Indian Institute of Technology Kanpur

National Programme on Technology Enhanced Learning (NPTEL)

Course Title
Engineering Thermodynamics

Lecture – 05
Concepts of Equilibrium and its State

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Let us start this lecture with a thought process from Rudyard Kipling who feels that I keep six honest serving men.

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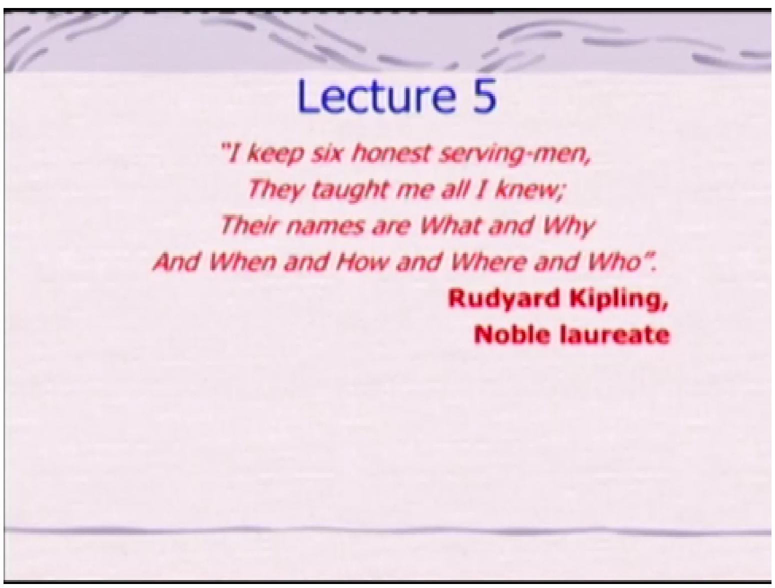

They taught me all I knew the names are what, why and when how and where and who okay this I consider like all these you know what why when how where and who are basically five Pandavas and Draupadi you can identify who is Draupadi okay you can think about that and let us you know before embarking into the new topic or the new thing in this lecture what we will be doing will be trying tore call what we learnt in the last lecture can anybody tell me we started the discussion on basically about various forms of energy an energy is very important.

So far the thermodynamic is concerned right and, so we looked at both microscopic forms of energy and macroscopic forms of energy and microscope a form of energy which will be interested in right and we will be working on that but the microscopic energy is more important because we will be utilizing this microscopic forms of energy which is also known as the unorganized form of energy am I right it is not organized properly and the task of thermodynamic is basically to convert this unorganized form of energy into organized form of energy.

So that we can utilize for our purpose you know in engineering applications right and after that we moved into a concept known as what we call equilibrium right and I took an example of connecting a copper rod to a hot bath that is something water hot water bath you know which will be maintained at a constant temperature around 100 degree Celsius right and the ice bath we connect so if you look and both are connected on the both the side of the copper rod and we consider the copper rod as our system.

Am I right we allow a lot of time to heat transfer to take place from the hot water bath to the cold water bath and then you people told me look it has attained the copper rod is attained the equilibrium actually it is not it was attaining what steady-state right but not equilibrium when I isolated that copper bar from the both the baths which are basically surrounding right and this is the system copper rod was the system and the hot water bath and the coldwater bath as a surrounding and isolated and insulated also then it attains a temperature right.

And that temperature means there is no gradient in the system which is your system this is the copper rod is your system of gradient of temperature therefore we call it as a basically reaching equilibrium today we will be discussing continuing to discuss on that what you call the equilibrium things and ocean edges.

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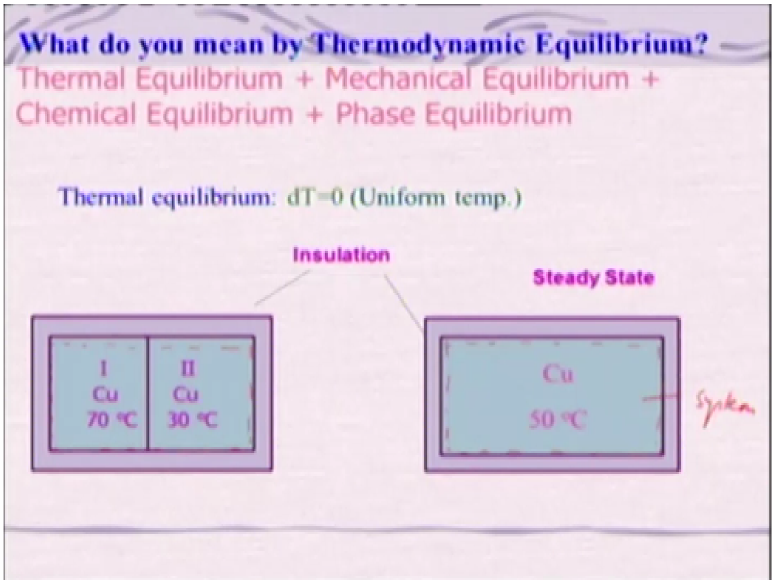

What do you mean by thermodynamic equilibrium that means when a system will attain the equilibrium in thermodynamic sense, right so let us take an example right, what we will do we will take a copper rod that is the what you call the first one copper one you know, so this is your copper rod one which is at 0 degree Celsius with a partition this Called as partition with another copper block which is at 30 degree Celsius right .Now both are separated says that you know no heat is transfer taking place although the temperature gradient is there one is at higher temperature as it is at lower temperature.

Now I will remove this partition right and then of course both will be come in contact you can assume that way or you can assume this partition is very thin right and then there will be some heat transfer and this is that became our system what you call this will be my system, right and then I allow for a longer period of time, so what will happen some heat will transfer from higher temperature to the lower temperature because that is the way how heat transfer from higher I mean gradient rate.

So after reach you know if you give a sufficient amount of time this whole system right it will be basically if you could look at this is my system and that will be attaining a temperature50 degrees Celsius like if you look at there is no gradient in this system I mean this is my system and in that there is no temperature gradient it is all uniform that and that we call you know as a what you call a system as a reach test equilibrium state right but is it thermodynamic equilibrium no it is not actually it is thermally equilibrium right.

We call it as thermal equilibrium because the uniform temperature is attended right but thermodynamic equilibrium will be having a very you know what you call a wider connotation right that means there will be various gradient will be there right there might be pressure gradient there might be a concentration gradient there might be you know phase change you know kind of things, so therefore a system can be said to attain a thermodynamic equilibrium only when it attains not only the thermal equilibrium but the mechanical equilibrium, chemical equilibrium and phase equilibrium right.

So these are the things we you know it must be satisfied then only you can call a system to attain you know equilibrium thermodynamic, so therefore one has to be little careful and let us understand what do we mean by mechanical equilibrium.

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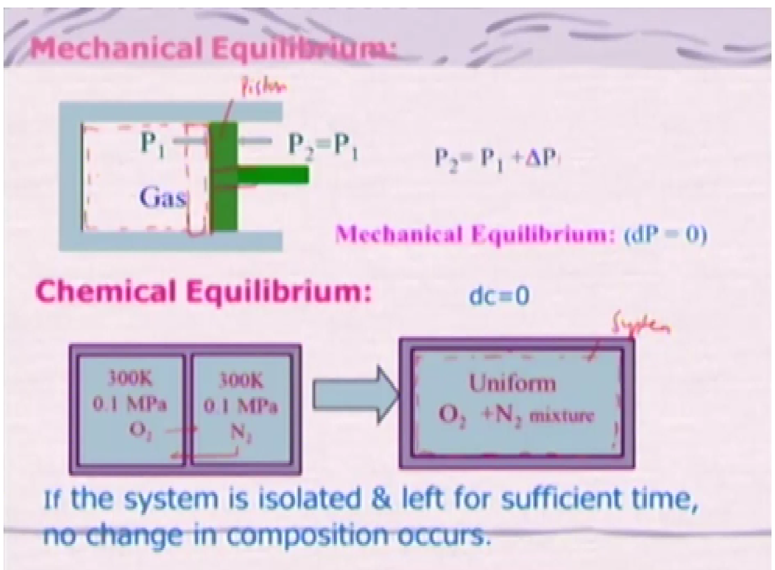

We will take a what you call a piston cylinder arrangement in which we will be taking a gas and this is our system this is our system and to start with this pressure acted by the gas on this piston this is our piston okay and will same as that what is being applied on the other side of the piston so it is in equilibrium right for example if I will increase the pressure let us say P Δ P what will happen what will happen the change in pressure is there on the this P2 side that means piston will be trying to push the gas right how long it will go on till it attains another equilibrium.

For example like you know in this case that piston can move to in this place let us say you know piston become moving to this one so that you know this gas will attend another pressure which will be same as that of the P2 and P2 is increased by ΔP then it will attain another equilibrium that means all thus molecule here right will be having the same pressure in the system are you getting my point yes or no, but that will happen under what condition one has to for example I if we I will increase this pressure you know is let us say.

If it is to start with1 atmosphere pressure I will give another attention to atmosphere pressure at the P2 will it happen or not think about it but what you can understand at this moment that if the system attains the uniform pressure after a change right there is no gradient in the system itself then it has attained a mechanical equilibrium right , so therefore the Equality of pressure you can say it is you know whenever system attends equality of pressure across the thing across the all the domain of the system then we call it as a mechanical equilibrium.

Now let us take another example rate of chemical equilibrium and chemical equilibrium you know like depends upon what basically based on concentration for example you know like suppose I will I am using some perfume right here I have just come suddenly and can you smell It if there is a perfume here is being there as spray here and after sometimes you could smell it right how because the molecule of the perfumes have traveled although there is no velocity in this room right.

It is going because of concentration gradient right that we call it as a diffuser, so and let us take a similar example what we had taken earlier these are two chambers one is containing oxygen right the first chamber which is at 300 Kelvin 0.1 mega Pascal's and it is this chamber the first chamber is separated by another chamber which contains nitrogen gas at 0.1 mega Pascal and 300 Kelvin right. And there is a partition here and what we will do we will remove this partition right and then what will happen oxygen will be trying to move in this direction right and nitrogen will be moving in the opposite direction because it is concentration of nitrogen is zero here and here it is very high.

So therefore it will be moving towards that and this will be after certain time what will happen what will happen to the concentration of oxygen and nitrogen it will be uniform across the whole system if I say this is my systems you know this is my system type so I cross everywhere it will be uniform provided you have given enough time for the diffusion to take place right and as a result the change in consensus will be zero in the system there would not be any change concentration is uniform. So then we call a system has attained chemical equilibrium right.

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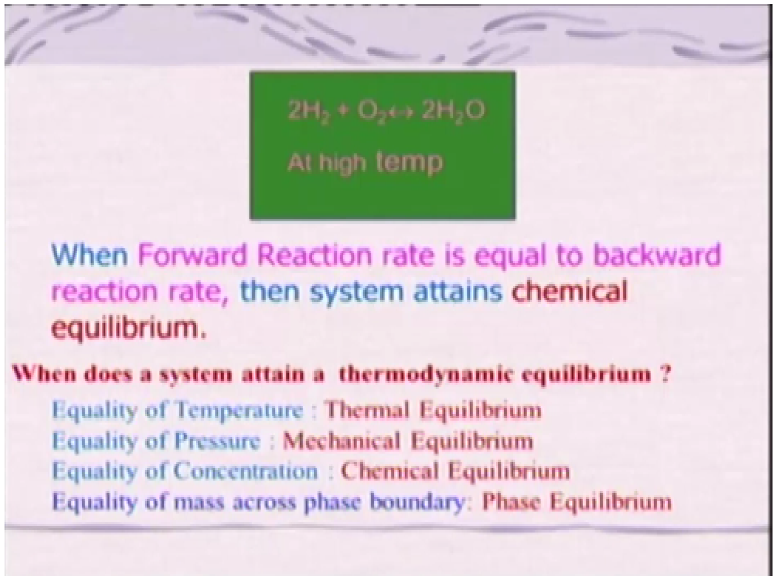

I mean this is a simple example I have taken but let us consider another example where two moles of hydrogen is mixed with one mole of oxygen right what will happen it will be mixed properly let us say all diffusion have taken place mixed and if it will attain a high temperature then what will happen it will go to two moles of water right and at the same time the water can be converted into oxygen and hydrogen as well both will be simultaneously taking place that means the hydrogen is reacting with oxygen going to the water and so also water can be dissociated to the hydrogen and oxygen provided.

You know it will be at a higher temperature otherwise no okay, so now we can call basically you know there will be forward reaction rate and there will be backward reaction rate because chemical reaction is occurring and there will be formation of new bond and also breaking up once you know of the this thing so all these things going on and then it will attain a equilibrium only when this forward rate of reaction is equal to the backward rate of reaction then system attains a chemical equilibrium rights.

So if you and similarly it will be happening like whenever let us say you are boiling water what will be happening the water at a particular pressure and of course at the boiling point you know100 degree Celsius for atmospheric pressure that will be what you call remaining constant and there will be change of the water vapor will be converted into the sorry water will be converted into its vapor and some of the vapor may be coming back to the water and it has reached equilibrium and that we call it as a phase equilibrium.

So to summarize that what is the thing that means a thermodynamic equilibrium can only take place if all these four equilibrium that is those are like thermal equilibrium, mechanical, equilibrium, chemical equilibrium and phase equilibrium are being satisfied in other words a system can attain equilibrium thermodynamically if all this for equilibrium can be attained by it if you look at thermal equilibrium basically equality of temperature and mechanical equilibrium equality of pressure in the system whenever I am saying it is basically equality of pressure and the chemical equilibrium is basically equality of concentration right.

And phase equilibrium is the equality of mass across the phase boundary that means whatever the let us say solid to the liquid or liquid to the solid you know can be the mass will be same remaining same so therefore it will be the phase equilibrium now we will look at like how stable is the equilibrium right that part will have to look at it.

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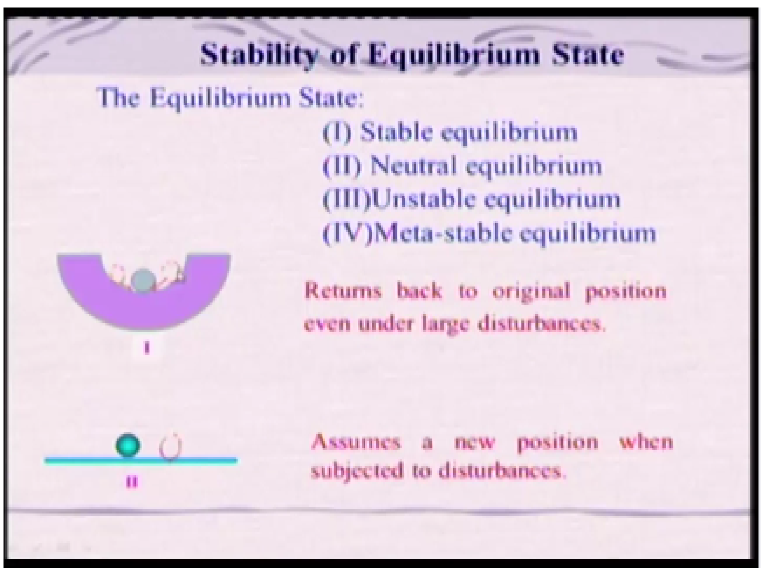

So that means this equilibrium States is there but it may be stable it can be unstable right or it can be neutrally stable it can be meta stable so the stability is very important part like if you look at equilibrium state can be you know divided into four categories one is stable equilibrium, neutral equilibrium, unstable equilibrium and meta stable equilibrium right.

So let us take a very simple example which most of you might have you know aware that let us say there is a ball which is here in a curved surface and if this ball due to something will move to let us say this place what will happen wall as due to some force it has gone to this place after certain time what will happen when the force is you know release what will happen to that ball will be returning back to this position and it will stay.

Similarly if there is a change in the position of the ball in the other direction right then again ball will come back and stay in the minimum you know energy state right if and under this condition we call it that it has a reach a stable equilibrium because if there is a change of the position of the ball it can return back to the undisturbed position right it does happen in our life am I right suppose somebody will scold at you right your mind will be agitated am I right yes or no.

Somebody can praise you will be later and then after that you will come to your normal position right that is nothing but your stable equilibrium either you are happy or you are happy your mind will be agitated right you are not in normal voice stable position, so that is the natural we do experience and which will be basically looking at kind of things and let us look at another example what we call as a neutral equilibrium suppose this ball is there in a flat surface you know well.

And now due to some force will be acting there will be some change in position, so let us say a ball will be coming over here depending on what it is having it may be right and it will come and attain another equilibrium position right that means this was a one equilibrium position it has come to the another equilibrium position and then we call this as a basically neutral equilibrium because it has assumed a new position right when subjected to disturbances right and we do also experience similar kind of things in our life.

For example you are very much you know happy with your family when you were doing your you know work in your family now you have come over here you are now in a stable position in this institute at this moment right maybe after finishing your course you will go and do a job or some other thing you will have also a good stable neutral position you will get right, yes or no? So this is a neutral position but if you look at come back to this table position when we can call because when you know it will be large disturbances are there then you know it is call it as a stable position right.

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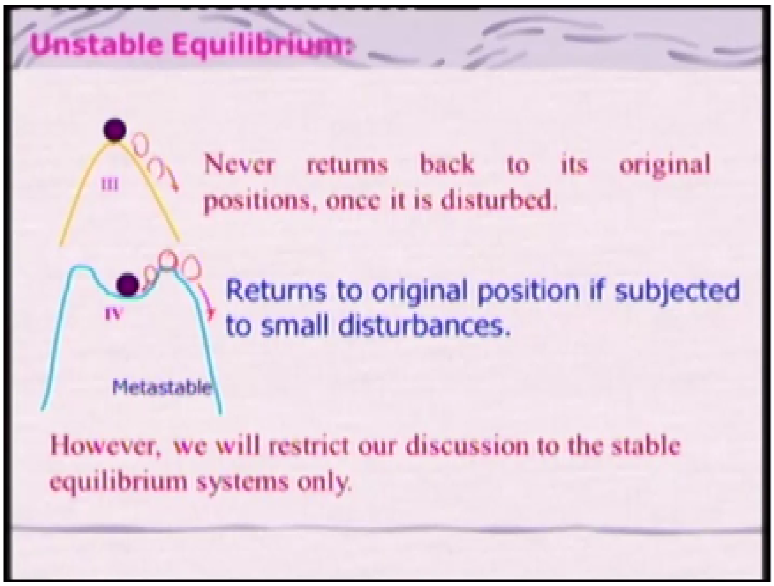

So let us look at the another case where if it is ball is there in this kind of a surface like lets in a mountain or something like that or hill and there is a you know you might have seen sometimes when you are you might have watched a mountain this is a stone which is lying in a very big stone on the top and then you might be thinking why it is not falling down and if it will fall down what will happen you know particularly when you go to the Himalayan region you may find similar things I had a similar you know experience.

I was thinking why if it will fall what will happen so if there is a little bit disturbances here right if there is a little bit distances what will happen the ball will roll down and it would not come back to its original position whatever it is having right so never returns back to its original position once it is disturbed right so that happens you know also with our day-to-day lifestyle now we are waking at it you know irritated for the smaller things right.

And you know like this is a position which should be avoided so let us look at another case like a which is having a what you call if the ball is in this position right and there is a change little bit changes here let us say if the ball is here and then it can return back to the original position but if the ball is the position has been changed to here, what will happen it? It may be little bit stable but however if will go over here it is going down it is becoming similar to the unstable equilibrium kind of things.

That means the if there is a small change it can manage right it can come back to his original position right but if it is subjected to a large change right then it cannot really return back to it's original position that is known as metastable positions if you look at like in a phase change lot of metastable positions do take place like we will be discussing about phase change then we will know particularly you can have you know sub cooled liquid even at a what you call a little higher pressure right.

And there is a also what you call there are several like iron you know like which is will be in cementite or in a metastable that can remain for years together and if you look at your glass you know glass also is in metastable if it is a little bit jerk you know it can break and other things not like toughened glass let other glasses so that will be meta stable and this metastable also we do experience particularly the people who get a very soft you know for example some people get heart attack right you know whenever the shock is very severe.

Due to some reason psychological or emotional or other thing said back you know they may collapse so that is also considered as I mean if they are stable I will in the time but small change they would not bother but if it is a big shock kind of thing will happen in their life they may be emotionally imbalance so that we can call it as a metastable situations, so however we will restrict our discussion to the stable equilibrium systems only and maybe I will be discussing little bit about the metastable when equilibrium when we will be discussing about phase change processes.

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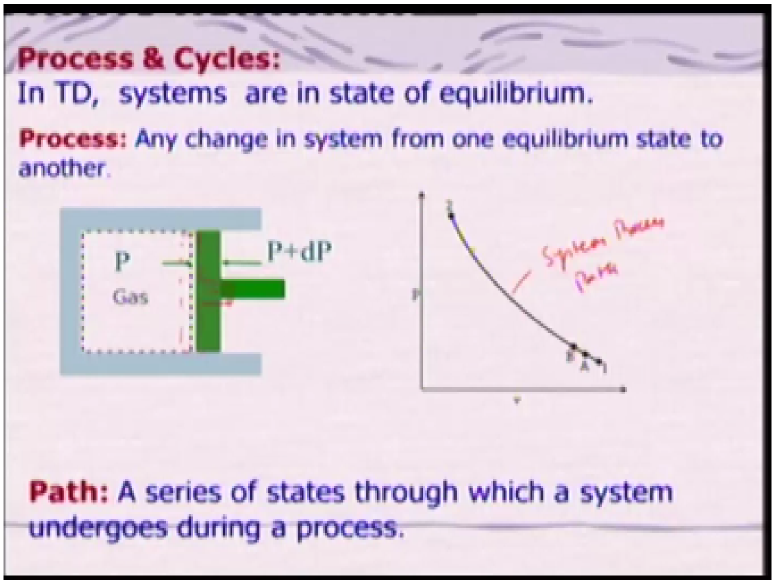

So now let us look at the because we will be looking at the vertical process and cycles in thermodynamic systems because the thermodynamic systems are in the state of equilibrium right and if you look at the process you know is basically will be taken by you know whenever a system is interacting with its surrounding so what will happen it will go from one thermodynamic equilibrium state to another thermodynamic state right.

And then that has to be basically you know state is known as what you call change in the equilibrium position one position to another during you know is known as a process, so let us consider a what you call piston and cylinder and it contains some gas and this we call it as basically system boundary kind of things if there is a small change in pressure what will happen that system will move and attains equilibrium position right.

The piston will move in this way and it will attain a equilibrium position for example let us say that you are at state1 at this point right and suppose you change a position as I told there is a small tiny pressure change and then it is moving then what will happen it will come to the position a and if you go on changing this pressure by a small amount so what will happen this will be you know this gas molecule which will be nearby and you know like you will be try to resist this motion and as a result there will be a you know pressure will be increasing in this point.

Because it is being compressed right and you will attend another state B and you go on attaining these various states as you change this pressure on the other side of the piston so the point you will be moving in this point like that and you attain a state - if I join this each you know position of the system as it goes and that we call it as a path or we call it as a process path that means a series of state through which a system undergoes you know during a process we call it as a what you call system path. This we call it as a systems process path, basically this path is taken during the process.

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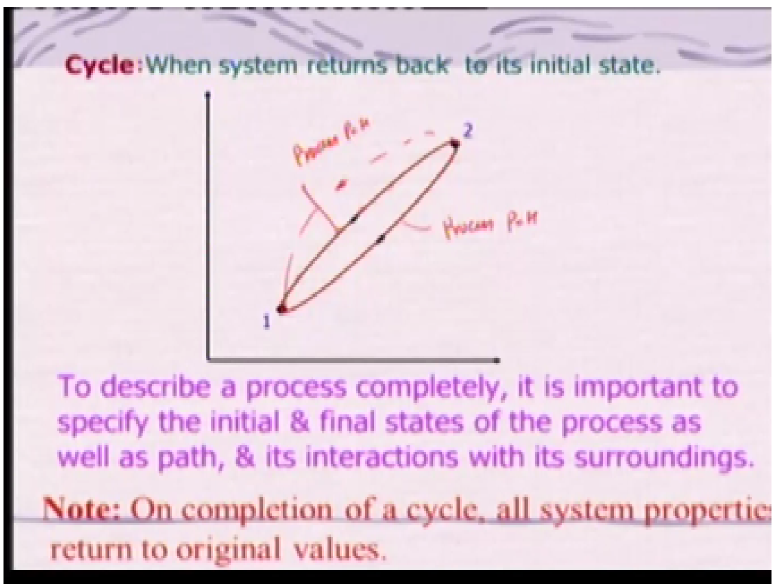

Now let us look at like when a system returns back to its original state let Us say you are here at station 1 and you are moving through this path during the what you call interaction of system with it is surrounding and then you reach a state 2 here and you can return back to this path to the state 1 right to another path or you can return back with the same path or we can take a another path here and come back here.

So this we call it as a cycle in the cycle if you look at that means it will be not depend on the path am I right, it will be it does not depend if it is coming back this cycle right so this is a point and it will be depend on the two state but of course if you look at the work done and other things you know energy interaction will be different for different cycle whatever you do but in case of a path if you want to define a process path this is my process path right one to two and this is another process path.

Now this if I want to define the process path what I need I should know the state1 I should know the state 2 and also I should know the path taken by the system right but where is the cycle we always bother about the two state or between which it will be of course it can take a different path so on a completion of cycle all system properties return to its original value that is the meaning what I was telling that means if it has return back you know following a cycle path the properties you know will be same as that when it was started.

But for this for the process path it need not, so to describe a process completely I am just repeating again it is important to specify the initial state and the final state of the process as the well as the path and its interaction with the surrounding right so this is very important when you describe a process completely right that means what you need you need to know the initial path right and you need to know the final path and also the what you call the path taken by the system during it is interaction with the surrounding one should know. So when in the thermodynamics will be looking at what you call a quasi static or quasi equilibrium process right.

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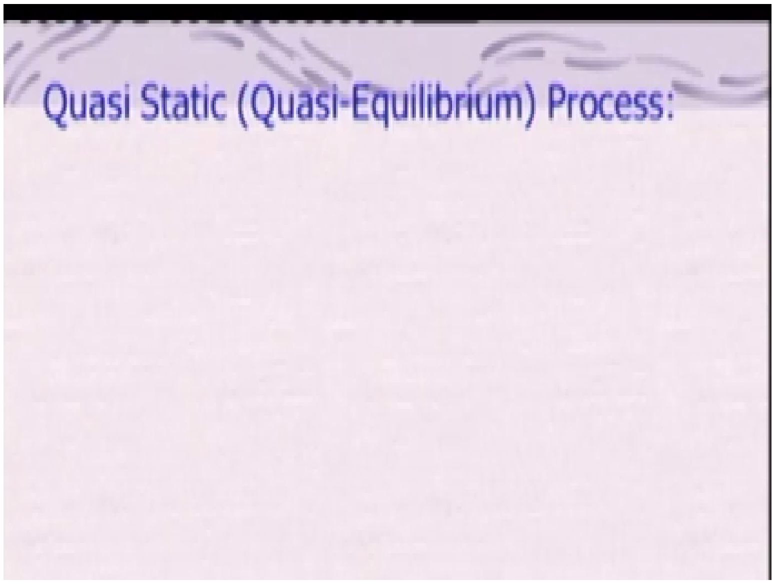

Quasi since you know it will be basically very, very slow manner or the change is not very much high.

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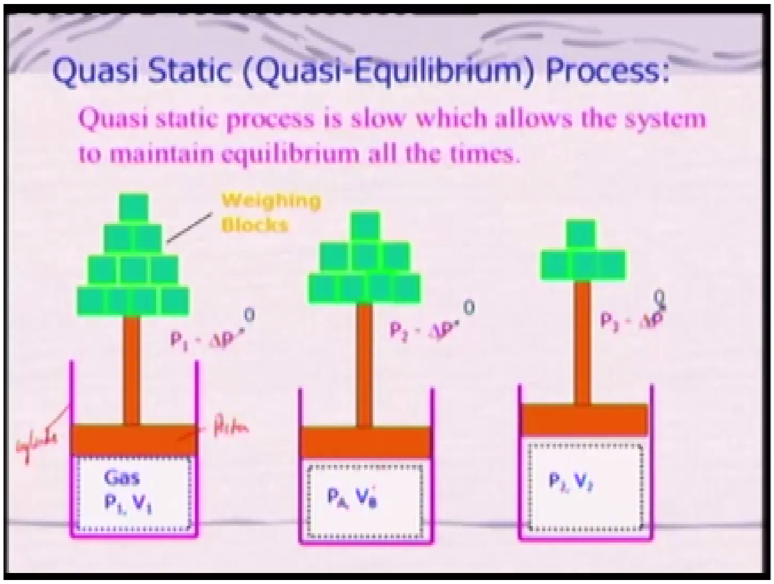

Suppose we will take this example right of our same piston and cylinder arrangement where the gas will be containing in this at a pressure p1and p1right of course there is a lot of weights are here which is being balanced by this gas pressure p1 and it is in equilibrium at the state one right and this you can say that let us say one kilograms of the weight is there let us say and then what I happen I will change you know what you call I will remove from here this weight blocks may be something like 5 grams right.

It is a very, very small as compared to you know1 kilo on kilo means what like 1 kgF force I am array 1 kg into this so and what will happen then of course I am assuming the friction between the cylinder this is my cylinder right and this is piston the friction between piston and cylinder is what is not the zero that means there is no friction between piston and cylinder which is not true in practical situation am I right.

Can you have a piston cylinder without any friction certainly no right but however you can minimize it let us say we are assuming it to be zero then what will happen you know this is a tiny mass which you have removed and as a result the pressure you know will change here that means pressure acting by the weighing blocks will change and there will be little bit increase in the what to call pressure PA and volume will increase okay.

And similarly you remove this another may be tiny block from here and then the it will attain the p2 andv2 where p2 is much lower than the p1you might have gone through several of them which I have not shown here and it has reach a v2or the volume is increasing so if you look at this is happening in a very, very you know small gradient a small differential here as a result that the process is taking place in a slower manner and which allow the system to maintain the equilibrium all the time right.

It is not suddenly like you are giving that means maintaining equilibrium all the time means what that means if there is a change in pressure in the gas of the system that pressure P will be uniform across the all the time in the system right the change is not like here only the pressure will be higher and there is a pressure will be different you know other away from the piston it is not that way so it is uniform all the time and that process is known as quasi static process. And in classical thermodynamics we will be assuming that it is all the time you know is in quasi equilibrium position.

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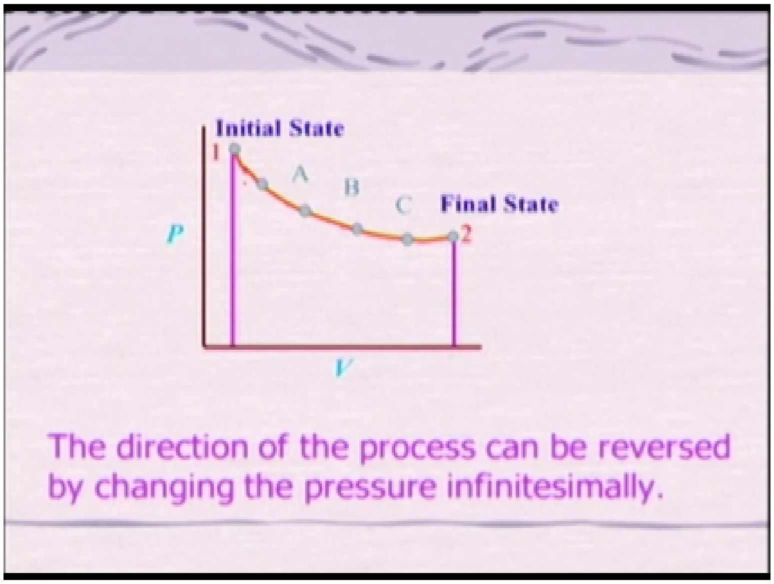

So you might be thinking why we are emphasizing on that right why you were emphasizing that it should be quasi equilibrium because of fact that suppose you were at state 1 and there is a tiny change and then you were coming to state A kind of things right or this position and then if I you know again put back that tiny weight which I had removed then it can go back to the state 1 okay but if it is too much it cannot.

So I mean like kind of things it can happen so and this process is a very, very slow process and we call it you know this thing as a result we can you know change the direction of the process from this to that or from this to that in a slower manner by changing the pressure or changing the you know this thing whatever the gradient is there in this example it is the pressure it may be internal temperature it might win concentration gradient you know depending on that so infinite as very small amount right.

Then a process can be reversible right but let me tell you it is hypothetically situations however you in practical problems would not be it will be friction will be there, there will be you know you cannot have slow process such a slow process you know then people would not look at but however when we are analyzed we can and some of the process can be similar to this it is not same okay so therefore will be in classical thermodynamic will be using the quasi equilibrium concept very often right. Is that clear because this is a very important concept you know which is the backbone of the classical thermodynamic the quasi equilibrium concept okay process, so therefore that means what we are calling a reversible process.

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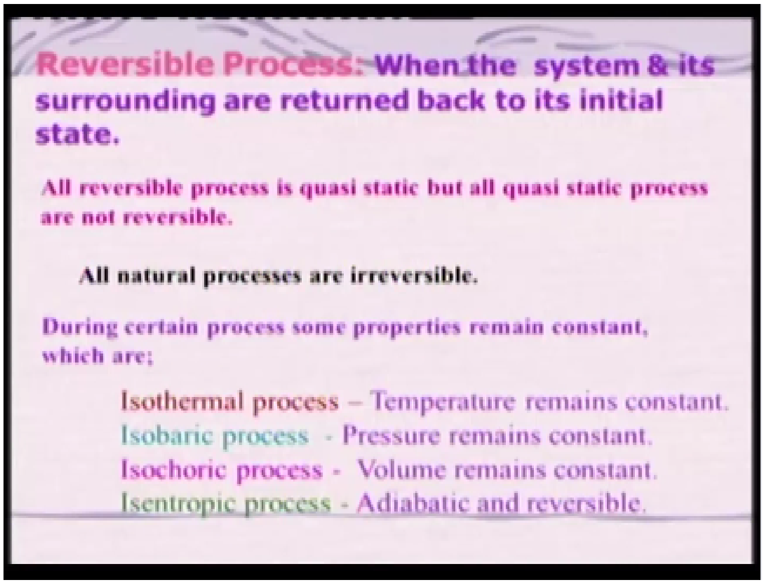

When system and its surrounding return back to its initial State right wherever it was there you know whenever system is the you know interacting with surrounding there will be some change in the system and also in surrounding and if you reverse it back both changes will be nullified you know it will return back to its original position we call it as a reversible process that means the process should be quasi static or quasi equilibrium all the reversible process must be quasi static but all quasi-static process need not to be reversible are you getting this point.

That means you know like it may be a slow process but however if it is not returning back which says original position by changing reversing it says that system and surrounding are not returning back to its initial State we cannot call it as a reversible although the process is slow okay so however all natural processes are irreversible okay, in engineering we try to make as reversible as possible but however it will be impossible to eliminate the what you call frictional so that it can be reversible fully it is not possible right.

And during certain process some properties may remain constant right which will be you know they might be having practical implication also like those properties you know those processes we can define in different ways which you know you might be aware if the temperature is remaining constant what we call that process isothermal a pressure rebounding constant we call it as a isobaric process if the volume remaining constant then we call it as a isochoric process and if it is adiabatic that means there is no heat transfer between system and surrounding.

And also it is reversible right then we call it as an isentropic process right, so these are the processes which will be discussing very often now and often and we will be using this processes by mimicking the natural processes or in actual cycles what will be will be idealizing and then doing that of course in some situation it may mimic the constant pressure process right or isothermal process kind of things so I will stop over here right and then we will continue in the next lecture.

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