Engineering Thermodynamics
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Lecture – 04
Thermodynamic Concepts: Properties. State. Equilibrium

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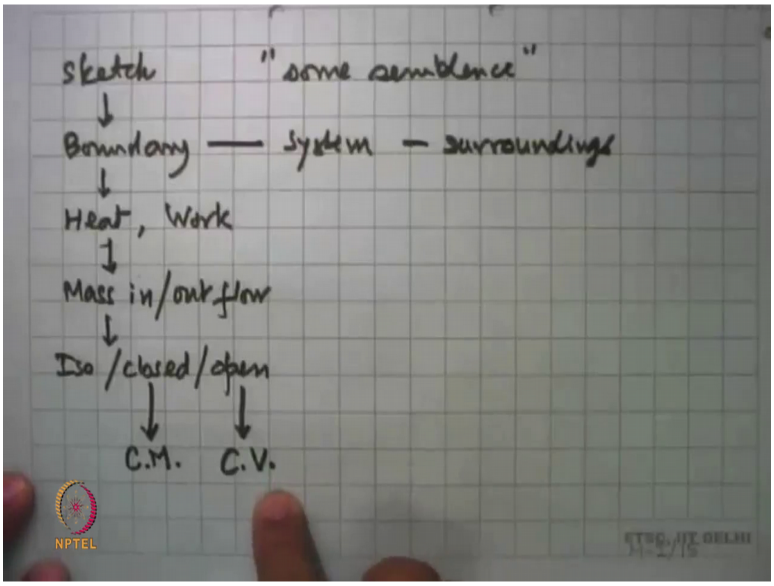

In the last class we the first steps in formulating a strategy for analyzing thermodynamic systems and that started by saying that we make sketch of the system; I have realistically representative of the real device. Then we define the system boundary and that tells us what is in it and what is not in it. We then look at I think is there heat or work class for the of the system and that is definition of heat and work. Then we asked is there any mass crossing the system boundary is going in or going out from the system. And then we defined these special types of systems isolated closed and open and said that if the closed system the equations will be formulated in the controlled mass approach CM. And in the open system we look at the systems and the equations the control volume approach CV energy.

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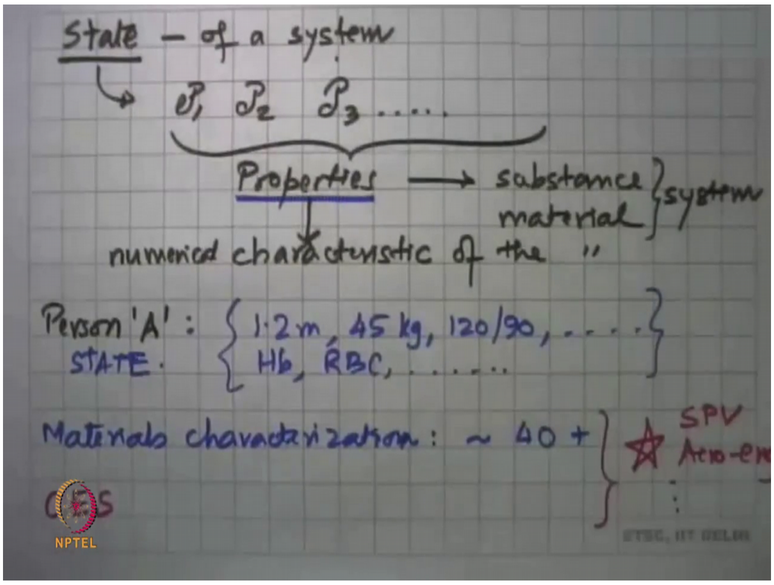

So, we will now pick up on this and say that we did not define what is the state? This is our next major concept that is coming up now and to define state this is the state of a system always and what we mean by state? If that we have a set of properties and we just call it P 1 P 2 P 3 and so on. And we say that it is these set of properties that define the state of the system; what we are implicitly saying is that we are not just properties of the system, but actually properties of the substance or the material this is this is system.

So, we are always now beginning to say that whenever we say properties of the system we actually need properties of the substance. We are not putting any restrictions on this at all as to what is the substance, is it liquid or whether it is a mixture will be pure, what pressure is it absolutely no spaces. Let us first define what is property? So, this is a characterization numerical characterization value based a numerical characteristic of the substance. That means, if we define that there is something they cannot put a number on it and to answer to that is yes, then you say ok. So, that causes the property and I am from this number 1.

So, let us take an example I said how do I characterize a person, person A that could be in a human being or living feature a dog or a cat or human; I say it is a human being. So, what are the properties by which I can define the state of this person and say what I will ok, you can say that this person is 1.2 meters in height, weighs 45 kg, the blood pressure of 120 by 90 and various other things. And these days if you go to any of these laboratories they will tell you that your hemoglobin is this much, your RBC is this much and various types of cholesterols of this much. And so many numbers will come out and one can say that all these in some way each one of them is a property of a person and all of these together are defining a state of this person.

What it is also telling us is like how many properties can I have and the answer is that if you look up the base materials are characterized, besides the microstructure you will come across about 40 volt properties of a substance. And since we did not put any restriction on what that property is anything that qualifies this thing that you can put a numerical value on the characteristic of the material this is the properties. So, this gives us very large number of properties; some of which are useful in this course some of these are not.

But, they think that one can look up is to see a package called Cambridge Engineering Selector. Well few lakh materials have been listed and their properties have been given and like this many of these properties. And this is a device from which we can say that I want a material with these properties which is the candidate material and the software packing will tell you then take up this material.

So, this is a very very important thing that is happening in today's agent point; every day many new materials are being discovered and essentially this is the crux of technological innovation and technological change in our time. We talked yesterday about solar photo vortex cells, the material of the cells the various things we put on it that is coming here. We talked about gas turbines, aero engines one of the big thing that is driving aero engine technology and we saw how much it has changed, if properties and the materials or substances used to manufacture everything. Unlike, this practically then nothing where today some innovation here is more driving what is required, what is required is dictated by thermodynamics and which is why we are learning this subject.

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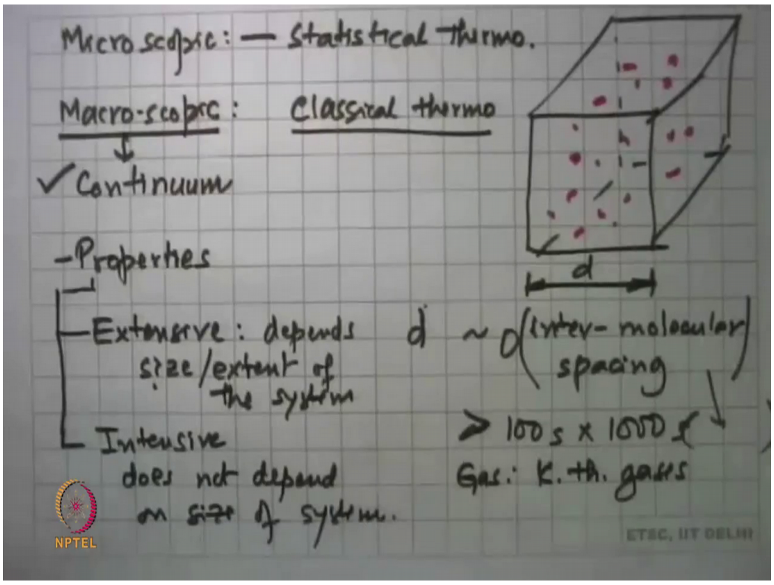

So, we come back and say well what are the properties that are of interest was in this thermodynamics. And we say that look if there is a substance and we just take say an elemental volume of that substance, then in this there will be lots of items and molecules in this in anyway. So, we are not going to worry about how many items are there or how many molecules are there and what each one of them it does. What we will, if that is to be done and we go to characterize it we have to go to the microscopic approach where, we start looking at each and every atom or each and every molecule in this. And then say what is the property from there and this is what we do in statistical thermodynamics.

In this course which is what is classical thermodynamics we do not worry about what each and every molecule is doing or maybe even what 10 molecules of doing, but we say that this is a big enough volume. So, that there are very large number of molecules. And so, if I take similar thing from anywhere else in the system they will all have on an average same behavior or the same properties. This is what we call the macroscopic approach and implicitly we are assuming that we have a continuum; that means, the size of this on an edge is such that it produces the volume in which there are very very large number of the atoms or the molecules. And that statistically we can characterize to behavior by certain numbers and that is what we this is the continuum approach.

So, we are saying that the individual molecules or atoms are not huge. If this dimension were of the order of the intermolecular spacing, then we call this distance d, if d is of the same order of the intermolecular spacing then we end up in the microscopic approach; we do not have a continuum and everything we learn is cannot be applied. So, if you are looking at in today's agent time nanotechnology and micro tube, then nanotubes where the dimension is of the order of this then this approach is not suitable. We have to go back over here and redo everything in a very different way and the answers are quite different from what we did things like this a major thing we did.

So, a lot of people working on it, lot of advance is taking place there I mean this is the crux of matter; what is micro and nanotechnology this. In our case we said that d is of the order of 100s or maybe 1000s of the intermolecular choice or even more. So, the individual atoms in molecule do not matter, we take all of them together and assign certain properties in there. In the cases of gases we have the well known kinetic theory of gases is a very very powerful tool, you had many aspects of what we see in real world in great thing by chemical reactions ok. So, what we are going to do is we are studying that part of thermodynamics, if we call proceed of the thermodynamics. We go by the microscopic approach, they assume that the substances are a continuum and now we begin to say what are the properties that I can assign you need macroscopic approach.

The macroscopic approach, the property would be the velocity say on each and every atom the temperature of each and every atom or molecule. And you have got millions and trillions and trillions of these how do I put it together; when you take statistics do some have adjacent. Then (Refer Time: 11:33) this is the if it was most probable answer for this. We do not go by probability we go by fix things what it here, but before I go there just to tell you that like just because, they are doing it does not mean this is not very important or exciting. This is in it would not write a very exciting field of moderate or physics and a lot of things that we do here actually be explains now here and you know very very rigorous in a very elegant way.

We would not go into the details of it later on, but when we look at say entropy it is the much more easier to competent from this approach; what it could be else then want see from this approach ok. So, let us now go back and see what are the properties that we have and we can say that we can classify properties in two ways; one is what is called an extensive property and the other intensive. Very simply extensive property is some number of the system or the characteristic of the system that depends on the size or the extent of the system. And intensive is something that does not depend on the size of the extent of the system ok.

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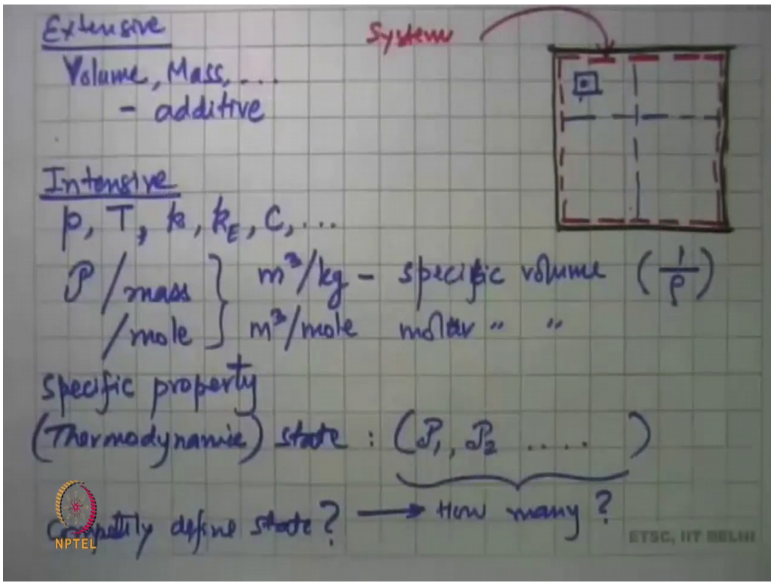

So, what is that mean? You go back and say that here is my system ok, here is say a room and in this we make our system which we say is everything in that air in this room except the walls of the room. So, the surface system boundary is right next to the surface, but not including this. So, that is the first thing we did with it define the system. They said what is included what is not included and next we say that what can I say about the system. So, I can tell you what the volume is, what is the mass and one can I do not think; let I can say what is the energy of this things like that. So, it means that if this is the system I get certain volume because, I take a portion of this I get some other volume.

So, it depends on the size of the system that we have been, I needs very these systems like we make subsystems which are completely independent of one another. Then adding that property for those systems will give you the property for the system. So, for instance we chop it up into 4 parts then the volume of this plus volume of this plus volume of this plus volume of this is the volume of the system. But, it has what we can say an additives property and the same can be said about the mass. So, remember mass is quantity of metal, we are not using the word weight that is wrong because that is the force.

So, this is an extensive property and many an analysis is much easier to do, he said look I do not know I have one system today which is got a certain volume. Tomorrow I am going to make another system which is much bigger than this, how can I take the result of this smaller one with the bigger one. And an extensive analysis does not help us remove that. And, that the main reason we then go to the intensive property and say look can I make a property which is independent of the size of the system that I take.

So, I take a little elemental volume there or I can call it that at this point in the system, if I can put some property and if it is say in everywhere it is the intensive property. It does not depend how big this whole system was and examples of that is the pressure, temperature and then you can say thermal conductivity, electrical conductivity specific heat. And we use some large number of properties which are extensive, but we make them intensive. So, we say that any property per unit mass or per unit mole is an intensive property. So, you take volume per unit mass that is meter cube per kg this becomes an intensive property and this we call in all these cases specific property; a meter cube per kg will qualify as specific volume and this is nothing, but the inverse of density.

They are much more familiar with density because, that is what you have learnt from school days. But, from now on in thermodynamics we always deal with specific volume; the two are just raised the (Refer Time: 17:57). So, this is mass per unit the volume per unit mass that is the specific volume or you can say what is the volume per mole. I mean that is molar specific volume and that helps us in analyzing things like how much nitrous oxide is found in the combustion process in a diesel engine further. So, this is an important thing we have done, we have converted an extensive property where in said intensive property ok. So now, we have said like I have to (Refer Time: 18:41) go back and say what is the state of the system where, where we started from.

We will now say that where I can specify the state thermodynamic state and now that is what we will worry about. We will drop the word thermodynamic, it may imply into the that we are looking at thermodynamic state, whether thermodynamic state is defined by a set of these properties; thermodynamic properties and this we will be again calling P 1 P 2 and so on. And the next question would come, how many properties do I need to specify? What we are saying is that if I have to completely and defined the state of a system, then how many properties do I need to specify?

We will come back to this question, when we come back in the third module on the properties. For now we will just say that irrespective what the system was in its thermo dynamic part; as limited set of we can specify with lot of property, but the subset of that with uniquely specify a state of the system.

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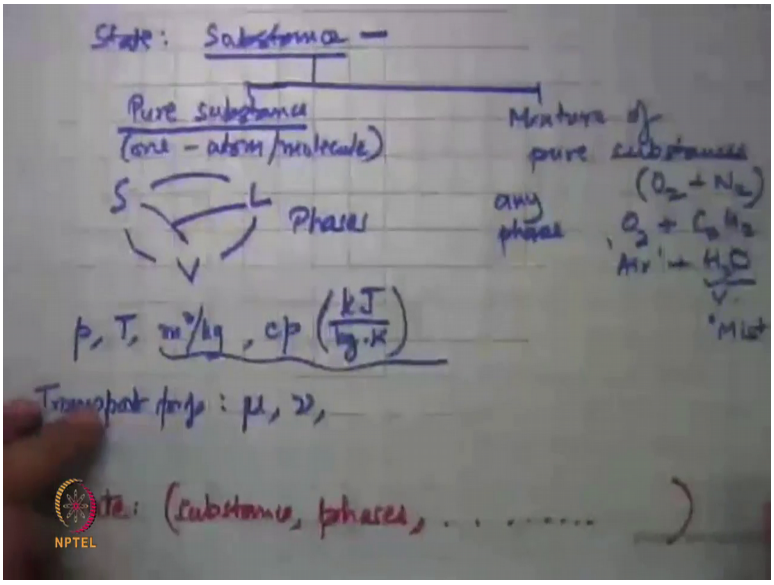

So, what we are saying is that the system material which is there so, the state and we are not talking of property means property of the substance we have known (Refer Time: 20:25) and I want the property in the system; was fortunate what is the substance in the system. And then we start getting its properties in the properties also substance. This substance could be just one type of a molecule which is what we will call a pure substance so, only one type of an atom or a molecule. And it does not matter whether this was solid or a liquid or a vapor or it was a mixture of these two or a mixture of these two or a mixture of these two or a mixture of all three.

It is a pure substance so, these are what we call as the phases of a pure substance and that is one arm of this. The second thing is substance would be a mixture of different pure substances for example, when say air technically this is two pure substances O 2 plus N 2. And every time if you want to look at O 2 plus N 2 analysis becomes a bit complex. So, in this course we will say can I say that this is one pure substance and approximately somewhere here. So, in some problems this is ok, but if you want to understand how much mux formation takes place, how much emissions take place we have to think of these two or it could be two completely different substances.

For example, in an noxious implies you have 2 chemicals different molecules coming in and that is what is required. Therefore, be even more of this and you can say that if air is treated as sort of a pure substance plus water in it in any form this becomes a mixture. And, we have this water we are not worrying what form it is, it could be a vapor, it could be small droplets that give us a mist or I this is the (Refer Time: 22:34); it will be rain drops liquid mass. So, here you have mixtures of substances give any phases, life becomes a complicated here. They are not to worry too much about this part, in this course we will cover only this knowing that the thermodynamics of this is can also be understood. But, it is matter of an advanced course in thermodynamics.

So, we come to the pure substance and say that there is only one atom and one molecule and we say that I have I can I would define certain properties and that is what be implement. So, we will worry about pressure, temperature specific volume these are the thermodynamic properties. Then there are transport properties, this also includes specific heat c c p whatever go and remember this is units are kilojoules per kg per K got in. This was specific volume, this is specific heat; the word specific is now coming in here. Transport properties include viscosity, kinematic viscosity things like that. So, we do not need this in this particular course; in fluid mechanics or anymore advance course we will worry about this, we would be quite happy to this ok.

So, what we have done now we said that you have a system, we state say what its state and we define the state by sub first study what is the substance operated 1 phase may be 2 phases 3 phases does not matter we specified that also. So, completely specify the state what we need to specify is 1, what is the substance, what are the phases that exists and then some properties of the substance. But, to the complete definition of a state what we have implicitly assumed in defining some of these things here saying this picture for example, when we said that here, here, here at any point we say that we measure the pressure and say what is the pressure.

And, if it is same everywhere we are putting it and they calling it pressure on the system a very intensive property. What we implicitly assume is a very important concept is that if we want to define the state of a system, this system has to be in thermodynamic equilibrium.

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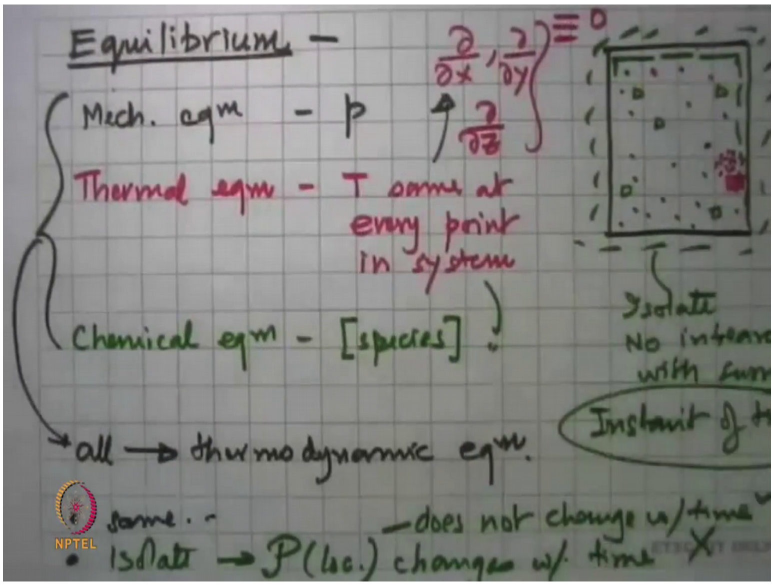

And this as a very very important concept and very simply let us define it and then we will go back and see what it implications are. If you take a system I am drawing a rectangle, but absolutely no necessity that it should be a rectangular you can make any shape, as long as it will include the system every one. And, if we say that in this system at any point that I take if the pressure at every point is the same then the system is in mechanically equilibrium. Now, we take this same thing and say if I measure at any number of points anywhere in the system and its temperature everywhere is the same then the system is in thermal equilibrium.

So, here T is same everywhere; here it was the pressure of this then comes in and we get a third-one and if he say that everywhere here the chemical composition is the same then the system is in chemically equilibrium. So, we have concentration of different species; species is nothing, but different types of molecules. And then this whole thing follows and if all these 3 types conditions are satisfied then the system is in thermodynamic equilibrium. So, we say well what are the characteristics of a system in thermodynamic equilibrium? We can say one if the temperature pressure and chemical composition at any point in the system is same; then the system will thermodynamically increase ok. So, the second argument that one can say that one can put the definition on it; like I take a system and then for that instant we isolated it and I say that this is the system.

So, I did the system body and I am now isolated this isolate means, there is no interaction with the surroundings. The system may have been having heat transfer with the surroundings and they want to see whether the system is in thermodynamic equilibrium we said ok, at this instant I just cut off the system from the surroundings and then I have wait and see 2 properties in the system change. So, if you isolate the system and if properties at any point so, any property at any location if it changes with time then the system is not in equilibrium. If at any location the property does not change with time then the system is in equilibrium. So, this issue of time that is not come in we are again it tells us now, like when we talk of equilibrium of a system we are always first going to make the system and say that at a particular instant of time only we can think of that the system is equilibrium will not.

Now so, one instant of time it is possible the system is not in thermodynamic equilibrium another instant of time will be thermodynamically equilibrium ok. So, an example of that would be that saying this is what this a room and these days we have a problem with mosquitoes. So, we put a mosquito repellent thing into the blood and this keeps giving out wafer of various chemicals which are mosquito repellents and we say that, if I take a snapshot at this point of time is this system is the room a is the room in equilibrium. The answer is where the composition here is different from the composition here.

So, the room air is not in thermodynamic equilibrium, but in the stop putting this out and wait for a long time then all these molecules with then completely different in the room. And, at any point of concentration of this repellant will become constant then we say that this room air is in thermodynamic equilibrium assuming that there is more temperature or pressure changes. What it also means is that the pressure and temperature are same everywhere, then these properties do not change with in any direction.

All these are identically 0, then we say the system is it equilibrium and once we have said that the system is in equilibrium then we can start assigning properties to it. So, whether it was extensive property or intensive property that we solve all those properties can be talked of only for system which is been equilibrium ok. Now, let us look at some real cases and several how good are these in terms of classifying this at being in equilibrium or not in equilibrium ok.

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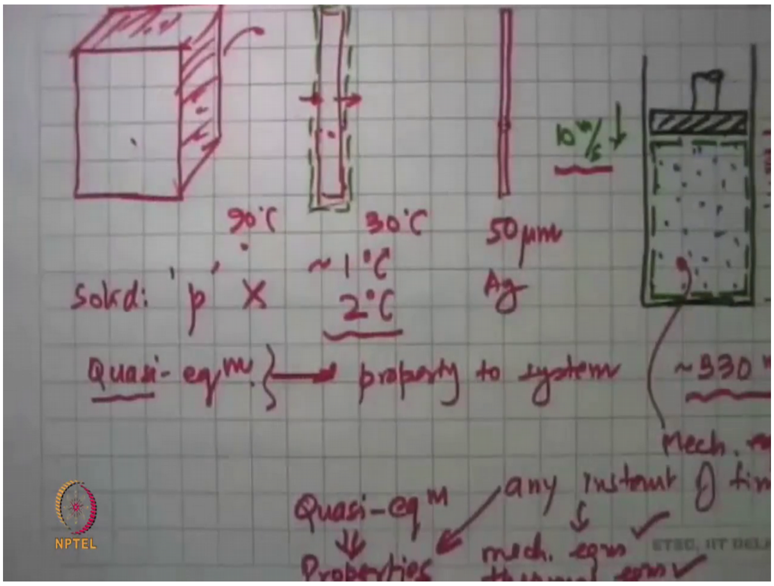

We take our say a piece of metal I am saying these surfaces 4 surfaces are insulated, this surface is heated the backside is cool. So, we are establishing a sorry system like this where, this side there is heat transfer to the system. This is the system, there is pick transfer of that the system and the system boundary includes all the metal that you see here. If this is thin and of a say material likes in the steel, there are temperature here if it is say about 90 degree C and the other side will maintain say 30 degree C then there are temperature variants in this. And so, this material is not in thermal equilibrium and so, that idea of that it is in thermodynamic equilibrium does not (Refer Time: 33:07). One of the issue that arises if this is a solid is that solid pressure is not defined.

So, talking about the pressure of a solid really does not make sense, we do not know at the most one can say that what is the pressure on the surface of the solid, but not what is the pressure inside the solid so, we know property. So, this is not in thermodynamic equilibrium, but if this thickness were very very less it was like a foil stainless steel foil 100 microns thickness or 50 micron micro meters in thickness. And, we say now I am employing temperature difference of 90 and 30 across it, when I approximate this as being in thermodynamic equilibrium. So, then we can say that look well implement in the variants are still there, but you might do it. I said forget in this was not in the steel, it was a steel silver foil then you say yeah temperature gradients here are still going to be there; I cannot strictly say that the thermodynamically.

But, if these temperature differences are say relatively modest say temperature difference of a couple of degrees Celsius, in depending on their regression then we can say the temperature difference this is very small. I can say that it is almost at the same temperature and I get said this is in a sort of thermal equilibrium. So, not strictly thermo thermal equilibrium and this we say yes for example, of Quasi equilibrium. Although, a means that the real system is not in equilibrium, but we are making certain assumptions and saying that then it is approximately like this. And so, I can consider it to be a equilibrium and in the temperature difference of that small I can say; the average of the temperature of these two is the temperature of the system and that is my system properties.

So, we needed this to assign a property to a system. If we did not assume this, if this was the case and somebody says what is the temperature of this material we cannot give an answer. There is no answer that is strict temperature; another example is from something that will keep coming back again and again in this course. They will cylinder pistol management and inside this there is a gas, that saw the moment assume that this is an ideal gas. And we say in engine say a part of a diesel engine or a petrol engine or any air compressor and we shall know this thing is moving back and forth at a certain speed; can I assume that at any instant the gas injectors is in mechanical units that is the question.

And, for that we do the same thing first define the system boundary and say look this is a system boundary which runs around the walls of the cylinder includes all the molecules inside it, but excludes the wall. We can move the piston, if somebody made a boundary like this we cannot even discuss the system.

And so, very precisely drawing the system boundary and wrecking what is in it and what is not in it is very very important. So, that is what we have done and within go back and say me that this piston is moving down nearly at the speed of 10 meters percent. And you say well if the pressure same every here and the way we will answer this question is to go back to what we have learn in this school physics. And so, that if the piston were to move very slightly say from here it moves better and stops; then what it has done if that the molecules just next to hit for a short distance are compress slightly. And then because there is a difference in the pressure this front keeps going out, the pressure behind it keeps decreasing and gradually the wave comes here.

And hopefully the pressure everywhere in the cylinder has become the same; otherwise the wave will come up here get reflected go back and in the few reflections, the pressure everywhere will become same. The speed with which this made travels is the local speed of some and that is the case with not just gases, but also with liquids and solids; if the same formula that comes from these. He there at say about ambient conditions I depend only on the temperature not common pressure. At a ambient condition the speed of the velocity the speed of some is of the order of say 330 meters per second which means that as the piston moves, a much faster rate this pressure wave went to an equalize the pressure.

So, might this in only a 10 meters per second, the equalization takes places as 330 meters per second until we can assume and say that look the equalization takes place much faster than the piston moves. So, during this motion even now this is slightly in not in equilibrium, but as gone that this velocity much less than this velocity; I can assume mechanical equilibrium in this and that say this is an assumption and the temperature also is equalized. So, we can say in all these problems where the piston is moving very slowly compared to the locals we have sawed, that this system at any instant of time and again this is the important, the system is in mechanical equilibrium and in thermal equilibrium.

And this is very very important because, when it tells us that at any instant of time if I have learned equilibrium or its not strictly an equilibrium we can say that this is Quasi equilibrium which means that at any instant of time I have Quasi equilibrium it means I can specify properties of that system.

So, every instant of time they are able to specify the properties of the system, this is very valuable to us ok. So, on again examples of chemical equilibrium, mechanical equilibrium and thermal equilibrium. And, real world systems in many of the cases extra element come to thermal equilibrium may not be like that, but we assume that take a small slice or make some other assumption and several ok. I can assume it to the thermal equilibrium or not and then will be we can do any calculations related to heat transfer, work transfer anything else. So, what we have done now is said well what is the equilibrium, what is the Quasi equilibrium. And, only thing remaining now is that if any of these three conditions are not satisfied, any of these three then the system is not in equilibrium ok.

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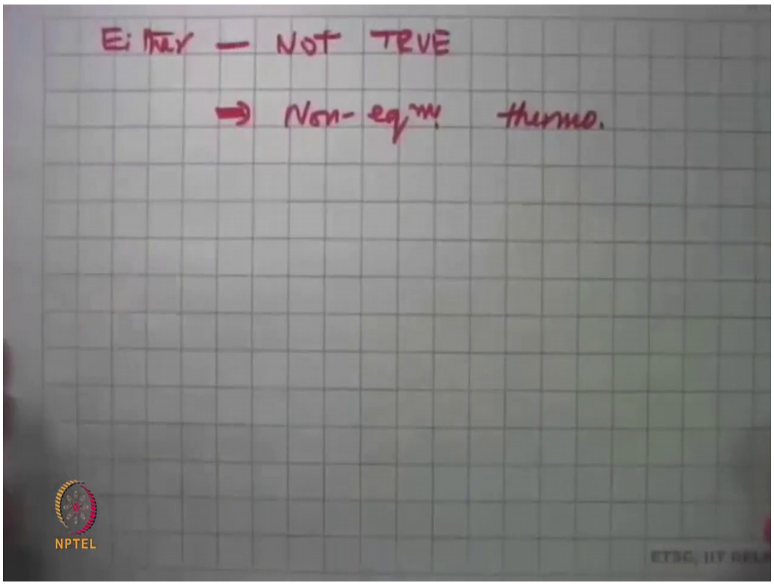

So, either of those not satisfied, not true this implies the system is it is a non-equilibrium system and what we are learning in this thermodynamics is not applicable. There is a separate branch of thermodynamics which deals pure limit non-equilibrium systems much more complicated at the graduate level or the research level, the undergraduate level is not worry about it. They say fine, if I want to get closer and closer and do a better and better analysis of the reality I need to go there, but at this point of time I think what happy to go to a Quasi equilibrium system and get at least some basic information ok.

So, that is non-equilibrium thermodynamics. Examples of that supersonic flow that is a non-equilibrium system or mixing of two different substances or very fast chemical reactions which are all non-equilibrium systems; we will not worry about that.