

**Engineering Thermodynamics**  
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**Lecture 02**  
**Thermodynamic Property, State, Equilibrium, Process**

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**Learning objectives**

1. Review of metric SI
2. Explain basic concept of :
  - *system, state, state postulate, equilibrium, and process*
3. Define intensive and extensive properties of system
4. Define density, specific gravity, and specific weight
5. Discuss temperature scale
6. Understanding pressure, barometer, manometer

So, in the last lecture what we went through was a review of our metric SI and the concept of system surrounding boundary, now we are going to talk about an intensive and extensive properties okay. So, let us look at a thermodynamic system which may consist of many species, for example you can look at a nitrogen hydrogen and NH<sub>3</sub> in the similar example which we had assume in the lecture for the production ammonia.

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**Properties of a system**

A thermodynamic systems may consist of many species.  
- A mixture of N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub>, in a reactor, at a given T and P

Predicting the state of a gas mixture (system) when the conditions of reaction are altered- we must have the knowledge of properties of the materials!

Essential features of a property are:

- a) A property should have a definite value when the system is in a particular state, and
- b) The value of the property should be determinable irrespective of how the system is brought to that particular state.

$$\int_i^f dZ = Z_f - Z_i$$

Now if you want to understand change of the state of the gas mixture if you change the condition, then you need to know the property of the materials. And the property of the materials in this case which depends on temperature and pressure and you have to choose the specific set of properties, properties such as odorless or other property which are relevant for portable water, for example is not relevant for thermodynamics. In thermodynamics the properties which are related to energy and its transformation are only useful in the analysis. So, the essential features of property would be that it should have a definite value then the system is in a particular state. Again I will say property such as odorless or tasteless are not useful in the thermodynamics analysis you have to choose properties which has a certain value which is related to the energy or changing energy.

So, a property should have a definite value on a system which is a specific state and the value of the property should be determined irrespective of how that particular state was achieved or was brought to that particular state. So, does not matter how this state was achieved, the property should depend on the final value. So, the change in the property from one state to another state can be clearly written in this expression whereas that is a specific property and its change is a change in its value from some initial state to the final state is given by the difference between these two and by the difference between the value of the Z into the particular state.

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Thermodynamic property

if  $Z=Z(x,y)$  then

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy = Mdx + Ndy$$

if  $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$ , then dZ is said to be an exact differential.

$$\Delta Z = \int_i^f dZ = Z_f - Z_i$$

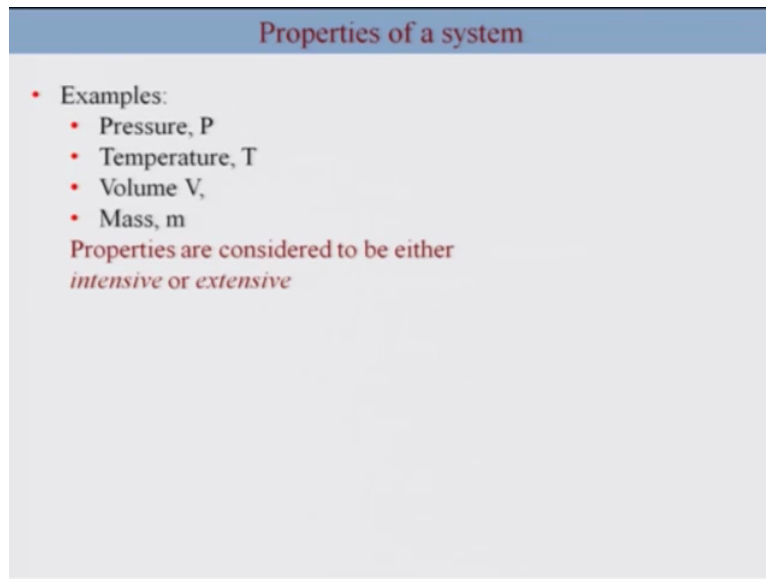
Thermodynamic property (Z) is independent of the path, and is a point function

Now let us little bit look at the mathematics so if you says that depends on the two variable X and Y you can write the differential of Z in the following form, where the partial differential in of Z with respect to X is given by M and this is N and mathematics tells us that if this

condition holds, then  $dZ$  is said to be an exact differential. Now in such condition you can integrate this in this form that means you can write  $\Delta Z$  as an integral of  $dZ$  from  $i$  to  $f$  and this would be given as the difference between  $Z$  of final and the initial values.

And therefore, thermodynamics property  $Z$  is independent of the path because of the exact differential and is a point function, so, this is a definition of the point function okay.

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**Properties of a system**

- Examples:
  - Pressure,  $P$
  - Temperature,  $T$
  - Volume  $V$ ,
  - Mass,  $m$

Properties are considered to be either *intensive or extensive*

So, let us look at common properties of a system the examples are pressure, temperature, volume and mass. The properties can be extensive or intensive so, just take an example let us consider a system this system can be simply water or any fluid okay, having a mass  $m$ , volume  $V$ , temperature  $T$ , pressure  $P$  and density  $\rho$ .

Now you divide this particular system into two parts okay and that you can do in this form where you have divided into two part one and part two. Now the mass certainly gets divided by two volume certainly gets also divided by two, on the other hand temperature of both the parts should remain same, the pressure should remain same and as well as the density, that is the what we can understand for all daily experience by taking water in a glass and dividing into two parts so. So, certainly certain properties are affected by this aspect of let say division of the volume which means it depends on the volume of the mass.

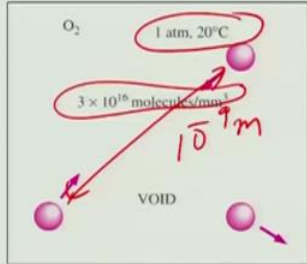
On the other hand, the other properties do not such a temperature, pressure and density. So, that becomes the basis for categorizing properties into intensive and extensive. So, intensive properties are independent on mass, examples are temperature, pressure and density and extensive properties are which depends on size or extend of the system mass, volume, total

momentum, these are the extensive properties okay. Now they are other properties which are called specific properties which are extensive properties per unit mass such as specific volume which is basically volume divided by mass and a specific volume becomes an intensive property. So, typically the specific properties are intensive properties such as specific volume.

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### Continuum Idealization

- Matter is made up of atoms
  - view it as a continuous, homogeneous matter with no holes, that is, a **continuum**.
- The continuum idealization
  - allows us to treat properties as point functions
  - to assume the properties vary continually in space with no jump discontinuities.
- This idealization is valid as long as the size of the system we deal with is large relative to the space between the molecules.
  - *This is the case in practically all problems.*
- In this course, we will limit our consideration to substances that can be modeled as a continuum.



Despite the large gaps between molecules, a substance can be treated as a continuum because of the very large number of molecules even in an extremely small volume.

Now in the typical matter what the matter if you know of this contains of many different atoms that falls we do not see these molecules or atoms around for us it looks like a homogeneous. And this is what we are going to use as an approximation we are going to use this system as continuous and this is idealization. But it is not so on and it is so bad approximation because if you look at the distance between these two atoms here in this case this will be of the order of  $10^{-9}$  meters okay. And for example this is an oxygen in certain volume at atmosphere 20 degree Celsius and there are these many molecules in the system.

So, if you look at this distance and divide by this distance the order of  $L$  by  $L$  is going to be extremely small and in such case this matter will look like continuous and this is not the approximation we are going to use. So, despite the large gaps between molecules a substance can be treated as the continuum because of the very large number of molecules even in extremely small volume. Now this allows us to do consider that the properties are also continuous.

So, it allows as their property vary continually in space with no jump discontinuity. And considering the system which we are going to look at the because of the size of the atom

which are extremely small this would be their practical case for all our problems okay. So, when I have to going to take sand particles or grain or asteroids which are extremely large or large in size. So, in this course, we will limit in our consideration to substances that can be model as a continuum.

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**Density and specific gravity**

**Density**  $\rho = \frac{m}{V}$  (kg/m<sup>3</sup>)

**Specific volume**  $v = \frac{V}{m} = \frac{1}{\rho}$

Sometime density is given in terms of Specific gravity:  
 $SG = \frac{\rho}{\rho_{H_2O}}$

$V = 12 \text{ m}^3$   
 $m = 3 \text{ kg}$   
 $\downarrow$   
 $\rho = 0.25 \text{ kg/m}^3$   
 $v = \frac{1}{\rho} = 4 \text{ m}^3/\text{kg}$

Density of liquids are essentially constants – approximated as incompressible substance during most processes

We will consider this kind of definition so if definition of density is very well known mass by volume specific volume is going to be volume by mass or one by reverse density. Now you have this specific gravity also which is the ratio of the density of the substance with a density of the water, now this density of water will be considering at 4 degree Celsius where the density of the water is maximum.

Now you can look at the specific gravity for various different substances some are greater than one some are less than one those which those having specific gravity that is let us then one will float on top of the waters layout okay. Now density of the liquid typically constant and we will be considering to be constant, so that is why they are part of called incompressible substances though there are slight change if you increase the pressure substantially, but otherwise we will be considering a constant density in this particular constant. So, furthers defined few things what is a definition of state in thermodynamics.

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**State and equilibrium**

(a) State 1

(b) State 2

**State**

- System is not undergoing change
- One can measure all the properties describing the condition

20°C	23°C
30°C	
35°C	40°C
42°C	

(a) Before

32°C	32°C
32°C	
32°C	32°C
32°C	

(b) After

A closed system reaching thermal equilibrium.

**Equilibrium**

- State of balance, no driving force or no unbalanced potentials within the system
- An isolated system at equilibrium undergoes no change.

So, let us consider a system which finally stops change in at all in our, so it undergoes the change and then reaches a point, where no change is in the properties are same. In such case the one can measure the properties all kind of properties. So, a specific step means a specific value of the properties, so if you fixed the values of the property you achieve as press particular state and this is an example you have a state one or with the mass 2kg 20 degree Celsius 1.5 meter cube you change the volume to 2.5 you change the state. You are changing just one property of the state and you are changing the state of the system.

So, that is how we going to define a state having a fixed set of properties. The other expect of thermodynamics where going to deal with is equilibrium the where is different kind of equilibrium. So, let us look at what is definition of equilibrium, so equilibrium is a state of balance there is no driving force or unbalanced potential within the system. So, let us take a case where you have variable temperature within the system okay. And after isolating this course system it reaches continuous constant value of the temperature throughout the system. So, a closed system reaching thermal equilibrium this is an example for that. Now if you take a system in isolated at equilibrium there will be no further change. So, as after this particular system if you isolate it there is going to be no change.

So, even if it a close system let say if at all isolated let it equilibrates to a specific temperature and then you isolate this isolate, then there will no further change in a system because there will be no interaction with this surrounding okay. So, that is how we are going to define the equilibrium there are many from of equilibrium or system it is state to be at equilibrium,



when all kind of equilibrium conditions are met (( ))(10:22). The equilibrium conditions are thermal equilibrium, mechanical equilibrium, and chemical equilibrium.

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**State and equilibrium**

*A system at equilibrium should have*

**Thermal equilibrium**


- No temperature gradient i.e., no driving force for heat flow

**Mechanical equilibrium**

- No change in pressure at any point in the system with time (pressure can change within the system with elevation)

**Chemical equilibrium:** If the chemical composition of a system does not change with time, that is, no chemical reactions occur.

**Phase equilibrium:** If a system involves two phases and when the mass of each phase reaches an equilibrium level and stays there.



So, let us look at one step by step in thermal equilibrium will be where there is no temperature gradient that means there is no driving force for heat flow. A mechanical equilibrium is, when there is no change in the pressure with time. So, there is no driving force for a fluid to flow, so a pressure can change within the system with elevation but in such case the forces will be balanced, then you have this chemical equilibrium. So, if there are no changes in the chemical composition of a system, then the system is at chemical equilibrium. So, for example we can consider like sugar dissolved in water and there is no changes in the chemical composition throughout the system and it will be say that chemical equilibrium. Now there is something called phase equilibrium. Now this is relevant, when you have more than one phase so phases such as liquid, gas, and solid.

So, if you have for example two liquids let us say oil and water, after you shake and you let it stay for while oil separates and water separates and there is no change in the composition of the oil and as well as in the composition of water after a while and there will be consider to be at equilibrium because they will need the thermal equilibrium they will need the phase a mechanical equilibrium as well as they are at two different phases.

So, hence phase equilibrium is this is a system which involves two phases and when the mass of each phase reaches an equilibrium level they has stays there. So, this is an example of phase equilibrium or so then we know that the state have a series of the properties or set of

properties and if you change one of the property the state will change. But it is not necessary that you have to define all the property to fixed a state there is a minimum number of properties which you must define or rest of the property gets fixed upon once you define this minimum number and that is how that is what the state postulates tells us.

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The state postulate

- The number of properties required to fix the state of a system is given by the **state postulate**:
  - *The state of a simple compressible system is completely specified by two independent, intensive properties.*
- **Simple compressible system**: If a system involves no electrical, magnetic, gravitational, motion, and surface tension effects.

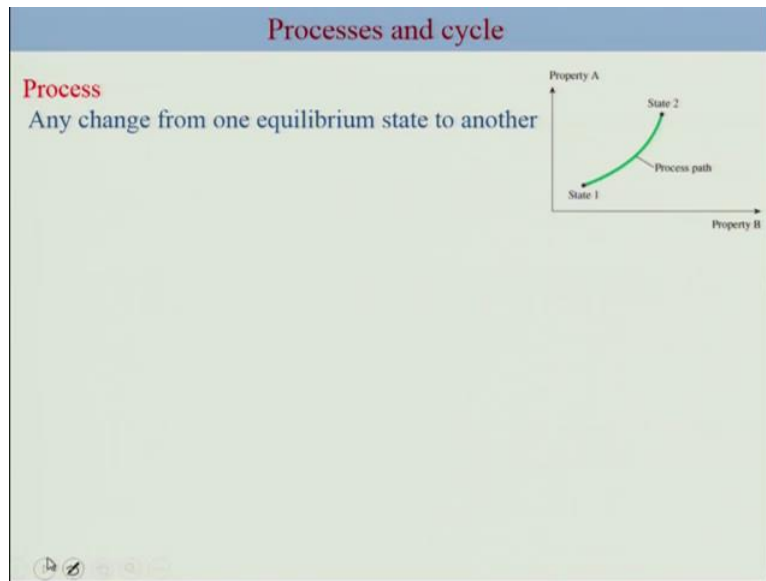
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So, state postulates is the state of a simple compressible system which is completely specified by 2 independent, intensive properties okay. Now what is a simple compressible system which is a system which involves no electrical, magnetic, and gravitational and surface tension kind of component? If you have those then you have to include another variable in order to define the state. Now this is an example of a specific state where to just two variable is been define temperature and specific volume okay.

Now you can make use of temperature and pressure also or this is relevant only for single phase, for single phase temperature and pressure are independent but for two phases first for example where water a liquid is converted into vapor, then the temperature pressure gets related. So, this is kind of one example where you know that at sea level when the pressure is one atmosphere water boils at 100 degree Celsius write and when we go to mountain the pressure is less than  $p$  atmospheric pressure and the boiling temperature also gets reduced. And in such cases when there is the phase change temperature is the function of pressure. The temperature of the boiling temperature is a function of pressure.



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Many state you can change along do a process. So, we will be defining the process here that any change from one equilibrium state to another. So, this is an equilibrium state and this is an equilibrium state or this is a process path okay. So, the process path is the series of state through which the system passes through. So, essentially it means that each of them along this green line is a state. And this is this is a specific state, this is a specific state of our interest or they are processes which are very fast, they are process which are very-very slow, a slow process where the intermediate point along the path or at equilibrium or Quasi equilibrium It is called Quasi equilibrium process. So, this is an example where you are using the slow compression in order to reach in order to make use of equilibrium thermodynamics what you are doing here...