# Thermodynamics: Introduction & Basic Concepts

Subject : Thermodynamics
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#### **Thermodynamics**

It is the science of energy transfer (particularly "heat" and "work") and its effect on physical properties of substance.

#### Thermodynamic System, Surrounding and Boundary

A thermodynamic system or simply a system is defined as a specified region in space or quantity of matter chosen for studying thermodynamics.

The real or imaginary surface that separates the system from its surrounding is called as boundary. It may be fixed or moving.

The region immediate outside the thermodynamic boundary is called as surrounding.

System and Surrounding put together is called as universe.

#### Microscopic and Macroscopic Approach to study thermodynamics

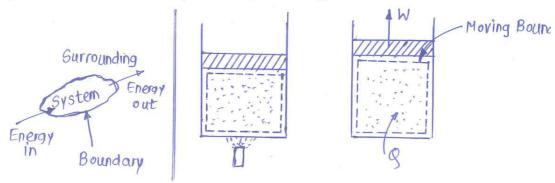
In Engineering, macroscopic approach is used wherein whole system is analysed in bulk without looking it on molecular level. E.g. pressure of the system can be measured by using a pressure gauge. Such a study is also called as "Classical Thermodynamics".

Microscopic approach is a more elaborate approach based on average molecular behaviour of large group of individual particles of system. Such a study is also called as "Statistical Thermodynamics".

# **Types of Thermodynamic Systems**

#### 1. "Closed system" or "Non-flow system"

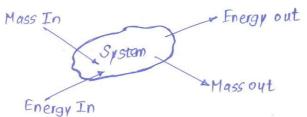
It consists of fixed amount of mass and no mass can cross its boundary i.e. no mass can enter in or leave a closed system, but energy in the form of heat and work can cross the boundary. E.g. Gas enclosed in valve less cylinder and piston arrangement.



Here, energy in the form of heat enters & energy in the form of work leaves the system. There is transfer of energy, but no transfer of mass i.e. mass is fixed. Therefore it is also called as "Control mass" system. Volume of closed system does not have to be fixed.

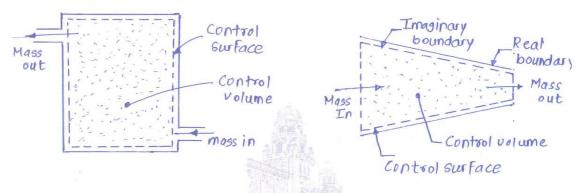
## 2. "Open system" or "Flow system"

Here energy as well as mass transfer takes place.



Thermodynamics of "Flow devices is best studied by selecting the region within the device as "Control Volume".

The boundary of a control volume is called as "Control Surface". It may be real or imaginary.



<u>Examples of open system:</u> - Almost all engineering applications like Compressor, Car radiator, Turbines, Condensers, Nozzles, Diffusers, Heat exchangers etc.

#### 3. Isolated System

The system in which neither mass nor energy transfer takes place is called as isolated system. E.g. Thermos-flask

### Thermodynamic property

Any observable macroscopic characteristic of a system by which its physical condition may be described is called as a "Thermodynamic Property".

These are of two types:

## 1. Intensive Properties

These are independent of mass in the system. E.g. Pressure, Temperature, Density etc.

#### 2. Extensive Properties

These are dependent on mass in the system. E.g. Mass, Volume, Enthalpy, Entropy, Internal energy etc. If the mass is increased, value of extensive property increases.

Specific extensive properties i.e. extensive properties per unit mass are intensive properties.

Examples:

- (i) Specific volume =  $v = \frac{V}{m}$
- (ii) Specific enthalpy =  $h = \frac{H}{m}$
- (iii) Specific entropy =  $s = \frac{s}{m}$
- (iv) Specific internal energy =  $u = \frac{U}{m}$

Properties are co-ordinates to describe state of system i.e. they are state variables.

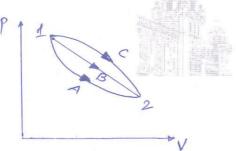
Any operation in which one or more of the properties of a system changes is called "Change of State".

The succession of states passed through a change of state is called the "Path" of change of state.

When the path is completely specified, the change of state is called a "Process". E.g. Constant pressure process.

A series of "change of states" such that the final state is same as the initial state is called as a "Thermodynamic Cycle".

Path function



From the above figure it is clear that, we can take the system from state point ① to state point ② via path A, B or C.

Since area under curve represents the work for each process, the work involved in each case depends on the path, the system follows in going from state ① to state ②.

Hence "Work is a path function" and therefore an inexact differential.

$$W_{1-2} = \int_{1}^{2} \delta W \neq W_{2} - W_{1}$$

#### Point function

"Thermodynamic Properties" are point functions, since the change in the "property" of a system in a "Change of state" is independent of the path the system follows during the "change of state", and depends only on initial and final states. For a given state, there is a definite value for each property. The differential of point function are exact.

$$\int_{V_1}^{V_2} dV = V_2 - V_1$$

Likewise, change of pressure, temperature etc. depend only on end states and not on the path followed by the system.

For a cyclic process, the final state is same as initial state hence change in any property is zero i.e. cyclic integral of property is always zero

$$\oint dV = 0$$
,  $\oint dT = 0$ ,  $\oint dP = 0$ 

# Thermodynamic equilibrium

It means complete equilibrium i.e. the system should obey

# 1. Mechanical Equilibrium

It means absence of any unbalanced force within the system and also between system and surrounding.

# 2. Thermal Equilibrium

It means temperature at all points in the system is constant.

# 3. Chemical Equilibrium

It means there should not be any chemical reaction within system.

# Quasi-static Process

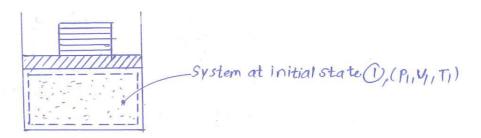
When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times, it is called as Quasi-static or Quasi-equilibrium Process.

It can be viewed as sufficiently slow process that allows the system to adjust itself internally so that properties in one part of system do not change any faster than those at the other parts.

#### Examples:

(i) Very slow compression of gas enclosed in a cylinder.

(ii)



If the entire weight is removed instantly the system will reach final state 2 following the path composed of non-equilibrium states.

But, if very small part of the entire weight is removed and time is allowed for the system to attain equilibrium, then slowly the system reach final state 2 following the path composed of equilibrium states.

# Significance

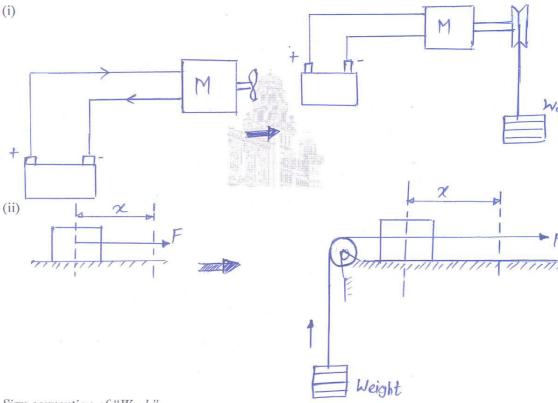
- (i) Easy to analyse.
- (ii) Work producing devices deliver the most work when they operate on quasi-static process.

Therefore, quasi-static process serves as standard to which actual process can be compared.

# Thermodynamic work

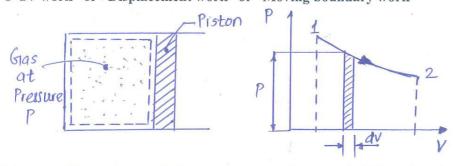
As per thermodynamics, "Work is said to be done by the system if the sole effect on things external to the system can be reduced to the raising of weight.

## Examples:



- Sign convention of "Work":
- (i) Work done by the system = "+ve", e.g. Expansion.
- (ii) Work done on the system = "-ve", e.g. Compression.

"P-dV work" or "Displacement work" or "Moving boundary work"



Let us consider a piston cylinder arrangement, wherein a fluid is undergoing a quasi-static expansion process.

Due to its pressure (P), fluid will exert a force (F) on piston face of area (A).

$$F = P \times A$$

Due to this force piston will be displaced by a small amount 'dx'.

Work = 
$$\delta W = F \cdot dx$$
  
=  $P \cdot (A \cdot dx)$   
=  $P \cdot dV$ 

Total work in moving the boundary can be obtained by integrating above equation.

$$W_{1-2} = \int \delta W = \int_{V_1}^{V_2} P dV \dots (A)$$

Above work is also called as Expansion or Compression work.

Equation A is valid only for closed system.

Equation A also reveals that area under process curve on a P-V diagram is equal in magnitude to the work done during a quasi-static expansion or compression of closed system.

## Heat

It is form of energy that is transferred across the boundary by virtue of temperature difference.

Heat flow into the system is taken as positive and heat flow out of the system is taken as negative.

A process in which no heat crosses the boundary of the system is called as an adiabatic process.

Heat is a form of energy in transit (like work transfer). It is boundary phenomenon

Heat is also a path function i.e. magnitude of heat transfer depends upon path followed by system during the change of state.

#### Similarities between "heat" and "work":

- (i) Both are energy interactions.
- (ii) Both are transient phenomenon (i.e. seen at boundary).
- (iii) They are not property of system.
- (iv) Both are path functions and inexact differential (i.e.  $\delta Q$  and  $\delta W$ ).

# Dissimilarities between "heat" and "work":

- (i) Heat transfer is energy interaction due to temperature difference only. All other energy interactions are termed as work transfer.
- (ii) Heat is low grade energy while work is high grade energy.

## "Reversible" and "Irreversible process"

A reversible process is defined as a process that can be reversed without leaving any traces i.e. both system and surrounding are returned to their initial states at the end of reverse process.

A process is reversible if the system passes through a continuous series of equilibrium states.

## Examples:

- (i) Frictionless relative motion.
- (ii) Frictionless adiabatic expansion or compression of gas.
- (iii) Isothermal expansion or compression.
- (iv) Extension and Compression of spring.

Process that are not reversible are called as "Irreversible process". A process will be irreversible if the system passes through non-equilibrium states.

Thus, if a system after undergoing an irreversible process is restored to initial state, it leaves a history of events in the surrounding.

## Examples:

- (i) Relative motion with friction.
- (ii) Combustion of air-fuel.
- (iii) Throttling.
- (iv) Heat transfer through finite temperature difference.

# Difference between "Reversible" and "Irreversible process"

Reversible Process	Irreversible process
(1) After reversing the process, both system	(1) Here After reversing the process some
and surrounding return to their initial state	trace is left.
without leaving any traces.	
(2) It is an ideal process.	(2) All processes occurring in nature are
	irreversible.
(3) It passes through a series of equilibrium	(3) The irreversible process is such that the
states.	change is spontaneous.
(4) Examples:	(4) Examples:
(i) Frictionless relative motion.	(i) Relative motion with friction.
(ii) Frictionless adiabatic expansion or	(ii) Combustion of air-fuel.
compression of gas.	(iii) Throttling.
(iii) Isothermal expansion or compression.	(iv) Heat transfer through finite temperature
(iv) Extension and Compression of spring.	difference.

# Zeroth law of thermodynamics

If two bodies are in thermal equilibrium with a third body, then they are also in thermal equilibrium with each other.

# Significance

It serves as the basis for validity of temperature measurement.