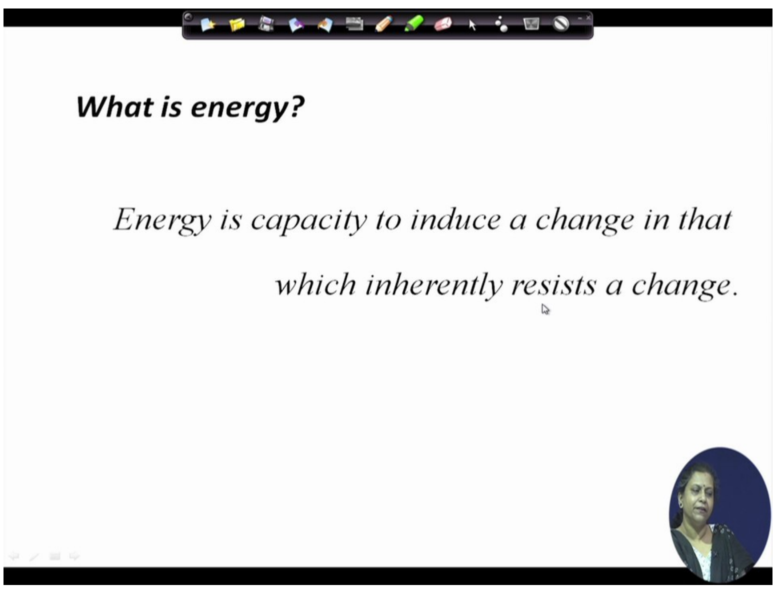

So therefore in order to understand energy the definitions which I would prefer to give is energy is the capacity to induce a change in that which inherently resists a change. If you go through this particular definition carefully, what do you find? You find that the word energy comprises of 2 parts what are the 2 parts? First thing is that there is some particular force which is trying to induce a change in the system.

The system is inherently resisting that particular change and this particular force which is being applied that particular force it overcomes the resistance to change of the system and then it performs the change in the direction of the applied force the same thing that you have learned in physics. In physics also we have learned that energy or the work done that was equal to or say the work done that is equal to F into dl, it should be dW which is equal to F into dl, right?

It is force into displacement. Just to keep a link or keep a paratue with that particular definition which you had some across in this case also I define energy in this particular way that it is a capacity to induce a change in a system which inherently resists the change, so therefore from this what do we see? We see in that case energy, what does it become? In that case energy becomes a product of 2 terms.

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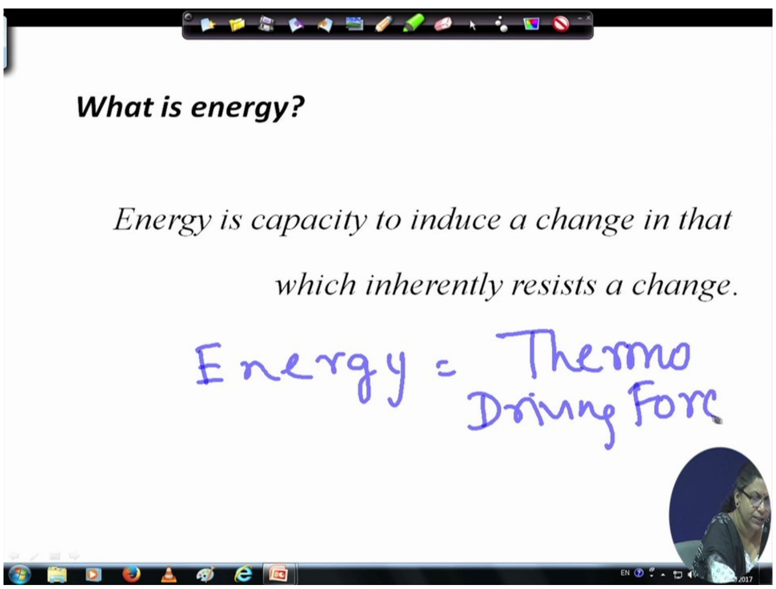

The first term is a thermodynamic driving force which inherently overcomes the change which a system provides to resist a change and once that change is overcome then this particular driving force it brings about a displacement of the system in the direction of the driving force. So therefore we find that just like physics we find that we define energy as the product of two quantities one is the thermodynamic driving force and the other is the thermodynamic displacement.

The important part here is the thermodynamic driving force and the thermodynamic displacement they are not defined in the same way as they are defined in physics, for our case defining the thermodynamic both these properties the thermodynamic driving force and the thermodynamic displacement both of them are thermodynamic properties of the system. Usually what do we find? A thermodynamic driving force is an intensive property whose difference in magnitude between any 2 parts brings about a change in some other extensive property of the system which is known as thermodynamic displacement.

So basically energy in thermodynamics it is a product of one intensive property whose difference in magnitude brings about a change in an extensive property of the system and the driving force it controls the extent and the direction of change in the thermodynamic displacement. For example in the piston cylinder arrangement that we were discussing just now.

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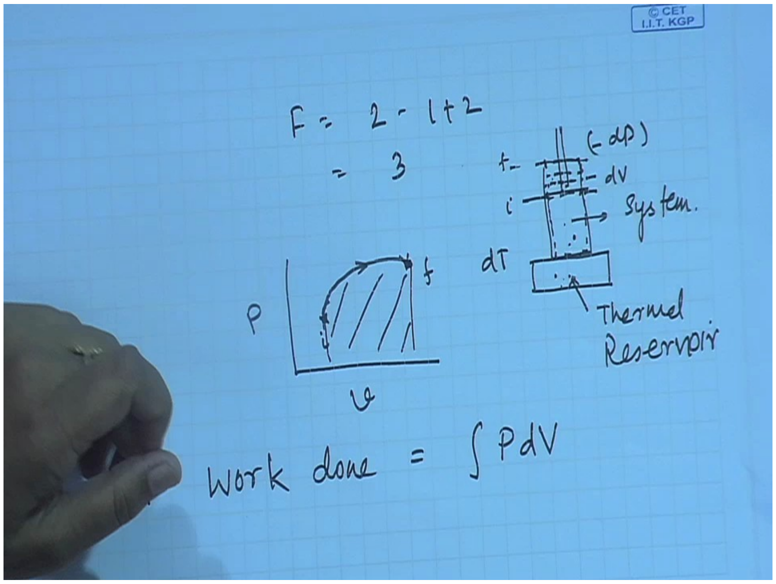

In this particular case we found that some amount of energy was flowing and due to this energy flow it was expanding and why was it expanding? Due to a pressure difference between the system and the surrounding.

So therefore the pressure difference P that was the thermodynamic driving force which was bringing about change in the volume, which is the thermodynamic displacement. So therefore for the pressure volume type of work, we find that work done or the energy transfer in this particular case it is equal to integral of PdV, right? Now one thing we need to remember in thermodynamics is that we can define the thermodynamic driving force and the thermodynamic displacement in any particular way but when multiplied they should give you the unit of energy.

For example we can define the thermodynamic driving force, yeah. So therefore the thing is it is very important for us to remember that whatever we are doing the thermodynamic driving force and the thermodynamic displacements are simply properties of that particular system one of them is an intensive properties which is the thermodynamic driving force.

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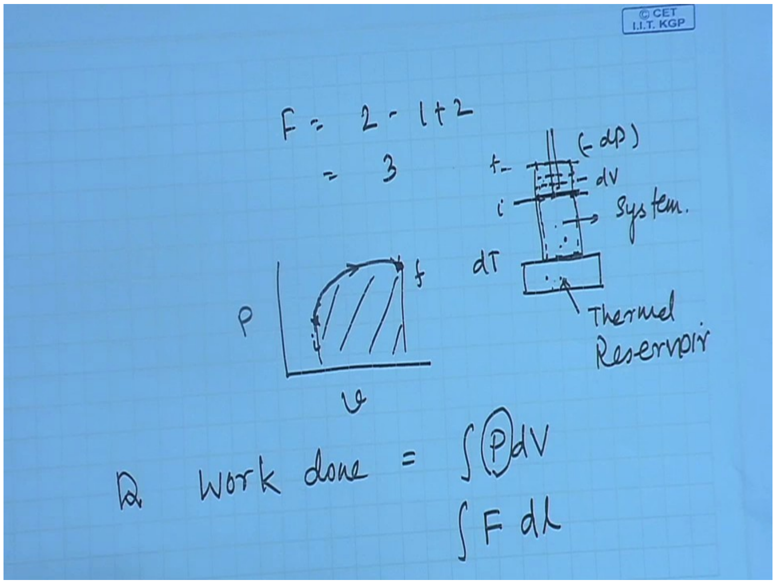

The other one is an extensive property which changes and that is a thermodynamic displacement and the choice of these two they are completely arbitrary for example in this piston cylinder arrangement we could have very well assumed instead of assuming this to be the driving force we could have assumed the product of the pressure and the piston area which is F as the driving force and the displacement of the piston as the displacement.

It hardly matters how we are going to define or rather how we are going to divide the energy into a thermodynamic driving force and the thermodynamic displacement it is important to remember that no matter how we are dividing it when we multiply the two it should have a unit of energy in this case there is just one thing which I would like you to remember that since thermodynamics driving force and thermodynamic displacements they are scalar quantities.

So therefore they are different from the displacement and driving force which we define in mechanics for example they do not obey the Newton's third law of mechanics and it is important to remember that although these two are scalar quantities but they are the collective property the motion of the large number of ultimate particles which exhibit Newtonian mechanics, right? But since they are completely random they are average of all the displacements and driving forces of a large number of ultimate properties, finally sum up to manifest as the pressure change which brings about the volume change.

So therefore it is important for us to remember that in thermodynamics we define energy as a product of the thermodynamic driving force which is nothing but an intensive property change and which brings about a change in any extensive property of a system which is the thermodynamic displacement. Usually since we deal with pressure volumes type of work so usually the redefined work done as integral PdV.

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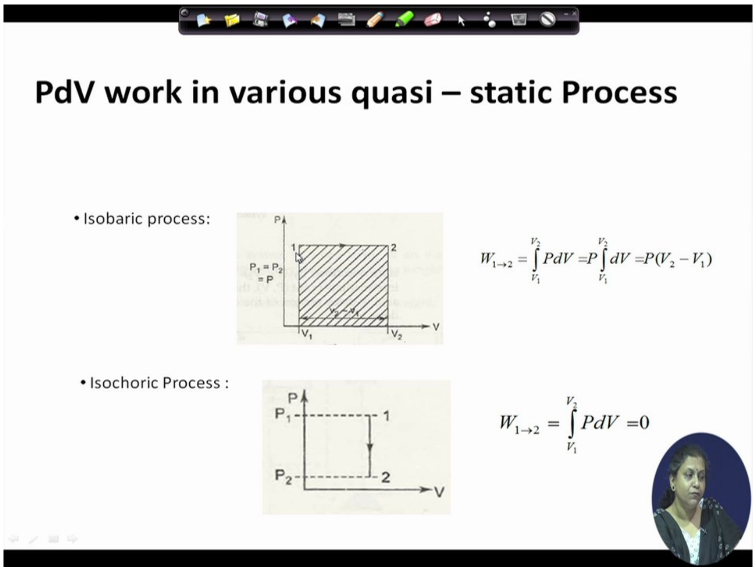

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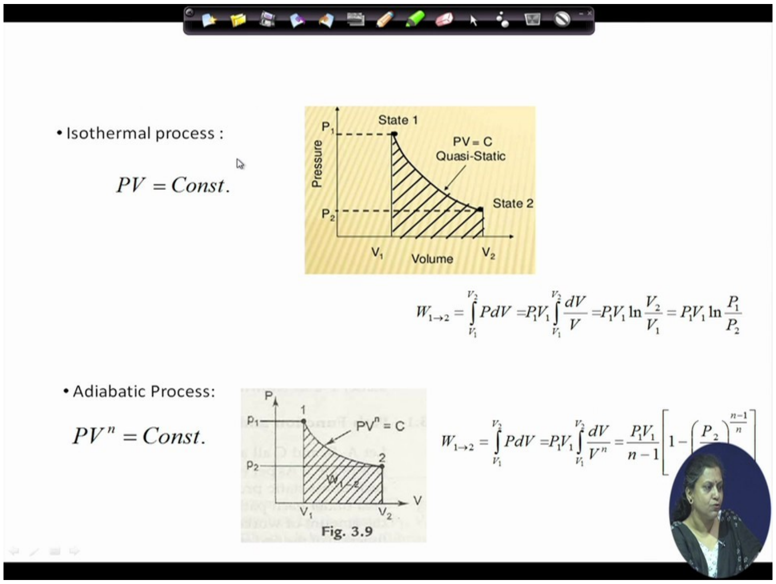

Now it is important for us to remember that the energy interactions between the system and the surroundings are usually in the form of work or in the form of heat, right? So here I am not going to go into details assume that you already know it or you can take it up as a home assignment I have just found out what are the different expressions of the work for different processes for different reversible processes Isobaric, Isochoric, Isothermal, Adiabatic processes. You can very well take these derivations as your home assignment in case you have any doubts we can have the interactive session during the course and the TAs' would be very glad to solve any doubt that you have.

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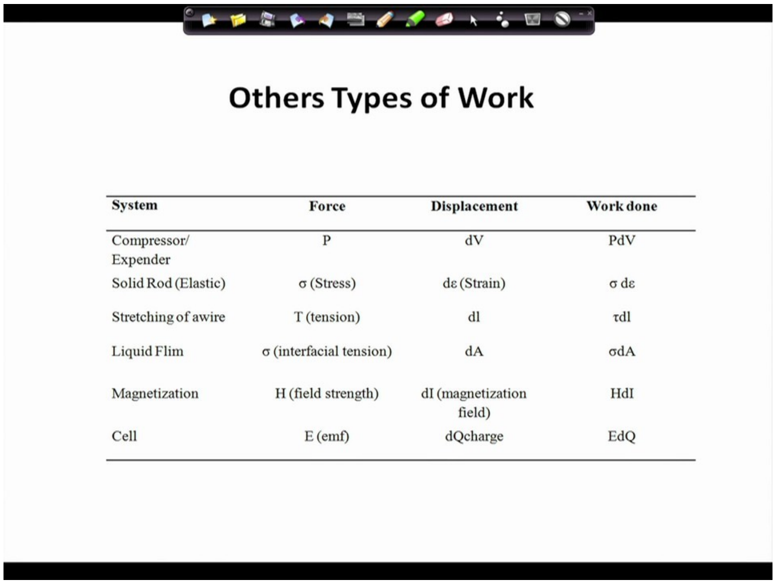

System	Force	Displacement	Work done
Compressor/ Expender	P	dV	PdV
Solid Rod (Elastic)	σ (Stress)	dε (Strain)	σ dε
Stretching of awire	T (tension)	dl	τdl
Liquid Flim	σ (interfacial tension)	dA	σdA
Magnetization	H (field strength)	dI (magnetization field)	HdI
Cell	E (emf)	dQcharge	EdQ

There are other types of works also which it is not only that PV type of work we can have other type of systems other than piston gas in the piston cylinder type of arrangement, but we will find that for each particular system that you consider, we can break up the work done into a thermodynamic driving force and thermodynamic displacement and when we multiply the two we get the unit of an energy, right?

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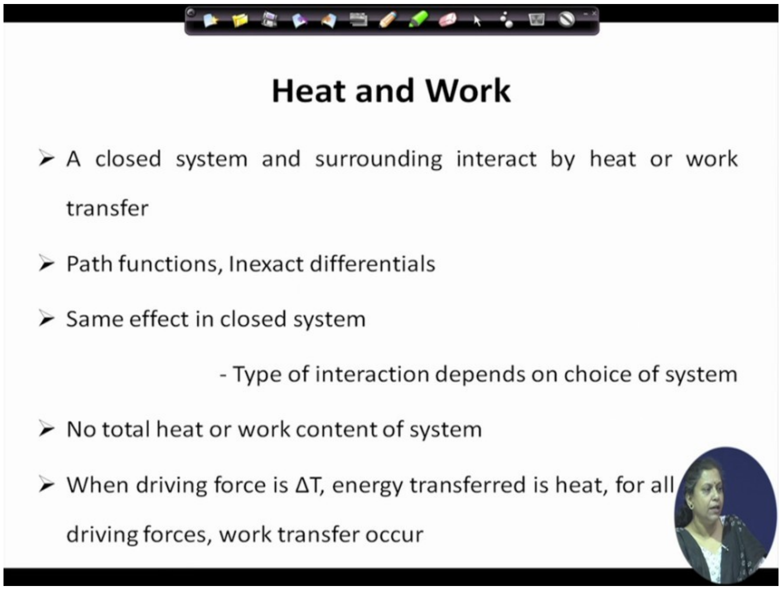

Now as I have already mentioned there are two types of ways by which a system and the surrounding can interact or can exchange energy, it can be either in the form of a work or in the form of the heat. For both of them we need a thermodynamic driving force and a thermodynamic displacement. When the driving force is the temperature difference than we call that particular energy interaction as heat, when the driving force is anything other than the temperature difference we call it as the work.

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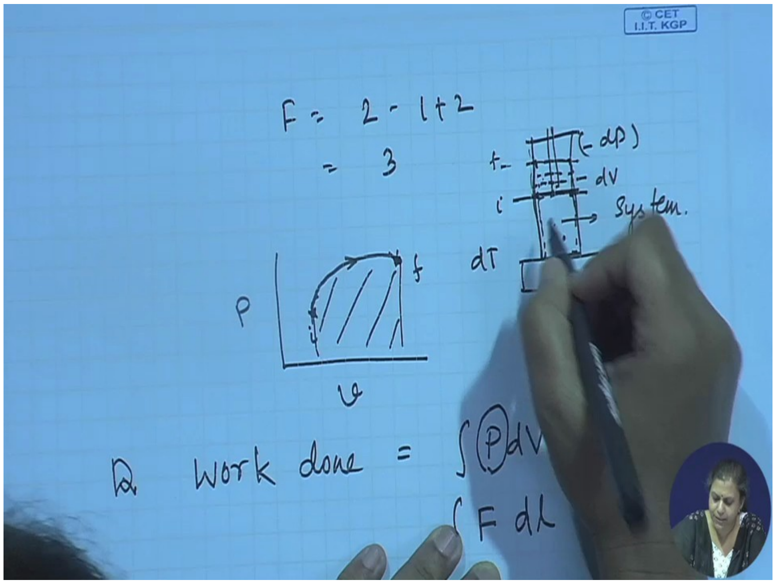

Now here I would like to mention one thing, since we are dealing with properties, so therefore this driving force and the displacement both of them can be the property of a system both of them can be the property of the surrounding or else one of them can be the property of the system the other of the surroundings. For example suppose I take up this particular arrangement I arrange my system such that my system comprises of not only the air in the piston cylinder arrangement but also some portion of the surroundings as well.

Now in this particular case we find that the pressure difference which was bringing about the volume difference everything was a property of this system. So therefore the energy change which took place here, is also a property of this system. Similarly, suppose I define my system somewhere outside such that this whole thing is a property or is or it lies in the surrounding then in that case we find that the whole energy interaction was a property of the surrounding. But suppose I have my system as the gas contained in the piston cylinder arrangement then we find that maybe not this case a better case is when work is done.

In this case what happens suppose I apply or I gradually increase the pressure here I find that the piston it keeps on coming down and it compresses the gas, so in this particular case what happens the pressure which is applied that is a property of the surrounding and the contraction of the compression of the gas or the volume decrease of the gas this particular volume is a property of the system.

So therefore for this case the energy interaction which occurs whose property should it be? Because in this case actually the energy interaction is occurring across the boundary which is a 0 thickness interface between the system and the surroundings and energy interaction occurs because there is the pressure of the surrounding forces of volume change inside the system under this condition we say that it is energy in transit, it is neither a property of the system nor a property of the surrounding.

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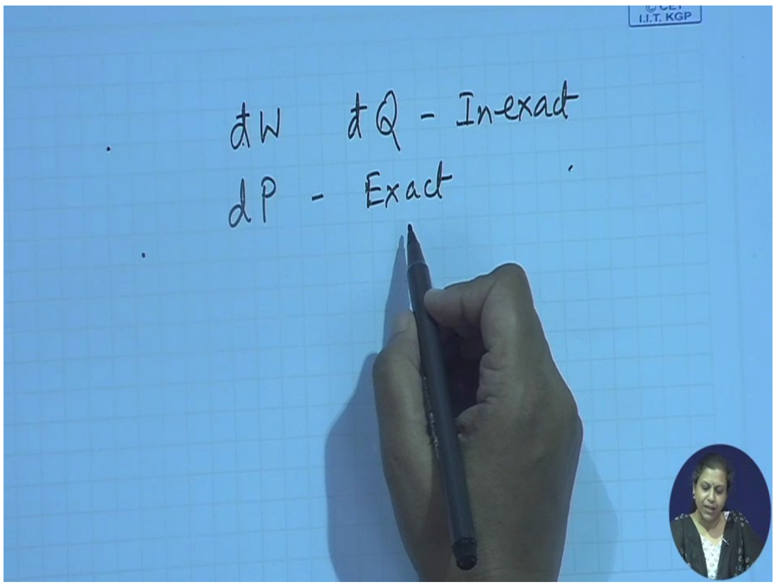

It is a path function it is energy in transit and as a result of which we consider this type of energy in transit as path functions whose differentials are inexact due to which we are going to represent heat and work interaction between the system and the surroundings by means of a different sort of a differential as compared to the exact differential by which we had depicted a property. This is something very important which I will be following in the class I would want you people also to follow this that we would like to differentiate between inexact differentials and exact differentials. The path functions will be shown by inexact differentials and the state functions will be shown by exact differentials.

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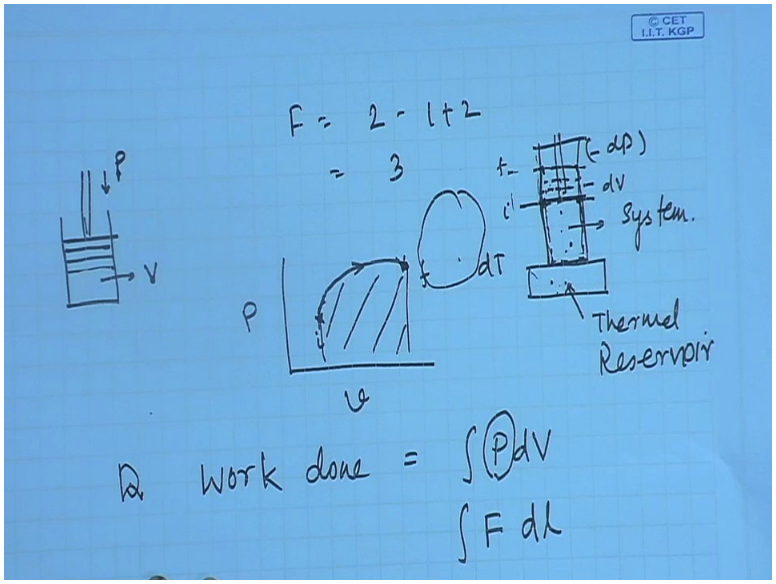

Now in this case so therefore I would like to mention that heat and work they are quite unique, why? Because they are the energy interactions between a closed system and their surroundings and we can have the same effect both by heat as well as by work. For example in this particular case the expansion of the system could have been brought about by pressure changes in the surrounding in which case we say that work is being done, in this case we say that work is being done on the system we can also bring about this same change by a temperature differential with the surrounding in which case we say that heat is being transferred to the system.

If you observe the initial and final state in this case and this case we find that they are the same but the change in this case was brought about due to work done on this rather work done by the system from the surrounding and then this case it was due to the heat transfer between the system and the surroundings, right? Now you have to remember that before the change and after the change is over we just see the change of state, we see the initial volume of the system, the initial temperature and pressure of the system, we see the final volume and the final temperature and pressure of the system.

We are in no position to understand how this change has been brought about once the change is completed, so therefore we can just see the change which has brought about. So therefore it is very important to remember that heat and work have meaning as long as the change is going on once the change is over we find a change in the property of the system we do not know how that change has been brought about.

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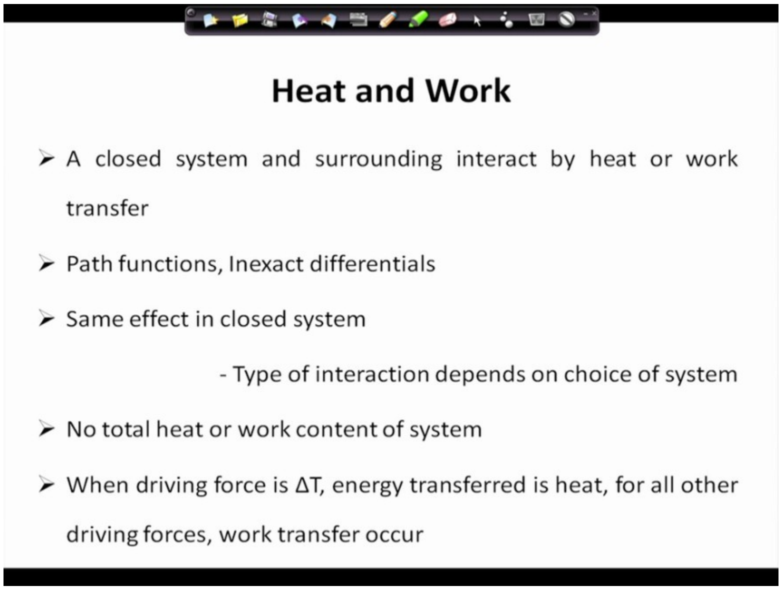

So therefore please remember there is no total heat or work content of the system there is a total energy content of the system but there can not be any heat or work content of the system they are just manifested as long as the process is going on and then they are manifested once the process is over by a change in property of the system which shows that there was an energy interaction between the system and the surroundings.

It does in no way show that there has been or in what particular form that energy interaction had taken place. Now before I end I will give you a very interesting example of how the choice of system dictates whether it is work done or it is heat transferred. During winter every day we heat up our water in our hostels by using an immersion heater most of us we have immersion heaters which we dip in the bucket of water and we heat the water.

Now suppose we assume that our system is just water in the bucket and nothing else then in that case how the water gets heated up? There is a temperature difference between the rod of the immersion heater and the water due to which energy gets transferred and it is heat transferred which heats up the water. Now suppose you think that well, no the water is not going to be my system, my system is the entire thing inside the bucket that means the immersion heater the water everything contained in the bucket. In this case how does the water get heated up? It gets heated up because of the electrical work which is being done on the rod by the battery.

So therefore in this case it is work done on the system it is important to remember why I was emphasizing so much on the choice of system, the choice of system is very important because that decides whether we are having heat interaction or work interaction as we proceed you will find that the choice of system may make your calculations difficult or it may make your calculations easier as well.

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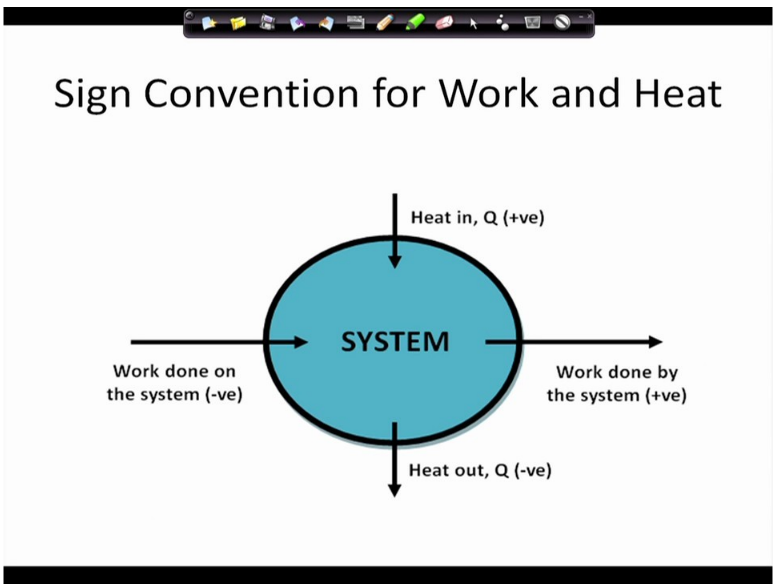

So therefore choice of the system is very important and before I end I would like to have like to discuss the sign convention which we are going to use for my work and heat in the entire course of phase equilibrium thermodynamics. The sign convention is that when heat enters the system it is positive and when system does work on the surrounding it is positive. So therefore we followed this sign convention and proceed for our next class, thank you very much.