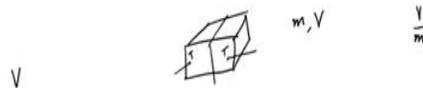


**Thermodynamics**  
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**Lecture 02 - Basic concepts and definitions – Part 2**

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- **Property:** A measurable macroscopic characteristic of a system
  - Thermodynamic properties relate to energy
  - e.g.: p, T, V
  - Extensive *extent of mass*  $V$
  - Intensive: *Independent of quantity of mass*  $p, T$
  - Specific  $v = \frac{V}{m}$  (sp. volume)



We define a property as a measurable macroscopic characteristic of a system. We are only looking at macroscopic thermodynamics. More importantly, thermodynamic properties relate to energy. We said that thermodynamics is a science which deals with conversion and transformation of energy. So, we are interested in properties which deal with energy. Some examples of those are pressure, temperature and volume. We will look at several other properties like enthalpy and entropy and so on as we go in this course. We have a further classification of these properties as extensive, intensive and specific.

Extensive properties depend on the extent of mass. Intensive properties are independent of the quantity of mass. And a specific property is an extensive property which, by some means, we make independent of the quantity of mass.

Let us look at an example of all of these. Let us say I have a box, which contains some mass. If I cut this box into two, does the mass of each part change? The mass of each part does change. So, mass itself is an extensive property. When I cut the box into two parts, each part has a volume

which is different from the initial volume of the entire full box. Therefore, volume also is an extensive property. Let us say I was measuring temperature. Initially, the temperature everywhere in the box was uniform. It had some value. I cut the box into two parts, hypothetically. Does the temperature of these two parts change? We do not expect the temperature to change. Therefore, temperature is independent of the size of the box or the mass of the box. Hence, temperature is an intensive property. Temperature does not change depending on how much of the quantity of a system I take. If I make the system into half or into three parts or four parts, it still is the same. Similar conclusions can be drawn in the case of pressure. If I cut the box into two halves, the pressure of each half will still be the same as it was before. It is independent of mass. Hence, pressure is an intensive property.

Usually, we do not deal with extensive properties much. There is a way to make an extensive property independent of mass. For example, a volume can be made independent of the quantity of mass by dividing it by its mass. It is called a specific volume, which we represent as  $v$ . Similarly, I can find other properties on a specific basis, for example, specific energy, specific enthalpy, specific entropy and so on. We will discuss these properties later on in the course.

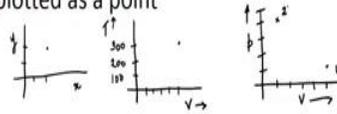
For extensive properties, we usually use capital letters, for example,  $V$  denotes extensive property (volume). There are of course some exceptions. For example, we use  $m$  for mass because we use  $M$  for molecular weight. We use  $T$  for temperature, which is an intensive property, because we use  $t$  for time. But for the other properties, we use small letters usually for intensive properties, for example,  $p$  is pressure (intensive property) which is independent of the amount of mass.

For specific properties, which are also independent of the mass, we use small alphabets, for example, we use  $v$  for specific volume. We use  $V$  for total volume. So, if I was to remove the exceptions, we use, for example,  $v$ ,  $p$  and so on for properties which are independent of mass (intensive properties). We use capital alphabets for properties which are dependent on the quantity of mass (extensive properties).

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- **State**
  - Set of all properties required to completely describe the system
  - Properties of the system are constant
  - State is a condition when the system is in equilibrium
    - Properties have definite values
- Any 2 independent properties can be used as axes and the state of the system can be plotted as a point



A state is the set of all properties required to completely describe the system. For example, when somebody asks you where you are, you need to give them information so that they can find you. You need to give sufficient information. Similarly, we can think of a state as all the things which you need to tell so that somebody can reproduce exactly the same system which you have, if they want to get there.

For example, you have air in this room. If somebody needs to recreate this room, they need to know what the air is composed of, what its temperature is, what its pressure is, and so on. So, all of the properties required to describe the system together is called the state. Since we are trying to define the properties, the property should not be changing. Because, by the time I measure it, it should not be some other value.

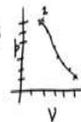
So, we need the properties to be constant. Or, if they are changing, the changes should be so slow that we can sort of specify their values after some time. For example, after a day, maybe the value of a property is something else, but at least today or at least at this point of time, it is some fixed value. After one hour, it may be slightly different. That is alright. In order to measure properties, we need the system to be in equilibrium, which means properties should not be changing. When the system is in equilibrium, the properties have definite values. Any two independent properties can be used at axes and the state can be plotted as a point.

We are used to, for example, plotting graphs of say,  $y$  versus  $x$ . If some distance in  $y$  is 2 centimeters and some distance in  $x$  is 2 centimeters, you can plot it and say that this represents that point where  $y$  is 2 and  $x$  is 2. In a similar fashion, we can plot various properties on graphs and they help us to visualize processes which happen. We can plot any property versus any other property. Which set of graphs we use depends on what we can see from the graph. For example, if the temperature is  $300\text{ }^{\circ}\text{C}$  or  $300\text{ K}$  and volume is  $5\text{ m}^3$ , I can plot this point on a graph, and say, this represents my state as far as temperature and volume are concerned. If the state changes after some time to some other value, I can also plot that. Similarly, I can also plot pressure versus volume. I can show what happens when the pressure changes or when the volume changes.

One example is that of a bicycle pump. I am filling a tyre of my cycle. Initially, the pressure inside my bicycle pump is low and the volume is high. Then I press the plunger down. Let us say, for the moment, I keep the outlet closed. When I press the plunger down, in the bicycle pump, the pressure increases and the volume decreases. I can plot this on a graph. Initially, let us say, pressure is 1 bar, volume is some 5 units. After a while, the pressure, when I press the plunger down, increases and the volume reduces. It means the new point must be higher on the  $p$  axis than the previous point and lower on the  $V$  axis.

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- A **Phase** is a quantity of matter which is homogeneous throughout
- **Path** is the locus of all the intermediate states which the system passes through when there is a change of state
- A **Process** occurs when a system changes from one state to another
  - Special processes where a property remains constant ✓
  - Cyclic process
  - Equilibrium: Mech., Thermal, Chemical, Phase
  - Quasi-static process



A phase is a quantity of matter which is homogenous throughout. We talk of, for example, a solid phase, a liquid phase, a gaseous phase for the air around. We can also talk of plasmas. In

this course, we are just interested in a solid phase, a liquid phase, and a vapor phase, and we look at some changes in phase between these.

A path is a locus of all the intermediate states which the system passes through when there is a change of state. For example, we just looked at a p-V diagram for a bicycle pump. Initially, the pump has some volume and some pressure. I press the plunger in. After sometime, it has some other volume and some other pressure. We have the initial state and the final state. If I do this process really slowly, I can also measure, at any time in between, pressure and volume at each intermediate state. I can connect all of those points. The locus formed by those points is essentially called as a path. It is a locus of all the intermediate states which the system went through between the initial state and the final state. Whenever there is a change in properties of a system, we say a process occurs. So, a process occurs when a system changes from one state to another. In a process, any property of a system can change, for example, the pressure can change, the volume can change, the temperature can change, mass can change, and so on. But there are some special processes where some property remains constant.

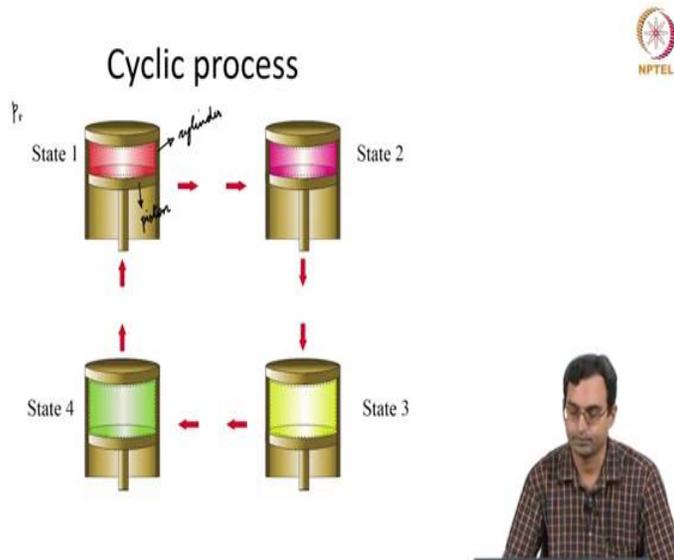
If I take a system, then by definition, the mass is constant, because when I talk of systems, I am generally talking of closed systems. So, the mass is constant. Suppose I have some mass of a gas in a rigid chamber. The volume is fixed as the walls are rigid. So any process happening inside this chamber is a constant-volume process. Such a process is also known as an isochoric process. Similarly, I can have some other process where the pressure is constant, and we would call that an isobaric process. A process where the temperature is constant is called as an isothermal process.

A process where there is no heat transfer across the boundary of a system is called an adiabatic process. In an adiabatic process, properties may change. We also have cyclic processes, which we will define later.

In order to define a state, we said that you need to have an equilibrium, which means things should be constant as a function of time. In order to have equilibrium, you should have mechanical equilibrium i.e. all forces must be balanced. You should have thermal equilibrium which means there should not be any difference in temperatures. You should have chemical equilibrium: if there are reactions, rate of forward and reverse reactions should be the same. You

should have phase equilibrium: if I have a mixture of two phases, for example, water and ice, the quantity of ice and the quantity of water should be constant i.e. there should not be net melting of ice into water or net freezing of water into ice. In order to have all of these equilibria and still have some change, we need to consider a quasi-static process. This process is such that the states achieved by the system are always near equilibrium. Anything which changes, changes so slowly that you can assume that the system is always under equilibrium.

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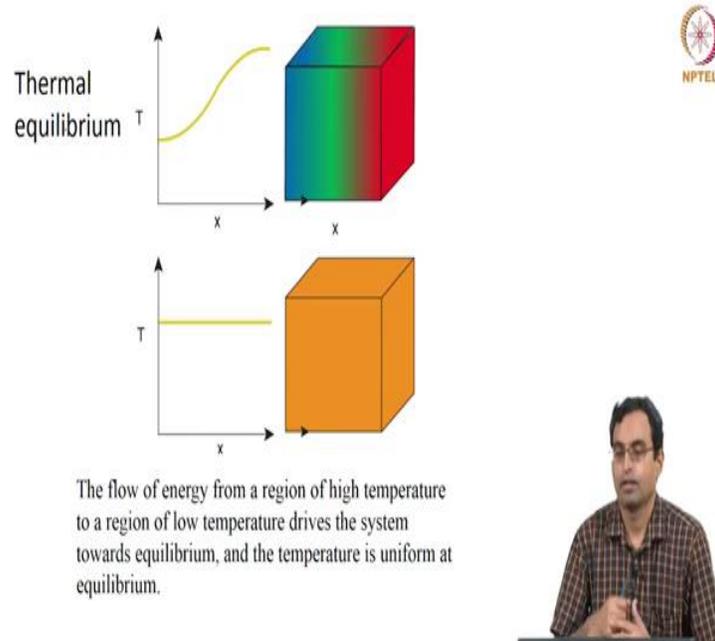
Let us look at a cyclic process. Let us say you have a piston and a cylinder, which is usually our most favored configuration for describing a lot of things. We will keep going back to piston-cylinder arrangements.

The piston-cylinder arrangement has some pressure and some temperature and volume. We call it as state 1. Very slowly, the temperature inside changes after some time. This process is happening slowly. It is a quasi-static process. The system is now in a new state (state 2). After some time, let us say I pull the piston down. The volume has increased. Temperature also might have changed. The pressure also might have changed.

This is some state 3. After some time, some other property changes and I come to some state 4. After a while, properties change in such a way that the system comes back to whatever the set of properties it had initially. It comes back to state 1. This kind of a process, where we reach the

initial state at the end of the process, is what we call as a cyclic process. So, the final properties are the same as initial properties. If initially, the pressure was  $p_1$ , finally, the pressure is again  $p_1$ . If I want to find out the change in pressure, it is essentially 0. Similarly, change in mass is 0, change in volume is 0, change in temperature is 0 and so on. So, there is no change in any property between the initial and the final state.

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We said that there has to be equilibrium in order to measure the properties of a system. Consider a box as shown in the figure where one side is hot, the other side is cold. If I ask you to measure the temperature of the box, you may not know where to measure as different parts of the box have different temperatures. So, we are not able to find out a single average value, which is representative of the temperature of this entire box. Whereas, if we leave it for a while, the temperature inside will be uniform. Now, if I ask you to measure the temperature of this box again, you can measure anywhere. Anywhere you measure, the value is the same. In this case, the box has reached thermal equilibrium. Hence, we are looking for systems under equilibrium, or very close to equilibrium, so that we can define the properties of the system.

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Mechanical  
equilibrium



In the quasi-equilibrium compression of a gas, the pressure is essentially uniform throughout the gas system, that is,  $P_B = P_T$ .



In a similar fashion, we also need to have mechanical equilibrium. If I have this piston cylinder-arrangement (shown in figure) and I was moving this piston really fast, either down or up, then the pressure near this piston and the pressure far away from this piston would not be the same. Then, if I ask you to tell me the pressure of the system, you would not be able to give me a single average value for the pressure. Such kind of a system is not very useful, because we do not know how to deal with it. Whereas, if the piston is moving slowly or if it is stationary, then everything inside is essentially the same. The pressures at different points would be the same or approximately the same if it is moving very slowly. Then, I can say any of the pressure values is a representative of the system.

So, we are looking for systems which are close to equilibrium even if they are changing or at equilibrium. Then we can define the properties very clearly. It is these kind of systems which we are going to deal with in this course. Quasi-static near equilibrium processes can be dealt with efficiently.