Basic Thermodynamics

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Lecture - 02

Zeroeth Law and Fundamental Concepts

Good morning I welcome you to the session of basic thermodynamics what we are discussing last class is the thermodynamic equilibrium of a system just to again repeat it.

For a system to be in thermodynamic equilibrium the property should remain invariant with time and that should be uniform within the system. This can be done by two ways either by allowing the system boundary to be such that system cannot interact with the surrounding. Another way of obtaining this that when the system properties are same as those of surroundings that means there is no imbalance between the properties of the system and the surrounding. To meet this thermodynamic equilibrium of a system three types of equilibrium are necessary these are like this.

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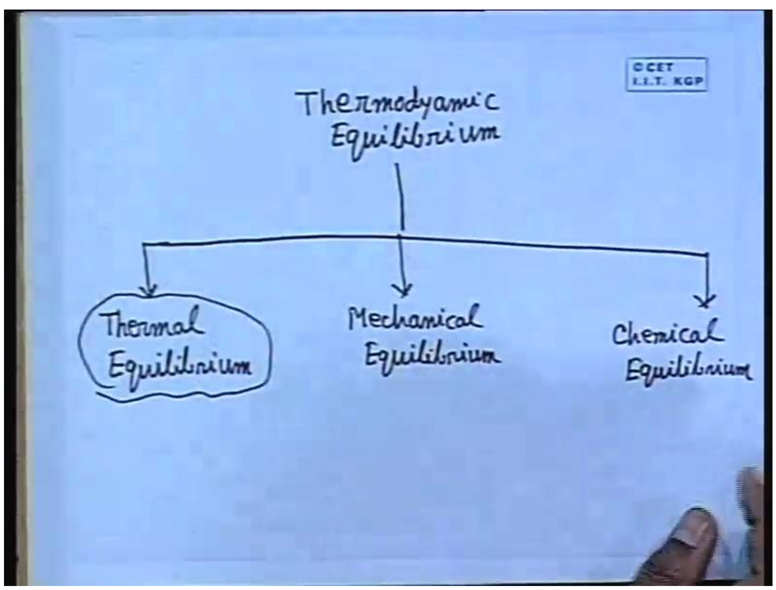

If we write thermodynamic equilibrium, it has got three types of equilibrium, one is thermal equilibrium another is mechanical equilibrium another is chemical equilibrium. These three equilibriums have to be maintained simultaneously to have thermodynamic equilibrium. Let us first discuss on thermal equilibrium. Regarding thermal equilibrium there are three issues which come into picture.

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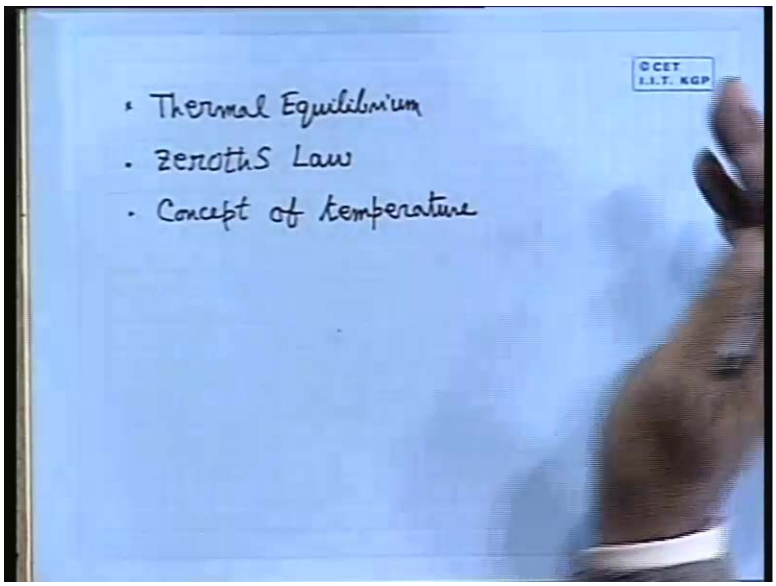

One is thermal equilibrium, what is thermal equilibrium? In this context very important law of classical thermodynamics is zeroths law and the concept of temperature. It is the thermal equilibrium and zeroths law which defines the temperature. Today, we know the concept of temperature. What is temperature if I ask you today that you can tell there are two ways of defining temperature? One is the microscopic way of defining, it is the average kinetic energy of the molecules that gives rise to the temperature of a body and this kinetic energy mostly composed of the translational kinetic energy. But if you define temperature from the classical physics point of view or classical thermodynamic point of view today we know the definition is very simple. It is the property of the system. By virtue of the difference of this property heat flows from a system of higher temperature to a system of lower temperature.

This is the definition of temperature which we can sense, we can measure property and the difference of which is responsible for heat to flow. Again we define heat as that form of energy which flows because of the temperature difference from one system to other. What is thermal equilibrium this is also very simple we know we have read it earlier also? Thermal Equilibrium is the equilibrium relating to the flow of heat that means if the two bodies are in contact so that heat can flow between these two.

So thermal equilibrium can only be achieved if their temperatures are equal that means no heat will flow, so thermal equilibrium means the equilibrium of temperature. All these things are known today. Off-course zeroeth law is the different way of expressing these two but we now discuss how these things originated in the classical physics at the being though we know these thing there is nothing new that what is temperature we know thermal equilibrium means the two system have to be at the same temperature.

So that they are in thermal equilibrium no heat will flow. But how this concept originated let us discuss that, the concept of thermal equilibrium and from which zeroeth law evolve and finally we arrived at a definition of temperature in classical thermodynamics. This is same definition how it was there I

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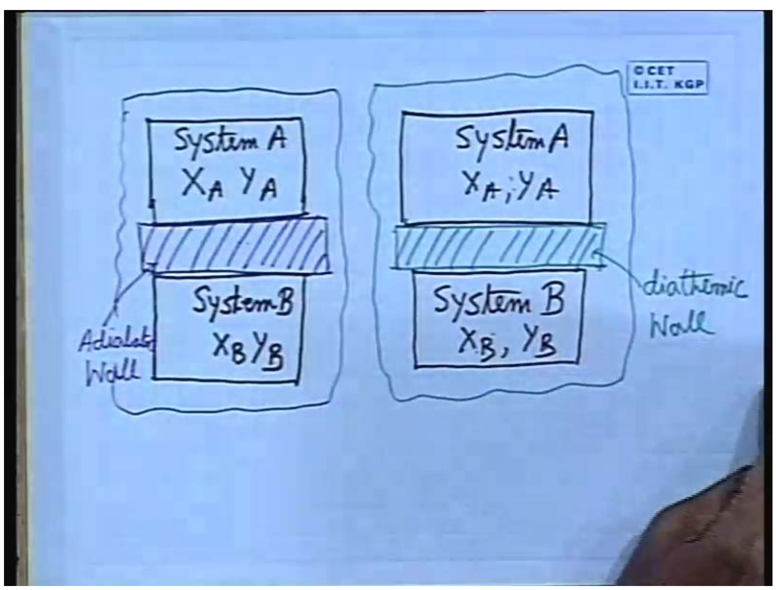

We will first discuss the concept of thermal equilibrium the way it originated in the classical physics this is important in studying thermodynamic to discuss this. Let us consider the two systems, one is system A and let us consider this system that it can be characterized by two independent intensive properties that mean the single component single phase system X_A and Y_A.

Let us consider another system which can be defined by any two such independent properties to define its states that is X_B and Y_B and let us connect these two systems by an adiabatic wall, what is adiabatic wall?. That is no heat can flow. All the terminologies are known today but it is true that this is known today but the way it originated in the classical physics I will describe that adiabatic wall. What is an adiabatic wall? The adiabatic wall is a wall which will be sufficiently strong to resist any stress developed because of the imbalance of the properties between system A and system B and it is a kind of wall in practice made of wood, felt, asbestos because originally it was conceived like that the experiments were done like that. Then people came in to the definition of adiabatic process? What is the adiabaticness? What is the diabaticness? All these things come afterwards. Initially it originated.

Let us have a boundary of that sort wood, felt, asbestos which does not allow the heat to flow and it is sufficiently strong to withstand the stresses developed because of the imbalance of the properties. This type of wall is adiabatic wall. If you separate them by adiabatic wall it has been found that now if entire thing is isolated from the surrounding then it has been observed that if number of combinations of X_A Y_A and X_B Y_B are available that means system A can assume any pairs of its X_A Y_A or any arbitrary values of X_A Y_A. Similarly any arbitrary values of X_B Y_B for system B they can assume any properties. So any values of X_A Y_A and X_B Y_B are available if they are separated by an adiabatic wall.

If the same two systems, system A with the same X_A Y_A and the system B with X_B Y_B they are available and they are separated by a metallic wall which are good conductor of heat for example. That is known as diathermic wall. If they are insulated from the surroundings, then it has been found that some process will take place by virtue of which X_A Y_A and X_B Y_B will change and the equilibrium will be attained by the two systems only certain restricted values of X_A Y_A and X_B Y_B that means we cannot have arbitrarily all possible value of X_A Y_A X_B Y_B like this.

Some restricted values of X_A Y_A and X_B Y_B will be possible so that no further change will take place between the two systems if they are separated by a diathermic wall this is the classical concept of thermal equilibrium. That means this gives rise to the definition of thermal equilibrium. Then the definition of thermal equilibrium comes in this way. This gives rise to the definition of thermal equilibrium which can be written now this way.

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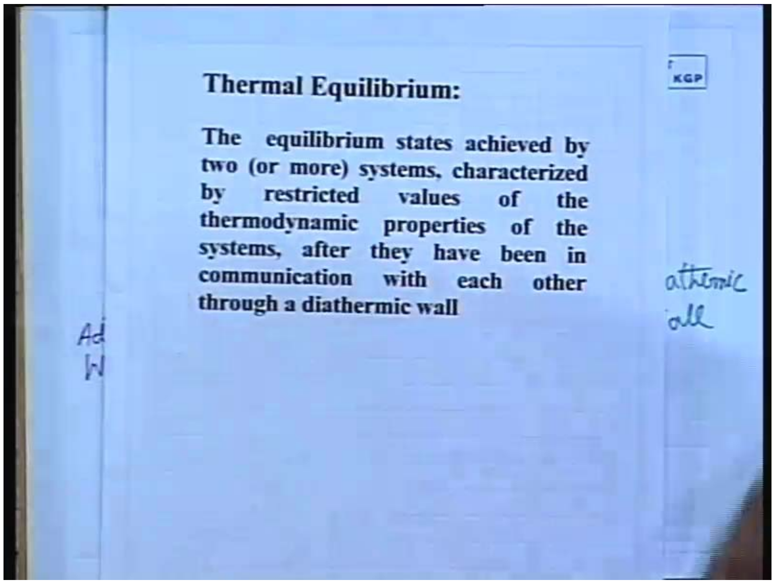

This is the original definition in the classical physics of thermodynamics the thermal equilibrium.

The equilibrium states achieved by two or more systems, characterized by restricted values of the thermodynamic properties of the systems, after they have been in communication with each other through a diathermic wall. This is an equilibrium state of a system between the systems which they achieve with restricted values of thermodynamic coordinates so in they are in contact by a diathermic wall that means all arbitrary values are not possible that is the concept of thermal equilibrium.

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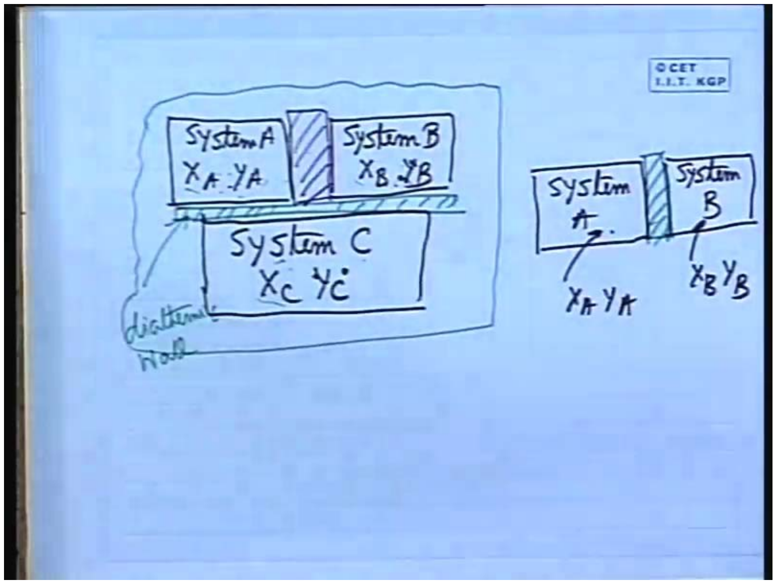

If we go little further what we will see now this experiment was made like this if there are two systems, system A with similarly X_A Y_A properties, system B with properties X_B Y_B. They are separated by an adiabatic wall. Let us consider a separate system C with properties designated by X_C Y_C all these systems are conceived for simplicity in understanding that they are specified by two independent properties and if they are separated that means system A and B are in communication with system C through diathermic wall.

That means this wall is diathermic wall already I have shown by this color diathermic wall, while this is adiabatic wall and everything is insulated that means if system A or B in communication by adiabatic wall and system A and B with C are in communication with diathermic wall then what happens that X_A Y_A and X_B Y_B changes as X_C Y_C change. That means this properties change X_C Y_C because of the interaction with system A and system B and system A and system B the properties also change and they attain some restricted values. For examples at some equilibrium we get some properties X_A Y_A some property values X_B Y_B for system B and X_C Y_C for system C.

If we remove this and put these two systems after achieving this equilibrium system A and system B then we will see that by a diathermic wall then what we will see that the system property that means the property X_A Y_A and X_B Y_B will not change. That means when they are in thermal equilibrium what I will not use here that means when they come to equilibrium with system C by a diathermic wall both system A and system B separately and individually then their properties will come to a uniform and invariant values they need they are in communication with each other by a diathermic wall their system does not change.

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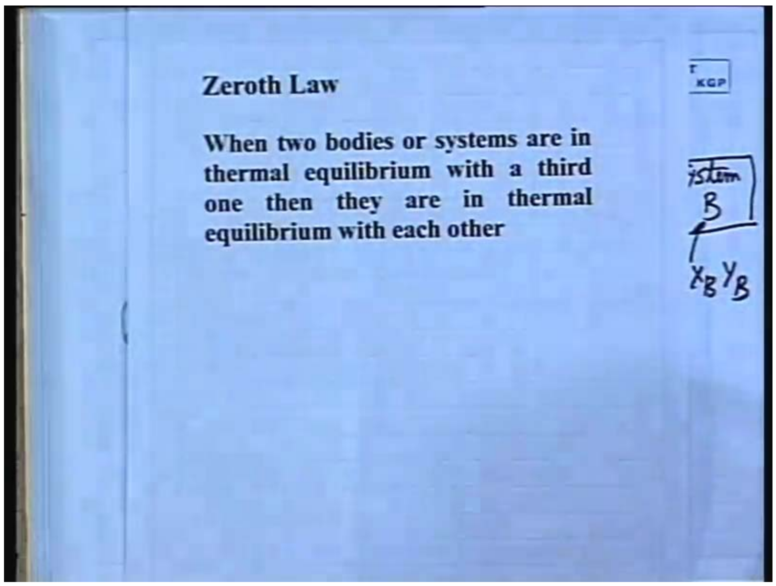

This gives rise to the definition of zeroeth law. This phenomenon is known as zeroth law of thermodynamics which is very important in classical thermodynamics which gives the definition of temperature. What is zeroeth law? When two bodies or systems are in thermal equilibrium with a third one then they are in thermal equilibrium with each other.

Today this is very known fact if you tell this to school boys at class seven eight level then they will tell this is known fact. But this is the way how it originated in the classical physics. We have to go through this origin so this is the basically zeroeth law.

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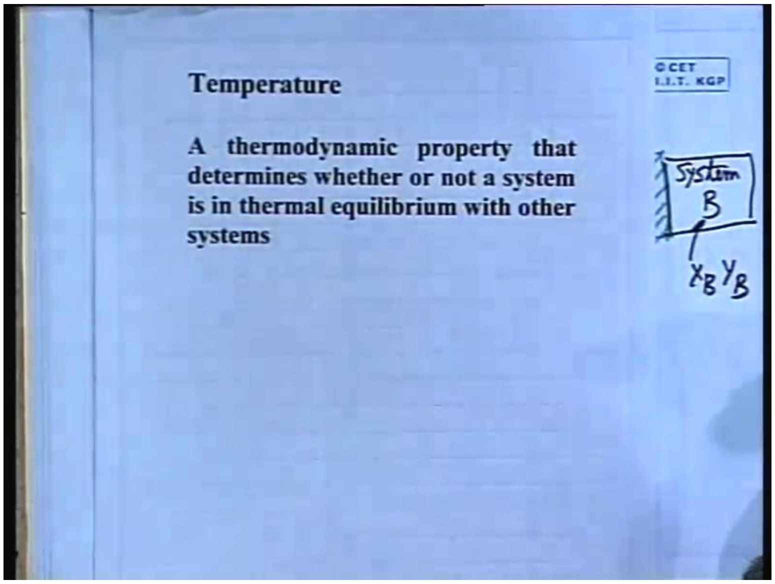

The concepts of these two things that the thermal equilibrium and zeroeth law gives rise to the definition of temperature in classical thermodynamics. If one ask you what is the definition of temperature in classical thermodynamics, how do you define? The temperature has to be defined without the definition of heat without going to the molecular level that it is not the average kinetic energy of the molecules then how do you define? That is giving by the classical thermodynamics. Afterwards we will define heat with the help of temperature as the property. Therefore without taking the concept of heat or without consideration of the molecular events we define temperature by zeroeth law in classical thermodynamics like this. It is a thermodynamic property that determines whether or not a system is in thermal equilibrium with other system. This is in short the concept of the thermal equilibrium.

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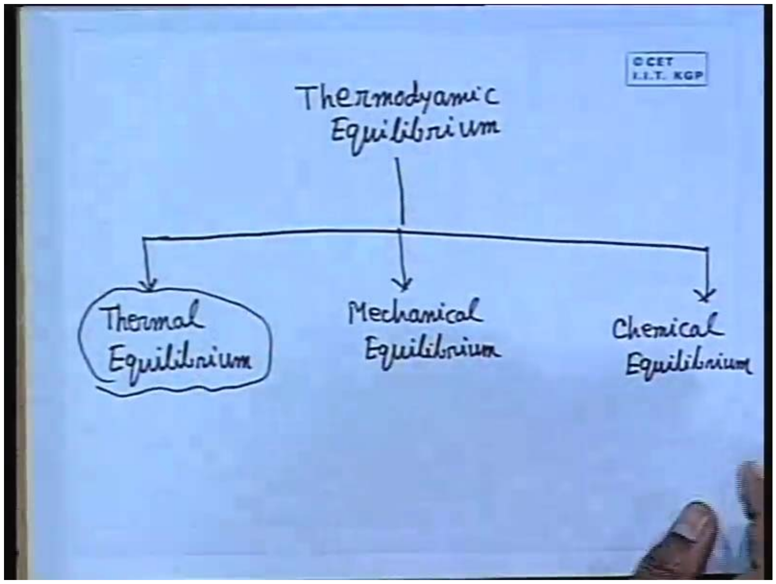

We come back to this thing that a system to be in thermodynamic equilibrium it has to fulfill the three equilibriums; thermal equilibrium, the mechanical equilibrium and chemical equilibrium.

Thermal equilibrium is the equilibrium of temperature that means when the temperature as same between two bodies there will be thermal equilibrium.

What is mechanical equilibrium? Mechanical equilibrium is the equilibrium with respect to work transfer between the system and the surrounding that means when there will be no imbalance of properties any properties that will cause work transfer. For example mechanical work transfer there has to be an imbalance in the pressure between the system and the surrounding. In terms of one of the primitive properties pressure, sometimes many books tell like that that if there is no imbalance between the pressure of the system and the surrounding the system attends the mechanical equilibrium.

Mechanical equilibrium in a broader aspect is the equilibrium when system does not go with any process involving work transfer but in a limited sense we can tell is a mechanical work transfer this is only responsible if there is the disbalance of pressure between the system and the surrounding. So there is no disbalance of pressure between the system and the surrounding then there is no question of mechanical disequilibrium that means the system is in mechanical equilibrium.

Another is the chemical equilibrium. Now you see all these non equilibrium is responsible for change of certain class of properties when there is no thermal equilibrium the property temperature goes on change. An equilibrium criterion is that all property should be invariant with time. Similarly for mechanical disequilibrium some other some properties will change that is pressure will change, volume will change some other associated properties also will change. This is sensed basically through the change in these properties automatically other properties will change because they are related depending upon the process constants that i will come afterwards.

Similarly chemical equilibrium is the equilibrium of the system with respect to chemical reactions and mass transfer that means if there is no disequilibrium between the system and the surrounding by which the chemical reactions or mass transfers do not take place then the system is in chemical equilibrium. That means a system has to be in chemical equilibrium it should not go for any process involving transfer of masses and the chemical reactions which causes the species density you see the multi component system.

The species amount or the masses of species to change with time they should not be invariant with time. That means chemical equilibrium is responsible for these changes that means for chemical equilibrium to be attain a system and surrounding has to be in equilibrium with respect to certain gradients. What is that gradients? That is the concentration gradients. That is the chemical affinity, the gradients of chemical affinity these are the things which causes the mass transfer and the chemical reaction to take place.

Similarly again I repeat for mechanical equilibrium pressure gradient has to be 0 and the gradients of other quantities which are responsible for other types of work transfer also that I will come afterward should be 0. Similarly for thermal equilibrium temperature gradient has to be 0 between the system and the surrounding. If all these things are met at a time then the system attains simultaneously thermal equilibrium, mechanical equilibrium and chemical equilibrium and as the whole the system attains thermodynamic equilibrium. This is the basic concept of thermodynamic equilibrium.

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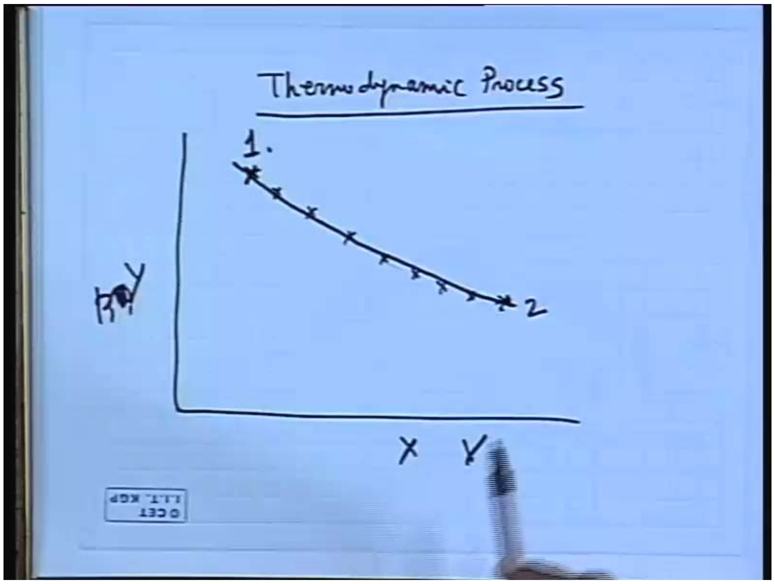

After this I go to the concept of thermodynamic process which is very important. Thermodynamic process Is a simple process that when a system interacts with surrounding. First of all define a system at an equilibrium state when a system interacts with the surrounding a process takes place how does it interact with the surrounding in terms of energy transfer also mass transfer may take place if the system is not a closed one then after some time it comes to another equilibrium state. So from one equilibrium state to other equilibrium states system comes through a natural process interacting with the surroundings.

Now question is very important in this regard process is very simple everybody knows that how to specify the process in thermodynamic coordinate diagram. That means for a example you see that if I express the system by two coordinate Y and X let pressure and volume here. Let this be the state one initial state and system is allowed to interact with the surrounding in forms of mass energy whatever may be very general open system and after sometime system comes again to an equilibrium condition. If we give infinite time the system will always come to an equilibrium condition when the properties will be same as that of the surrounding it will come to a dead state but sometimes we forcefully stop this process so that we forcefully make this system at another final equilibrium state let this is two.

We can tell the system has changed from state one to state two by a process but to specify that process in the thermodynamic coordinate by a continuous line then what we will have to do we will have to define the intermediate states the succession of intermediate state through which the system has passed so that we can define the process as a continuous line on a thermodynamic coordinate diagram. How to do it? Because if we tell that this is one of the intermediate point this is one of the intermediate point that means these points we can show only if the system is in equilibrium at that state but when a system natural process occurs from one state to other state system is in dynamic equilibrium system is not in thermodynamic equilibrium. All the processes are non equilibrium in nature means the properties are varying with time and also properties may not be uniform within the system. Therefore a natural process can never be shown by such a specified path.

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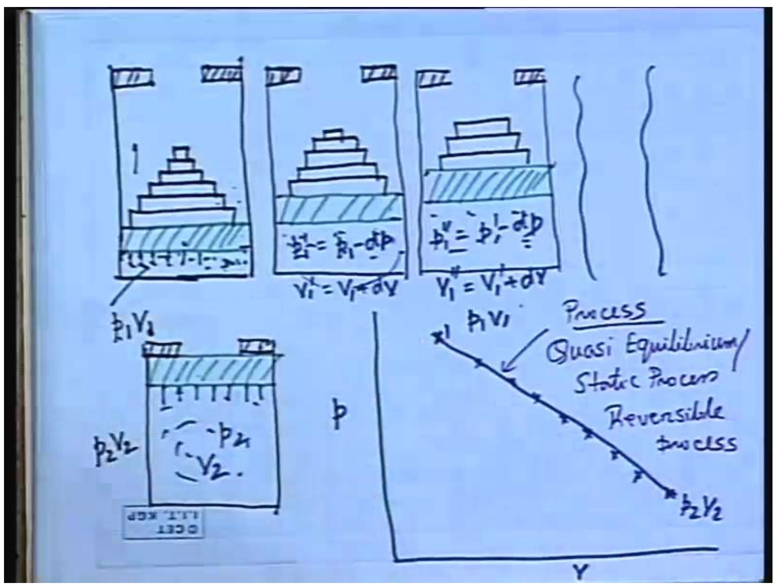

To understand this let us go to this. Let us see a arrangement like this. Any difficulty you now ask me. This is very important concept. Let us consider a cylinder in practical case and a piston and a and let us consider the piston is loaded with some weights which are divided. You have read all those things earlier any confusion is there you please ask me sir this is my confusion number of weights.

Let us consider that there is some gas within the cylinder and consider this gas as a system. This gases exert some pressure and at the initial state let us consider the weight of the piston along with the external weights balance this pressure p. Let this pressure is p_1 and initial volume is v_1 the system is at state one. Let us consider there are two stops which allows the piston not to go beyond this. Now what happens? This is a system at equilibrium state which is specified by its pressure p_1 and volume v_1 how it is in equilibrium? Now this pressure p_1 exerted on the piston balances the piston weight and the external weights, P one into the pressure force.

So that this is in equilibrium the gas has a fixed volume, fixed pressure and along with that other properties are fixed if it is a system where two properties are required to fix its states. Practically if we now release all the weights simultaneously or a considerable portion of the weight from the top what will happen there will be a pressure imbalance between the gas and the surrounding. So piston will move upward piston will move upward and it will heat the stop and ultimately it will come here. If we finally make this just remove this what will happen the piston will come here and at that time an equilibrium state will be achieved with the gases inside and let this gas pressure will be p_2 and in that case what will happen this pressure will balance the piston weight and the reaction of the stop.

Practically what will happen there will be some oscillations here and ultimately it will be fitted like this so the reaction and the weight will be balanced by this p_2 and let the volume is v_2. So the final state will be p_2v_2. We know the initial state and final state now while going so very fast the piston will move any intermediate state if you want to observe by any instrument measuring pressure, temperature other things you will see they are not only varying with time they may not be uniform also throughout that is very first process because we want to make it very fast.

We keep a high imbalance in the pressure remove all the weights then it will come to it and practically all natural processes are like that but instead if we conceive a process like this which is infinitely slow like this instead of releasing the weight one by one if we do like this we release the weight like this, instead of doing this if i take a small weight out that means we create a very small amount of pressure imbalance. So that the in that case the piston will move very slowly and come to a equilibrium position like this that means there is weight we remove only this one stop is there as usual.

This gas is there and this pressure let it is p_1 dash which is equal to p_1-dp pressure is reduced by this and v_1 dash which is equal to v_1+dv. Piston has moved a infinite small distance because the imbalance is very small and if this way we remove the weights let us consider another picture that we have removed another weight slowly if we think in terms of infinite resolution of the weights and go on reducing the weights like this and piston will be ultimately coming to this position slowly and in that case the third position is that this is v_1 double dash it is p_1 dash minus dp similarly v_1 double dash is v_1 dash plus dv.

Slowly and gradually if we remove the weight in such a way that all the time we restrict the piston to move infinite small distance, under a infinite small imbalance of the pressure. Piston comes from an initial pressure p_1 and volume v_1 to an intermediate pressure which is slightly less than p_1 volume is slightly more than v_1 and then again slowly if we remove and if we do like that after a long time if you do it with infinite resolution of this weight the piston will come here and if we do this then what are the differences then all the intermediate state points are almost equilibrium.

They are in the limit of thermodynamic equilibrium. To conceive it in an ideal case to be exact thermodynamic equilibrium we have to stop the process. That is just like consider the walking of an old man he walks certain distance small distance then he stops again walk stops the small man with the heart disease walks this is a very good example he stops walks and so then all that means he covers the distance in such a way that infinite small distance he travels and then it comes to an equilibrium state everything within the system becomes uniform and invariant with that. But even if you do not stop if you do it continuously and gradually removing this weight then in all the succession states we can think of a sort of equilibrium in the limit equilibrium process.

In this case what happen that if you now pv that this is your state one p_1v_1 then all the states if you come like this you can specify by process then let this is your p_2v_2 and all these succession states you can specify and you can join this as a single curve and you can specify the process that means this is the thermodynamic processes.

The process can be specified provided the intermediate succession states are in equilibrium. This type of process is known as quasi equilibrium quasi static process, quasi means almost. I will discuss that length this thing reversible at the present movement you just write it that it is known as a reversible process the concept of reversible process we will come afterward.

One of the criteria for reversible process is the quasi equilibrium process. This process is quasi equilibrium or quasi static that means almost static process that means process is almost static infinite small departure then again rise but even if we it is done continuously this gap this means this continuous there is the infinite one in finite infinite number of small elemental process is we conceive.

So that system departs from one state and goes to the other state only under an infinite small imbalance of the properties between the system and the surrounding. In this way this system moves. In this case what will happen infinite long time will be required for a system to come from one equilibrium state to other equilibrium state? This way only we can specify a process. Very important thing at this moment we must know that whenever we specify a thermodynamic process performed by a system in thermodynamic coordinate diagram we always consider the system the process is a quasi equilibrium or quasi static or a reversible process.

Next I will go quickly time is short for this today's class which I have thought that I will complete this thing.

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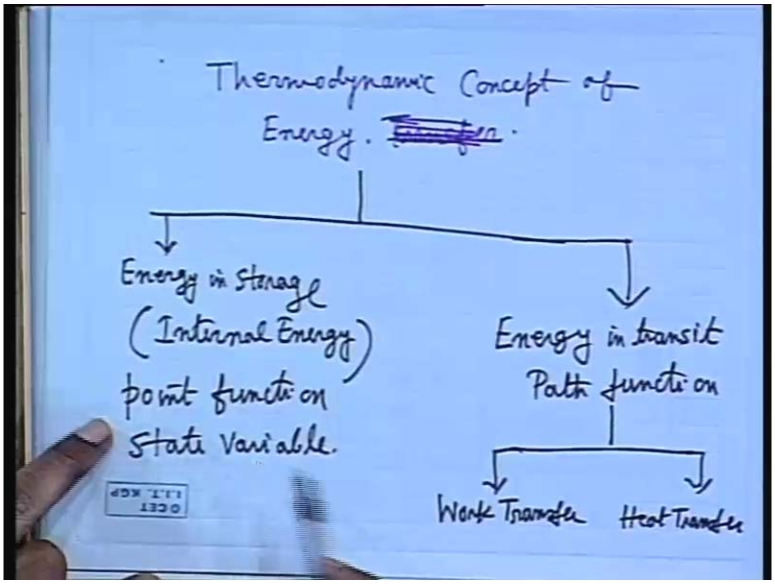

The thermodynamic concept of energy transfer let me write thermodynamic concept of energy transfer. This is very important. In thermodynamics the concept of energy transfer knows thermodynamic concept of energy rather you cut the transfer thermodynamics concept of energy.

In thermodynamics energy has been given two status that I will tell you in first law. One is the energy as a state variable property of a system, energy as a point function another is energy as a path function two forms of energy one is energy in storage that is system can store energy for an example let us see that a mass of gas at high temperature what do you tell that gas is storing the gas at the system storing what type of energy because of its temperature internal energy. Internal energy stored in the gas you consider a fuel sometimes we tell the chemical energy of the fuel which can be converted into heat by burning then that heat can be converted into mechanical work but always we tell that chemical energy that is the bonding energy of the molecules.

There are various ways a system can store energy by virtue of its temperature that internal energy that is more precise the intermolecular energy chemical energy another thing is that mass of gas is there you start the gas you creates the motions of the microscopic particles. Then we consider the gas as a system then we can tell because of the motion of the particles the system stores some energy which is the kinetic energy of its particles another form of energy is the potential energy.

What is the definition of potential energy that means if you place a system in a conservative force field because of its position in a conservative force field a system's energy stored in the system because non dissipative work is done to place the in a conservative force field that is stored in the system as an energy always we tell that for example gravitational potential energy in the gravitational field of what always we have some energy stored within us because of which we can shift our self from one position to other. These are the energy that you are acquainted with or the energies which can be stored in a system.

So thermodynamics tells this energy all together as an internal energy of a system that is system which has these stored energy internal within it and that is the point function or state variables. Another energy comes in to picture these are not stored within a system these are energy transfer that means these cannot be conceived when a system is in equilibrium state. This can be conceived only in the form of transit when there is a process takes place. These types of energies are classified into two groups. Work transfer and heat transfer no other groups.

Therefore now I can write the thermodynamic concept of energy is that one is energy in storage very important this thing i am telling one is energy in storage which is known as internal energy in general though we mean by internal energy colloquially intermolecular energy by virtue of temperature not that all form of energy which is stored internally within system. This is a point function because I know that internal energy is a property state variable that means this is associated with the state of the system another form of energy is energy in transit which is the energy which is transferred between a system and the surrounding.

These are path functions and these energy in transit or energy transfer again can be divided into two groups one is work transfer another is heat transfer. I have given the examples of energy in storage internal energy of a system point function or state variables. Energy in transit only comes into play when two systems are interacting with each other or systems surrounding interacting with each other.

One form of this energy in transit is heat that is the energy in transit by virtue of a temperature difference and flows in the direction of the negative temperature gradient means high temperature to low temperature. And all other form of energy transfers is all work transfer. Usually mechanical engineers will be little bias to tell work means mechanical work it is f dot ds no all other form of energy transfer it may be an electrical energy transfer.

If you put a voltage across a resistor which allows a current to flow an electrical energy is being transferred to the resistor as a system that is work transfer. But we use an adjective to separate it from different categories of work transfer. That is another adjective is used mechanical work transfer, electrical work transfer, magnetic work transfer you understand? But all are coming under the category of work transfer only heat is the different category of transfer which takes place by virtue of the temperature difference. These are the two different concept of energy in thermodynamics one is the energy in storage another is the energy in transit that is the path function.

We see that there are different form of time is up what is the time five minutes left five minutes left. So think today we are late I will stop here today just I will ask you that if you have any queries you can ask questions only because I will always give five minutes time for questions I will be happy to answer your questions from whatever I have taught today of course a very less amount of things had been told today please.

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That is a very simple thing why natural processes cannot be specified by path? Because to specify a path of the process in thermodynamic coordinate how can you specify a path or specify a continuous curve? If you have got intermediate points so you understand because to specify a path how do you draw a curve very simple thing go back to school level class five six level geometry that to draw a curve you know you have to know the number of points you do not know the equations before hence. So numbers of points have to be joined that means the number of state points have to be known.

So whenever a state point is specified in thermodynamic coordinate the thermodynamic system has to be in equilibrium. How do you specify the system pressure or system. One example, any two properties x and y. If you have to show an intermediate points with x and y for the thermodynamic system for any natural process in any intermediate state this x and y are not constant within the system.

You cannot specify at the beginning I told that if you tell. My intermediate points is having this pressure and this volume but unfortunately if you measure continuously the pressure and volume for an example in a natural process where a gas expands we will see even the pressure equilibrium is not there internally within the gas. How can we specify the gas by a single pressure or a single temperature moreover they are invariant with that because the two things are clubbed a non equilibrium states where the system changes rapidly and continuously with time there is no equilibrium within the system itself.

So it does not attain a uniform value of the pressure. Therefore to specify any intermediate points to draw the curve we require that particular criterion of equilibrium that should be uniform within the system and momentarily invariant with time. That is why all processes are natural processes cannot be specified by a path only it can be done if the process is quasi equilibrium.

Thank you.