

# GATE / PSUs

# STUDY MATERIAL THERMODYNAMICS



THERMODYNAMICS

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# MECHANICAL ENGINEERING GATE & PSUs

## STUDY MATERIAL

# **THERMODYNAMICS**

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### **CHAPTER-1**

## **INTRODUCTION AND BASIC CONCEPTS**

#### BASIC TERMS

- → Thermodynamics: It is that branch of science which deals with conversion of energy. In other words, it is that branches of science which deals with relationship between heat and work and change in the properties
  - The four laws of thermodynamics define fundamental physical quantities such as temperature, energy, and entropy that characterize thermodynamic systems. The principal of thermodynamics are summarized in four laws.
  - Zeroth law of thermodynamic: If any body A is in thermal equilibrium with body B and C separately then B and C will be in thermal equilibrium.
  - The first law of thermodynamic: It is states that energy is always conserved; it cannot be created or destroyed. Energy is invariably conserved but the internal energy of a closed system changes as heat and work are transferred out of it or in.
  - The second law of thermodynamics The entropy of isolated system not in thermal equilibrium almost always increases and it also tells whether the particular process is feasible or not.

The third law of thermodynamic: It is states that the entropy of a pure crystalline substance at absolute zero temperature is zero.

- $\rightarrow$  There are two approaches to study the thermodynamics:-
  - (i) Macroscopic Approach {classical Thermodynamics}
  - (ii) Microscopic Approach {Statistical Thermodynamics}
- $\rightarrow$  In Macroscopic approach, the behavior of the gas is described by the net effect of action of all the molecules, which can be perceived by human senses.
  - (i) The structure of matter is not considered
  - (ii) Only a few variables are used to describe the state of matter.

The values of these variables can be measured.

- $\rightarrow$  In Microscopic approach, the behavior of the gas is described by the summing up the behavior of each molecule.
  - > A knowledge of the structure of matter is essential
  - ➤ A large number of variables are needed to describe the state of matter.

The values of these variables cannot be measured.

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 $\rightarrow$  Thermodynamics System: It is a certain quantity of matter or region in space where our attention is

for analysis.

- (i) Everything external to the system is known as the surrounding or the environment.
- (ii) The system is separated from the surroundings by the system boundary.



#### Figure: A thermodynamic system

- $\rightarrow$  Boundary: It is the real or hypothetical envelop to the system. Boundary is not included in the system. Inside boundary is system.
- $\rightarrow$  Both system and surrounding together comprise a universe.

#### **CLASSIFICATION OF SYSTEM**

- $\rightarrow$  There are 3 types of system
  - 1) Closed system
  - 2) Open system
  - 3) Isolated system
- 1) **CLOSED SYSETM:-** It is a system in which there is no mass transfer between system and surroundings and there is energy transfers in closed system.

**Example:** (*i*) Piston cylinder arrangement without any valve.



Energy transfer is in the form of mechanical work

• This system is also called control mass system.

2) **OPEN SYSTEM:-** It is a system in which both mass and energy cross the boundary of the system.

**Example:** (*i*) Piston cylinder arrangement without any valve.

- Control volume:- It is a open system where the volume remains constant.
- All open systems are not control volume but control volumes are open system.
- Boundaries of control volumes are called control surface. In control volume, boundaries are fixed (rigid or hypothetical).
- 3) **ISOLATED SYSTEM:** It is a system in which neither mass transfer nor energy cross the boundary of the system. E.g. Thermoflask
  - Thermodynamics universe is an isolated system
  - 100% heat insulation is not possible Ideal condition
  - For thermodynamic analysis of an open system, for example an air compressor as shown in figure, attention is focused on a certain volume in space surrounding the compressor, it is called control volume, bounded by a surface called the control surface.



#### Difference between the control volume and closed system:

- A closed system is a system closed to matter flow, though its volume can change against a flexible boundary.
- When there is matter flow, then the system is considered to be a volume of fixed identity, the control volume

#### **CLASSIFICATION OF BOUNDRIES**

- Boundaries can be classified in to:
  - (i) Real Boundaries (ii) Imaginary Boundaries

#### 1) Real Boundaries



#### 2) Imaginary Boundaries



- Boundaries can also i.e. classified in to:
  - (i) Rigid Boundaries (ii) Flexible Boundaries

Note: Flexible boundaries are not fixed, its keep on changing.



#### **PROPERTY OF A SYSTEM**

> Thermodynamics properties: any observable or measurable characteristics of a system is called property of a system

For e.g. : Temperature, pressure, mass, kinetic energy, volume, potential energy, internal etc.

- > These are all macroscopic in nature.
- When all the properties of system have definite values the system is said to be exist at a definite state.
- Properties are the coordinates to describe the state of system.
- Any operation in which one or more of the properties of a system changes is known as a change of state.
- The succession of states passed through during a change of state is known as the path of the change of state.

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- Process: When the path is completely specified, the change of state is called process eg. Constant pressure process.
- Cycle: It is defined as a series of state changes such that the final state is identical with the initial state as shown in fig.



A process and a cycle

The properties can be classified into two groups:

- (i) Relevant properties: Those associated with energy and its transformation.
- (ii) Irrelevant properties: Which are not associated with transformation and energy. E.g. odour, taste.

The property is a state function and not a path function. Its differential must be exact

Specific volume: It is the ratio of volume to the mass of the system is called specific property.

$$v = \frac{V}{m}$$

Molar volume: It is the ratio of volume to the mole number of the system is called molar property

eg.

$$v = \frac{V}{N}$$

- Heat and work is not a property of the system.
- Property can be classified in to two:
- 1) Intensive property : It is a property which will not depend upon the mass of the system. For eg.
  - Temperature, Pressure, density, specific internal energy.
  - > Extensive properties per unit mass, such as specific volume, is intensive properties.
  - > An intensive property is independent of the size of system
- 2) Extensive property: It is a property which will depend upon the mass (extent) of the system.e.g. Mass, volume, internal energy, enthalpy, entropy

#### **THERMODYNAMICS**

- > The value of an extensive property varies directly with the mass
- Difference between Extensive property and intensive property

Extensive property	Intensive property		
1.Its value depends on how large a portion of	1. Its value remains constant whether we		
system has been considered.	consider the whole system or a part of it.		
2. It depends on mass of system.	2. It is independent of mass of system.		
3. Energy, enthalpy, entropy, volume, area,	3. Pressure, temperature, density, thermal		
hear etc. are its examples.	conductivity and viscosity are its examples.		

If 'p' is any parameter of the system & 'dp' is an exact differential, then we can say 'p' is an property of the system.

$$\int_{1}^{2} dp = p_2 - p_1$$

Work is not a property of this system because

$$\int_{1}^{2} dw \neq w_2 - w_1$$

But pressure is a property of this system

$$\int_{1}^{2} dp = p_2 - p_1$$

State of a system: it is the condition of its existence

$$\underbrace{T_1, P_1, \rho_1, v_1}_{\text{State of this system}}$$

Phase of a system: A quantity of matter homogeneous in physical structure and chemical composition is called a phase. E.g.: Ice is phase {homogeneity in physical structure and chemical composition}

Oil in water is not a single phase system, but it is two phase system.

- Homogeneous system: A system which has got only one phase is called homogenous system.
   E.g.:- Ice, water, air
- > within the thermodynamics range of temperature, air is treated as homogenous system.

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Heterogeneous system: A system which has got more than one phase is called heterogeneous system.

e.g.: Boiling water

- > Pure substance is homogeneous and invariable in chemical composition throughout its mass.
- A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phase is the same.
- Thermodynamic Equilibrium: A system will be in thermodynamic equilibrium only if all the following three. Equilibrium satisfied:
- i) **Mechanical Equilibrium:** A system is said to be in mechanical equilibrium if there is no unbalanced force within the system if system is isolated from the surroundings.
- **ii)** Thermal Equilibrium:- A system is said to be in thermal equilibrium if there is no heat transfer within the system if system is isolated from the surroundings.
  - Temperature at every point should remain the same in thermal equilibrium, but in mechanical equilibrium, pressure at every point within the system should remain the same is not a necessary condition.
- **iii)** Chemical Equilibrium:- A system is said to be in chemical equilibrium if there is no any chemical reaction within the system when the system is isolated from the surroundings.
  - quasistatic process is a thermodynamic process that happens infinitely slowly and no real process is quasistatic. Hence in practice, such processes can only be approximated by performing them infinitesimally slowly.
  - Infinite slowness is the characteristic feature of quasi-static process
  - A quasi-static process is thus a succession of equilibrium states
  - > A quasi-static process is also called reversible process.



**Figure:** Infinitely slow transition of a system by infinitesimal force

Figure: A quasi-static process.

#### **Reversible process/ Ideal process:**

A reversible process is one which is performed in such a way that at the conclusion of the process, both system and surrounding may be restored to their initial states, without producing any changes in the rest of universe.

- A reversible process is carried out infinitely slowly with an infinitesimal gradient, so that every state passed through by the system is an equilibrium state.
- Reversible process coincides with a quasi-state process.

#### Examples

- 1. Evaporation.
- 2. Frictionless adiabatic expansion and compression process.
- 3. Electrolysis.
- 4. Frictionless relative motion
- Irreversible process / Natural process: A process is said to be irreversible, if the system passes through sequence of non-equilibrium states
- Any natural process carried out with finite gradient is an irreversible process.

#### > The causes of irreversibility:

- 1. Unrestricted friction.
- 2. Mechanical and fluid friction.
- 3. Heat transfer with finite temperature difference.
- 4. Involvement of dissipative effects.
- 5. Lack of equilibrium during the process

#### **Examples:**

- 1. Relative motion with friction.
- 2. Diffusion of gases.
- 3. Dissolving of sugar or salt in  $H_2O$ .
- 4. Plastic deformation.
- 5. Heat transfer by convection
- > Adiabatic wall: Which does not permit the flow of heat
- > **Diathermic Wall:** Which permit the flow of heat
- > Zeroth law of thermodynamics is the basis of temperature measurement.

#### **MECHANICAL ENGINEERING**

Thermometer	Thermometric Property	
Constant volume gas thermometer	Pressure (P)	
Constant pressure gas thermometer	Volume (V)	
Electric resistance thermometer	Resistance (R)	
Thermo couple	EMF (e)	
Mercury in glass thermometer	Length (L)	

Conversion of temperature unit:-

$$\frac{{}^{o}C}{5} = \frac{F-32}{9} = \frac{T-273.15}{5}$$

- The advantage of a thermocouple is that it comes to thermal equilibrium with the system, whose temperature is to be measured, quite rapidly because its mass is small.
- Thermocouple circuit is made up from joining two wires 'A' and 'B' made of dis similar metals. Due to seebeck effect, a net emf is generated in the circuit which depends on the difference in temperature between the hot and cold junctions. This emf is measure by a micro volt meter to a high degree of accuracy.



- Reverse effect of see back effect is peltier effect. Cooling and heating of two junctions of dissimilar materials when direct current is passed through then, the heat transfer rate being proportional to the current.
- Before 1954, two fixed points, the ice point and steam point, were used to quantify the temperature of a system. After 1954, only one fixed point, the triple point of water 273.16 K is used and it is the standard fixed point of thermometer.
- > Choice of metals depends largely on the temperature range to be investigated.
- Time-constant is the amount of time required for a thermo couple to indicate 63.2% of step change in temperature of a surrounding media.
- Energy of a system: After specifying the system

$$E = U + K.E. + P.E. + Electrical energy + magnetic energy + chemical energy + ----$$

$$\mathbf{E} = \mathbf{U} + \mathbf{mgz} + \frac{Mc^2}{2} + \dots$$

If temperature is more, (mgz +  $\frac{Mc^2}{2}$  + ---) may be neglected E = u

#### **Classification of energy**

- i) Stored Energy
- ii) Energy in transit
- i) Stored Energy:- It is that form of energy which is stored within the system in some form and characteristic of the system and is a property of the system stored energy will not cross the boundary of the system. Internal energy may cross the boundary in the form of heat.
- > Potential energy, kinetic energy, internal energy, chemical energy are property of the system.
- ii) Energy in transit:- It crosses the boundary of the system during a thermodynamic process, it is not a property of the system.
- Work: work is an energy in transition which crosses the system because of the difference in a property different from temperature.
- Work is a path function since it depends up on the path.





Clockwise cycle gives positive work or work done by system and negative work represented by the counter clockwise cycle means work is done on the system.



Mechanical work:- Work is said to i.e. done when point of application of a force moves by a distance 's'

 $W = F \times S$ 

Thermodynamic work:- It is said to be done when the sole effect external to the system can be reduced to lifting of a weight.

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