Thermal Physics
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Lecture - 31
Basic Concept of Classical Thermodynamics

Hello and welcome back to this NPTEL course on thermal physics. Today, we are going to start week 7 of this course. Now, in the previous weeks, we started from this kinetic theory of gas, which is a microscopic theory. And we have found out that macroscopic parameters like pressure and temperature can be realized in terms of the microscopic parameters. Similarly, in the next section we have looked into the transport properties like viscosity and conductivity, thermal conductivity and diffusion.

And we have seen that the microscopically microscopic parameters like molecular mass, molecular mean velocity, this can lead us even surely to the macroscopically measured parameters like coefficient, coefficient of viscosity coefficient of diffusion and thermal conductivity of a fluid. Now, we have talked about ideal gas in the first phase and eventually we looked into the non-ideal gas. And we have introduced different equations of states.

Primary focus was on Van der Waals equation of state and we have seen that we can actually the, so called real guests behavior is only realized over limited pressure and volume and temperature regime. Now, when we were discussing real gases, please remember we have not discussed much about the microscopic properties of the gas anymore. Although the origin of this Van der Waals was constant A and B it has a microscopic origin, what I meant to say.

And then we have discussed about the origin of in the temperature measurement and zeroth law of thermosdynamics. Now, this week onwards, we are going into the domain of classical thermodynamics. Now, in classical thermodynamics, everything is macroscopic in nature. So, we do not talk about the molecular assembly anymore. Of course, towards the end of this discussion like course, we will cover certain topics called chemical potential, which once again we are taking us back to the microscopic level.

But for now, the majority part of the remaining of the course will be talking about macroscopic properties macroscopic systems. So, in the discussion of classical thermodynamics, it is important to understand few definitions before we can start. And so, in today's lecture, it will be primarily on the fundamentals of classical thermodynamics and we will talk about different definitions, we will talk about differences.

I mean what is the system, what are the surroundings, we will talk about the different processes parameters etcetera. So, without delay let us begin.

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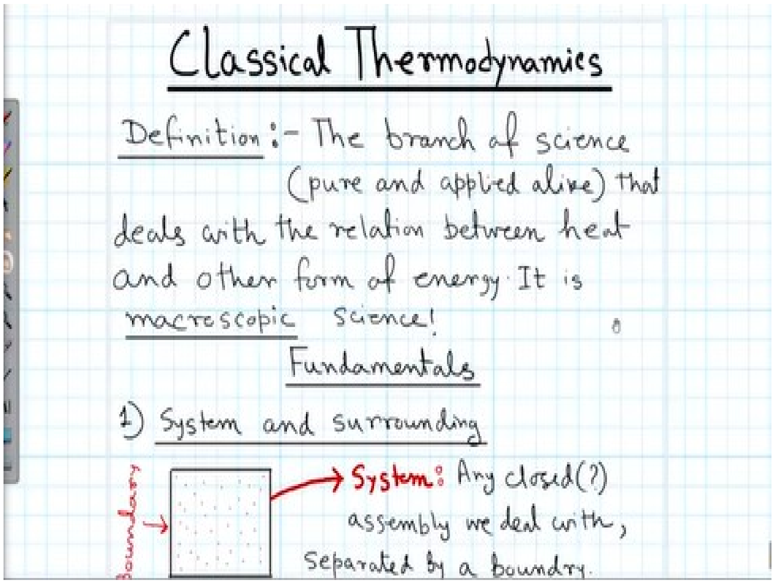

Classical Thermodynamics

Definition :- The branch of science (pure and applied alike) that deals with the relation between heat and other form of energy. It is macroscopic science!

Fundamentals

1) System and surrounding

System: Any closed(?) assembly we deal with, separated by a boundry.

So, the first definition is of thermodynamics itself. The term thermodynamics it means, the branch of science, which is both pure and applied that deals with the relation between heat and other forms of energy it is macroscopic science. Once again I am pressing on the fact that this is macroscopic science not microscopic anymore. I mean it can be made microscopic as I have already described.

You know, we can look into the chemical potential of the system but that comes on a later phase. Initial first few centuries of development, first 200 years of development of classical thermodynamics, it is primarily macroscopic because the concept of molecule, concept of atom was not accepted at that time. Not that it was unheard of people knew about it, some people speculated about it.

But it was not well accepted until early 20th century, when the atom model was beyond doubt, it was established. And we have discussed about Perrin's ground breaking work on Brownian diffusion, which actually helped a lot in establishing the atomic model, either in the presence of atoms and molecules anyway. So, now in this case when we say that it is a branch of science, it means pure science and applied science alike.

Although thermodynamics to begin with started off as a pure science as a branch of physics, but later it was found out that not only physicist but chemists lot use thermodynamics the concept of thermodynamics a lot. Later on, when with the development of statistical thermodynamics, the mathematicians took over. So, there is a whole lot of contribution from pure mathematicians in the runs, of course, the theoretical development of statistical thermodynamics I am talking about.

And although thermodynamics started off as a branch of pure science, it turns out that most of the engineering application needs a knowledge of thermodynamics. So, now nowadays, not only pure science students, but also the students of all core engineering branches like forget about I am not talking about very specialized branches where you know, which does not come under the core engineering branch.

But core engineering like chemical, mechanical, even computer science and civil they need to study currently nervous in detail. So, let us go into some more fundamentals of this classical thermodynamics. So, one very important concept to begin with is what is meant by a system and what is meant by the surroundings. Many times, we talk about thermodynamics and we start with the sentence that let there, be a thermodynamic system.

Now, what is the system exactly, the system is we can define a system as any closed of course, I have put a question mark here, I will tell you why this question mark is after some time, any closed assembly we deal with separated by a bounded. So, in a system it is mandatory to have a boundary. So, I have just depicted a very familiar system of gases, I am not talking about ideal gas anymore, it could be ideal, it could be real, whatever, it is the gas.

So, we have a box full of gas molecule. So, the wall of this box works as a boundary and this whole thing is our system. Now then, if this is system then what is surrounding.

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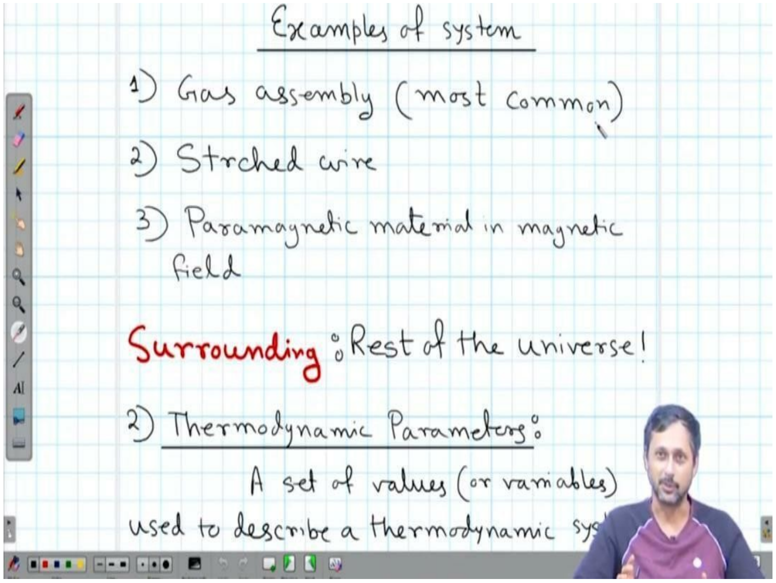

Examples of system

1) Gas assembly (most common)
2) Strched wire
3) Paramagnetic material in magnetic field

Surrounding : Rest of the universe!

2) Thermodynamic Parameters :

A set of values (or variables) used to describe a thermodynamic sys

And there are some typical examples of system one is the gas assembly, which is most common and once again, when we will be discussing classical thermodynamics, most of the time we will be talking about a gas assembly. Because this is how we learn of course, the same concept, same principle can be worked can be applied for other systems. For example, a stretch wire we have elastic wire, which is under some tension.

That can be used as having that can be a thermodynamic system. We have a magnetic material, paramagnetic material could be a salt, could be an alloy which is placed inside a magnetic field that is very well described by a thermodynamic system. And let us say there is a surface fill. So, we all know about surface tension, when we have soap solution, we have bubbles. The surface of a bubble is actually a very good example of a thermodynamic system.

We can model that using you know, very simple thermodynamic relations. So, these are all systems. Now, what is surrounding? The surrounding is rest of them. So, when we talk about system, we talk about for example, let us come back here. So, whatever is outside the boundary, we do not care what is outside, we just call it the rest of the universe. I mean, it is a heavy term I can understand.

But let me tell you, this is how it works, there is a system and there is the rest of the universe, which is not part of the system, and these are called the surrounding. Now, next comes the concept of thermodynamic parameters so, what are these parameters. So, parameters are a set of values or variables used to describe a thermodynamic system.

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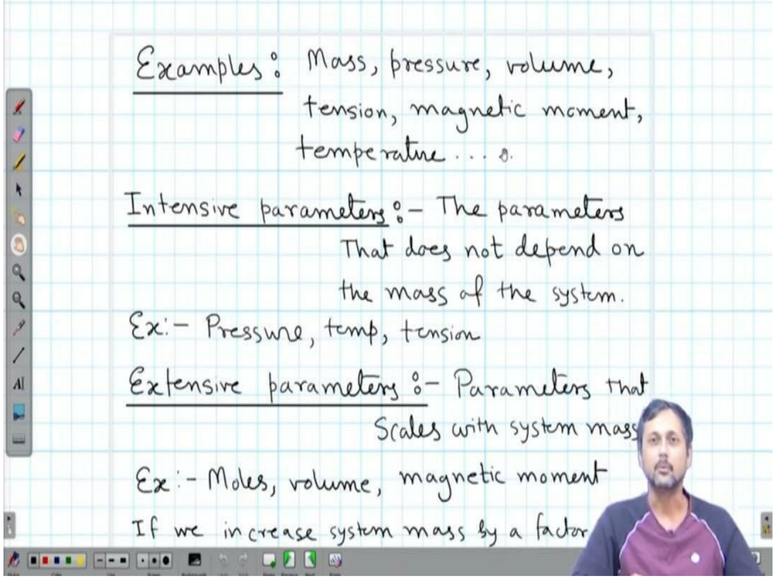

Examples: Mass, pressure, volume, tension, magnetic moment, temperature . . . .

Intensive parameters :- The parameters That does not depend on the mass of the system.

Ex:- Pressure, temp, tension

Extensive parameters :- Parameters that Scales with system mass

Ex :- Moles, volume, magnetic moment

If we increase system mass by a factor

So, examples are you know mass, pressure, volume, tension, tension means could be surface tension, could be the tension applied of force applied in a string, even that is called attention, we all know about magnetic moment, temperature. So, all these are examples of thermodynamic parameters. Now we can categorize these thermodynamic parameters into two broad classes, one is the intensive parameter the other is the extensive parameter.

Now, what are intensive parameters? Intensive parameters are those which does not change when we change the mass of the system. And extensive parameters are those which scales with mass.

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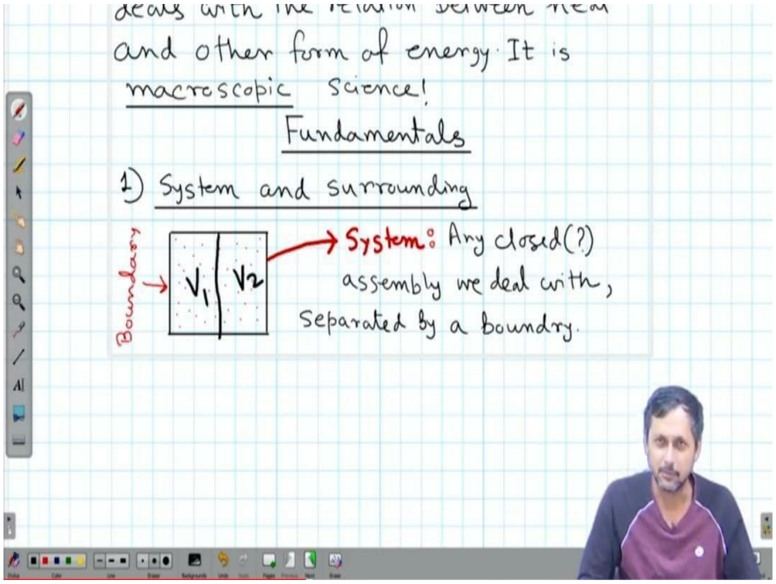

deals with the relation between heat and other form of energy. It is macroscopic science!

Fundamentals

1) System and surrounding

System: Any closed(?) assembly we deal with, separated by a boundry.

So, let us take once again a simple example, I have this box here. So, what happens if I just put a partition in any arbitrary partition? So, let us say the initial pressure was P so, when I put this partition arbitrarily without, you know affecting the other part, I am just saying okay, let us say I have a magic one, I just waved that one and that partition appears. If I can do that without disturbing anything else in the system.

What will be the pressure on left side and what will be the pressure on right side? The pressure is exactly the same and it is exactly same with the initial pressure. If the initial pressure is P, it should be P once again. So, if I now have, but then look at the volume, this will be V 1, this will be V 2 and total volume will be V 1 plus V 2. So, pressure after I partition this so, when I am partitioning it, I am basically partitioning the mass whatever mass is available.

Let it be you know, whatever the total mass of the gas molecule, I am just putting a random partition into it. So, what changes the volume changes. Does the pressure change? No. Does the temperature change? No. Unless and until we are you know, during the process we are you know, robbing the wall of the container which in reality will take happen because I do not have a magic wand I cannot just put a partition arbitrarily.

So, you have to apply some force it has to be pushed through. So, there could be some small temperature change, but if we ignored that, the temperature does not change. So, we see when we divide the system into two, temperature does not change pressure does not change, but volume changes. So, pressure and temperature these two are the example of an intensive variable, which does not scale with the mass does not scale with the system.

It does not change with the number of molecules in the system. But volume on the other hand is one parameter which changes with system mass or number of particles. So, I mean, in a sense mass itself is a expensive variable, because if you divide the system the mass change, if you divide the system number of moles changes. So, that is where we have the concept of intensive and extensive parameters.

So, basically, what I mean to say is if I similarly if I just now you know, keeping the pressure and volume and pressure and temperature same, if I now want to increase the volume of the system, what do we need to do? I think you understand basic thermodynamic principles already because we have been studying this for during your you know, plus 2 standard itself. So, if I have the box, and I want to increase the volume keeping the pressure and temperature only way we can do is we can increase the volume of this box.

Take a new box and put some extra number of molecules. So, that the pressure and temperature remains unchanged and the volume increases. So, that means if we scale it by is just opposite to the division actually divided, we are not dividing we are putting something more. So, basically, whenever we are scaling it by a factor x, the extensive parameters also scales, so volume changes, but pressure temperature remains unchanged.

So, these are just some examples and so, as I have said already, we will be focusing primarily on the gaseous system. So, this is easy to understand and of course, we will take other examples when we will be taking more examples of extensive and intensive variables.

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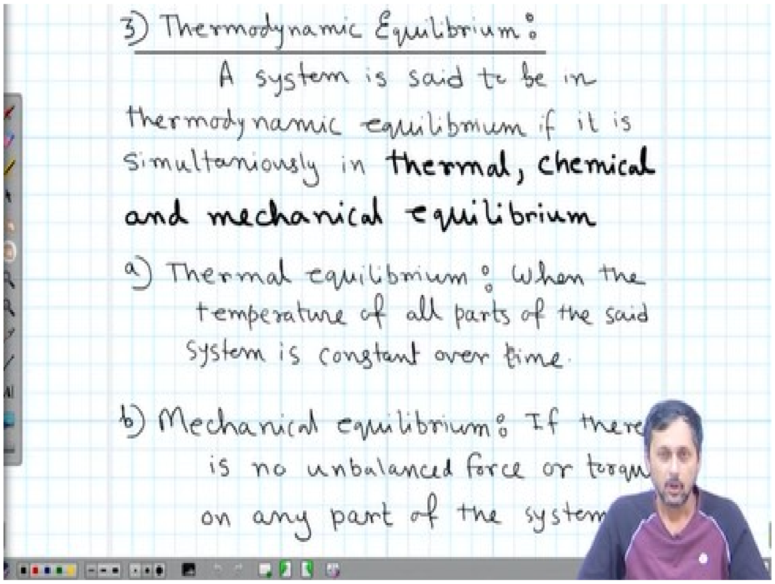

3) Thermodynamic Equilibrium:

A system is said to be in thermodynamic equilibrium if it is Simultaniously in **thermal, chemical and mechanical equilibrium**

a) Thermal equilibrium: When the temperature of all parts of the said system is constant over time.

b) Mechanical equilibrium: If there is no unbalanced force or torqu on any part of the system

Now, next and very important concept is that the concept of thermodynamic equilibrium. Now, a system can have many different types of equilibrium, it can have thermal equilibrium, it can have mechanical equilibrium, and it can have chemical equilibrium. So, let us first explored them one by one first is equilibrium. The thermal equilibrium is when there the temperature of all parts within that system is constant over time.

So, once again if we go back to this gas assembly. Let us assume that we so, let us just go back to this one forget about this V 1 V 2. Let us assume that we have not toured this partition, we have just putting one side of this in contact with the heat part. So, what happens we know that from thermal equally the concept of thermal conductivity that this wall will be somehow getting warmed and given that this is not an insulating wall.

So, it will get wall and the molecules will carry this extra thermal energy from this part to the other parts unless and until an equilibrium of temperature is achieved. So, this is the, I mean as long as there is a temperature gradient this transport flow will go on. So, that means, when there is a gradient present, temperature gradient present in the system, system cannot be said to be in thermal equilibrium.

So, another way of putting it is thermal equilibrium is when there is no temperature gradient in the system. Or another in the same thing in a different wording is when the temperature of all parts of the set system is constant over time. It is also important to have this constancy maintained over time. So, if I just measured it for, you know, for one second, it stays the same. After 5 minutes I measured a different value.

So, that means the system is not exactly in thermal equilibrium, but as low heating processes going on. So, it is not only all parts should have equal temperature, but it should stay equal over time. Next one is mechanical equilibrium, if there is, there has to be no unbalanced force or torque on any part of the system. So, I have this pen in hand. So, if I just, you know, rotate it like this. So, of course, that means when I am rotating it.

When I am doing this, there has to be certain amount of torque I am applying pressure on this side, applying pressure in this direction, applying pressure in this direction and this direction and it is applied at two separate points. So, that is why it is rotating. So, there is a torque. I am applying pressure equally from both sides, it is holding steel. So, this is a balanced force this means it is in mechanical equilibrium.

But the same force when applied in different places it is not in mechanical equilibrium. So, this is the concept of mechanical equilibrium.

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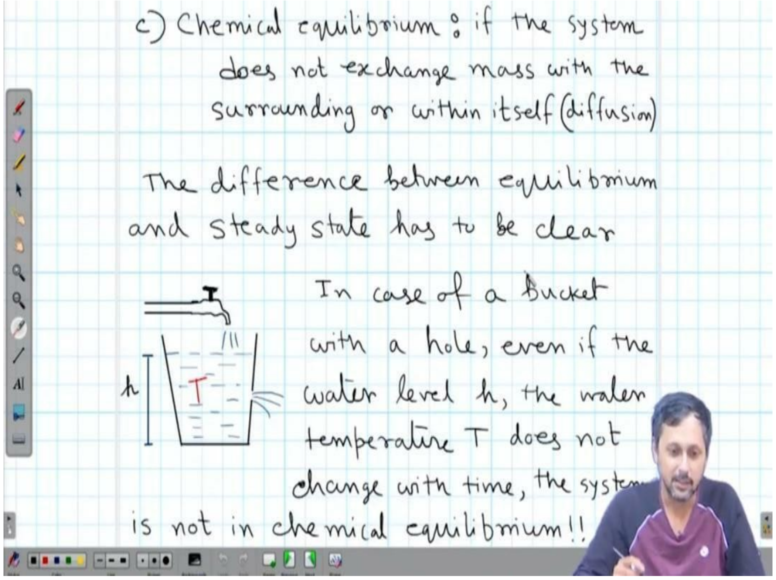

c) Chemical equilibrium : if the system does not exchange mass with the surrounding or within itself (diffusion)

The difference between equilibrium and steady state has to be clear

In case of a Bucket with a hole, even if the water level h, the water temperature T does not change with time, the syst
is not in chemical equilibrium!!

And finally, the chemical equilibrium: Now what is chemical equilibrium? Chemical equilibrium means, do not confuse it with chemical reaction, chemical reaction is a system I mean inside a system if some chemical reaction is taking place. That is also an indication that the system is not in chemical equilibrium, but a broader definition of chemical equilibrium is that the system is not exchanging any particle with the surrounding or within itself.

So, that means the system is a closed system, it is not changing any particle. I will come back to that definition of closed system and also there is no density gradient present inside the system. We all know about density gradient. So, there are three types of equilibrium thermal equilibrium, no temperature gradient, mechanical equilibrium, there is no unbalanced force or torque and number three chemical equilibrium that there is no density gradient.

So, we have so, basically, the second mean that the mechanical equilibrium means there is no viscous force also, that is also some kind of an unbalanced mechanical force. So, when we have a system, let us say 1 gas assembly, when there is no viscous forces, you know acting with each other that means there is no velocity gradient, when there is no diffusion taking place or there is no thermal conductivity taking place that means the system is in total equilibrium.

So, all three has to be achieved thermal, chemical and mechanical equilibrium has to be achieved, if we want to get a thermodynamic equilibrium. So, all three combined produces a state in which we call it thermodynamic equilibrium. So, that is why diffusion although it could be totally understood in terms of kinetic theory or mean free path and collision theory. It cannot be considered as thermodynamic equilibrium.

And also, there is a crucial difference between steady state and equilibrium. So, just take an example we have a bucket here, water I think I have given this example before also in one of the lectures, if I am not very long. So, let us say there is a tap water is falling into the bucket and there is a hole in the wall through which the water is going out. Now, we can always change the flow rate of this tap adjust the flow rate of this tap says that the flow rate here.

The inflow here and the outflow here, they are equal to each other, it is possible. So, that means we can reach a state in which the number of water molecule that is coming in and number of water molecules that are going out will be equal. That means there is no unbalanced force mechanical force on the system and the temperature is also equal that if I allow the flow for long enough the temperature will be equal to the incoming tap water.

So, temperature, no problem that means it is in thermal equilibrium, no unbalanced force mechanical equilibrium. I mean, manuals force inside this bucket of course, there is gravity pulling here, forget about that inside the bucket no. But actually, to be honest, in this particular diagram, there should be some sort of unbalanced force present. So, I can do one thing, I can just join it here and I can make this hole somewhere here.

So, there is no problem you see, now the water now the water will flow. So, now the water inside will not experience any mechanical force mechanical difference. But is it in chemical equilibrium? The answer is no, because molecules are coming in and molecules are going out. So, you can say that it is in a steady state, but not because it is not in a chemical equilibrium. Although it is in thermal and mechanical equilibrium, we cannot call it a thermodynamic equilibrium.

So, this one is a classic example of a steady state, which is not in thermodynamic equilibrium. But we will see many cases in many times in next few classes or for the remaining lectures, that there are systems which has achieved steady state as well as thermodynamic equilibrium at the same time. Anyway, we will come back to that. Now, this is a case when the system is exchanging particle with the surrounding.

If you remember, I have put a question mark here, when I said closed, so that means it is not necessary that a system will be closed. A system can be open system as well, that takes us to the, that makes us revisiting the definition of system.

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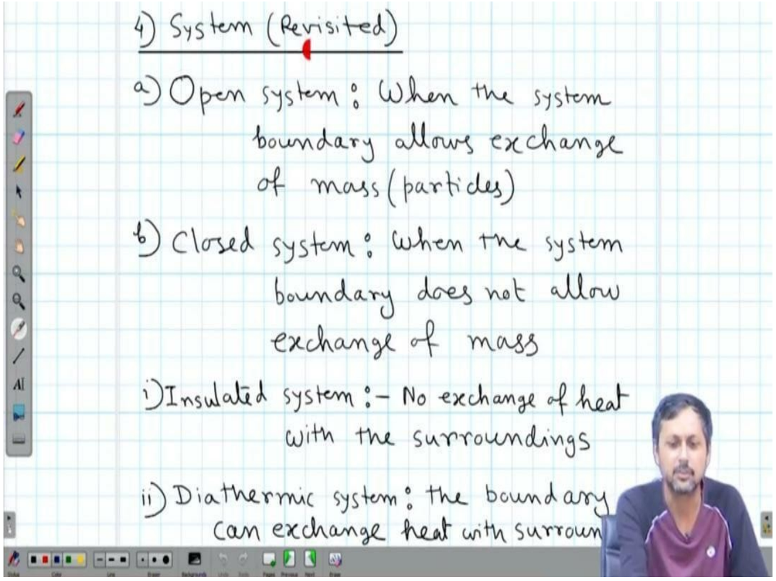

4) System (Revisited)

a) Open system : When the system boundary allows exchange of mass (particles)

b) Closed system : When the system boundary does not allow exchange of mass

i) Insulated system :- No exchange of heat with the surroundings

ii) Diathermic system : the boundary can exchange heat with surroun

So, we have two types of system one is called the open system, the other is called the closed system. The open system is the one that in which the boundary allows the exchange of mass. For example, if you remember, we have discussed about effusion. Effusion is what? A box or container which contains gas, and there is a tiny hole through which gas can leak out. So, there is the process of effusion. Now is this one is an open system; it is not exactly a closed system.

You remember osmosis, I think we all know about osmosis. In osmosis what happens we have we talked about osmotic pressure when we were talking about Einstein's theory of diffusion. So, the water molecule can pass through this semi permeable membrane. So, that is an open system. But most of the time we will be talking about closed system when the system boundary does not allow the exchange of mass but exchange of mechanical energy and exchange of thermal energy can be allow.

Now, depending on whether the system allows exchange of thermal energy, we can divide it even further. We can call it an insulated system or an isolated system. An isolated system is in which there is no thermal energy exchange with the surrounding. Insulated, isolated basically the same thing and we can have a non-insulating system or it is sometimes called the diathermic system. Diathermic system is when the boundary which is a diathermic boundary that allows the exchange of heat with the surrounding.

So, we could classify the systems in two broad categories open and close. And inside closed systems also there could be insulated system or isolated system and there could be non-isolated system with exchanges the amount, which allows heat energy exchange. So, this is where we and let me tell you that most of the time we will be talking about closed systems. Open system is something very difficult to deal with in classical thermodynamics.

Sometimes in engineering thermodynamics it is being dealt with, but in our case, we will be sticking mostly to the closed system and different types of the closed systems.

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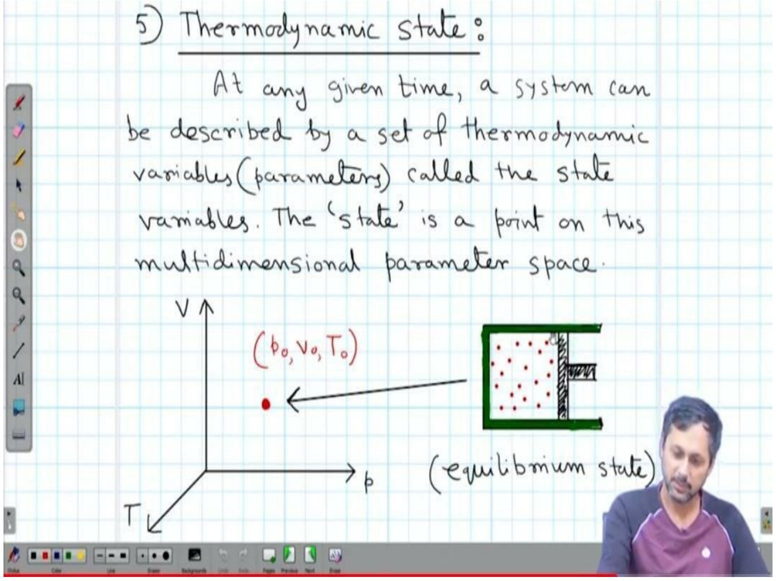

5) Thermodynamic state:

At any given time, a system can be described by a set of thermodynamic variables (parameters) called the state variables. The 'state' is a point on this multidimensional parameter space.

Now, next concept is thermodynamics state. So, let us assume once again let us assume a gas assembly, let us say we have a system in which we have gas molecules trapped inside a piston. Now, of course, I am free to move this piston but this is not what I am doing right now, I am just saying that this piston is fixed here. So, my pressure volume and temperature is fixed. Of course, I have to allow it enough time.

So, that this thermodynamic equilibrium can be reached, there is no exchange of molecule with the surrounding the wall is not, you know open, it is not an open system. And let me assume that there is no mechanical force. So, if we give it long enough time it will be equilibrated and we have P 0, V 0 and T 0 as the pressure volume and temperature. Now, this three for this particular case, this three quantity P 0 that means, the pressure V 0 that is the volume T 0 is the temperature, these three quantities will define the system uniquely.

Of course, now, there is one more parameter here, which I forgot to mention, that is the number of moles or we can call it n 0 or new. So, let me write n only, n being the total number of molecules. So, if I specify these four parameters, it will actually uniquely determine this system. And now, let us say that we want to change the state of this system. So, this combination of these three parameters is called a thermodynamic state.

So, this is a collection or this is a point in a multi-dimensional parameter space. A state is actually a point in a multi-dimensional parameter space. Do not confuse yourself, we all know about PV diagram we all know we have done it many times in the last few classes itself, we all know about TP diagram, we have also discussed that during real gasses. So, do not confuse yourself when I say multi dimensional what I did here, just to see, up to three we can draw very easily.

So, forget about n we will let us assume it is a closed system. So, n is fixed so, we just accept any fixed number. We draw three axes P V and T and this particular combination of pressure volume and temperature can be represented by one point on this three-dimensional axis system that you understand. So, this is what I mean by multi-dimensional. Now, if I make it an open system, I can have this another axis I mean of course, we cannot draw that, but you can imagine you can visualize.

That we have four axes, and then it is P V T and n or n 0 whatever you call it, four parameters makes one point in this case just because for easy visualization, we have used three parameters. And let us say it is constant. Now, if I want to change this now if let us say I am applying some mechanical forces. Now, after some time I stop and I allow enough time for this gas assembly to let us say, I am just going from going outwards. So, the volume increases.

So, temperature will drop, pressure will drop, but after some time, it will be in a steady state or rather not steady state, it is thermal equilibrium both steady state and thermal equilibrium. So, not only thermal it will be thermal mechanical and chemical equilibrium. So, the path from one point and then what happens. Then you realize that the next set of P V and T will be another point on this 3 dimension curve. So, we have one state here and another state there.

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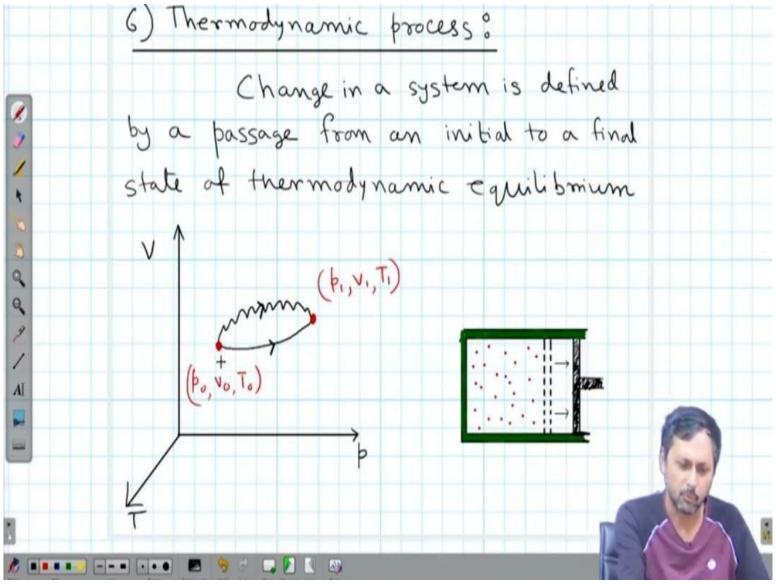

6) Thermodynamic process:

Change in a system is defined by a passage from an initial to a final state of thermodynamic equilibrium

And exactly that is what I have drawn here. And connecting these two points is a path that defines a thermodynamic process. So, the definition of thermodynamic process is change in the system or the path or the passage through which a system goes from an initial state to a final state, final state of thermodynamic equilibrium. And please remember, typically we can represent only the equilibrium state.

If it is a non-equilibrium state, it is not possible to represent this as a point in this PVT diagram. And so, thermodynamic process is the path connecting this to thermodynamic states. Now, you see, I have drawn two paths here, so, I should put the arrow as well. So, I have drawn two paths here; one is a smooth line, one is a zig zag line. So, basically what I tried to tell you about is there are different paths or different processes through which a thermodynamic system can go from one state to the other.

The two states initial and final states are necessarily equilibrium states, in between it is not necessary to have and equilibrium state. So, the process could be an equilibrium process, could be unknown-equilibrium process. So, you start here from tomorrow's lecture in the details of thermodynamic processes. And let us see where we go from there, because I will tell you something that maybe today's lecture seems very boring to you, but these are important.

I mean if you take any standard textbook, that textbook will not probably follow this particular order of events. But more or less this topic will be covered as a fundamental topic of classical thermodynamics. So, my suggestion would be after listening to this lecture, take any standard textbook which has listed and read the first chapter of classical thermodynamics and you will have a better idea of what I am trying to tell you. See you again in the next lecture, bye.