Basic Thermodynamics

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1 Syllabus

Subject	BASIC THERMODYNAMICS	Sub. Code	09 ME 3DC BTD
Credits	04	L-T-P	3-1-0

- 1. Introduction: History of Thermodynamics, Macroscopic V/s Microscopic View point, Thermodynamic system and Control, Thermodynamic properties, Process and cycles, Homogeneous & Heterogeneous systems, Thermodynamic Equilibrium, Quasi-static process, Pure substance, Concept of continuum,
- 2. Temperature: Zeroth Law of Thermodynamics, Measurement of temperature-the reference points, Comparison of Thermometers, Ideal Gas, Gas thermometers, Idea gas temperature, Celsius temperature scale, Electrical Resistance thermometer, Thermocouple, International Practical Temperature scale.
- 3. Work & Heat : Work transfer, *pdv*-work or displacement work, other types of work transfer, Free expansion with Zero Work transfer, Net work done by a system, Heat transfer, Heat transfer-A path function, Specific heat and Latent heat, Point to remember regarding heat, Transfer and work transfer.
- 1. First Law of Thermodynamics : First Law for a closed system undergoing a cycle, First Law for a closed system undergoing a change of state, Energy-A property of the system, Different forms of Stored Energy, Specific Heat at Constant volume, Enthalpy, Specific Heat and constant pressure, Energy of an Isolated system, Perpetual Motion machine of the First Kind-PMM1, Limitations of the First Law.
- 2. Second Law of Thermodynamics : Qualitative different between Heat and work, Cyclic Heat engine, Energy reservoirs, Kelvin-Planck statement of Second Law, Clausius'statement of the Second Law, Refrigerator and Heat pump, Equivalence of Kelvin-Planck and Clausius statements, Reversibility and Irreversibility, Causes of Irreversibility, Conditions for eversibility, Carnot cycle, Reversed Heat engine, Carnot's Theorem, Corollary of Carnot's Theorem, Absolute Thermodynamic temperature scale, Efficiency of the Reversible heat engine, Equality of Ideal gas temperature & Kelvin Temperature, Types of Irreversibility.
- 3. Entropy : Introduction, Two reversible adiabatic paths Cannot Interact each other, Clausius' Theorem, The property of Entropy, Principle of Caratheodory, The Inequality of Clausius, Entropy change in an Irreversible process, Entropy principle, Applications of Entropy principle, Entropy transfer mechanisms, Entropy generation in a closed system, Entropy generation in an open system, First & Second Laws combined, Reversible adiabatic work in a steady flow system, Entropy and direction: The second law-A directional law of nature, Entropy and Disorder, Absolute Entropy, Entropy and Information theory, Postulatory thermodynamics.
- 1. Real and ideal gases: Introduction; Vander Waal's Equation Van derWaal's constants in terms of critical properties, law of corresponding states, compressibility factor; compressibility)" chart. Ideal gas; equation of state, internal energy and enthalpy as functions of temperature only, universal and particular gas constants, specific heats, perfect and semi-perfect gases. Evaluation of heat, work, change in internal energy, enthalpy and entropy in various quasi-static processes. Ideal gas mixture; Dalton's law of additive pressures, Amagat's law of additive volumes, evaluation of properties. Analysis of various processes.
- 2. Pure substances: P-T and P-V diagrams, triple point and critical points. Sub-cooled liquid, saturated liquid, mixture of saturated liquid and vapor, saturated vapor and superheated vapour states of a pure substance with water as example. Enthalpy of change of phase (Latent heat). Dryness factor (quality), T-S and H-S diagrams, representation of various processes on these diagrams. Steam tables and its use. Throttling calorimeter, separating and throttling calorimeter.

Resources

- Thermodynamics an Engineering Approach by Yunus Cengel and Boles
- Fundamentals of Engineering Thermodynamics by Howard N.Shapiro and Maichel J. Moran
- Engineering Thermodynamics by Achuthan second edition.
- Thermal Science and Engineering Dr D.S.Kumar
- Thermodynamics is a science that deals with all aspects of energy conversion, energy exchange and energy saving by Prof A.Venkatesh
- Engineering Thermodynamics by P.K.Nag
- Video lectures by Prof Som, IIT KGP, NPTEL, www.nptel.iitm.ac.in

2 Introductory concepts and Definitions

Thermodynamics is that branch of science which deals with energy and its interactions. Much of the definitions and the quantities in thermodynamics are borrowed from various branches like physics, chemistry, Electronics, Electrical and various other fields of science and engineering. The study in thermodynamics is on energy and their interactions among the systems (machines) of importance for a Mechanical Engineering graduate.

2.1 Why thermodynamics for Mechanical Engineering students?

Here few basic examples are shown in order to give a glimpse of usage of thermodynamics for mechanical engineering students. In this course we lay down the basic fundamentals used for thermodynamic analysis as



Figure 1: Role of Thermodynamics in general use

applicable to mechanical systems. This is one region where an practicing mechanical engineering student would spend much of his time in his career and hence the importance for the subject.

2.2 Concept of system, Control Volume

Concept of system in on sense equivalent to the concept of free body diagram in Engineering Mechanics. **System** is the region in space with well defined boundary where in mass and energy interactions takes place. Simply stating "a system is a region where in the study of what ever we want can be done". The red shaded region in



Figure 2: system

Figure 2 or the broken line can be used as the boundary of the system. Well defined boundary is a necessary for defining a system as the interaction of the system either the mass or the energy usually happens across the boundary only.

Classification of systems

• Closed system or Control Mass - Mass of the system remains constant. Only Energy Transfer occurs across the boundary. In the piston and cylinder arrangement shown in Figure 3(a), the gas enclosed in



Figure 3: Closed system and Open System - Image Courtesy Howard N.Shapiro and Maichel J. Moran

the cylinder when the two values are closed is taken as system. From figure 3(a) it is observed that at this instant when the two values are closed no mass is transferred out of the cylinder. The boundaries of the

system can move, deform and also are rigid as can be seen from the figure 3(d). Figure 3(d) can also be considered as closed system at this instant of time where in there is no mass flow shown explicitly from the opened valve. In the figure 3(d) top surface (a-b) of the system does not change hence rigid, the side walls (a-d) and (b-c) the length of the boundaries deform and the bottom surface moves along with the piston which is a moving boundary.

- Open system or Control Volume Both mass and Energy cross the boundary as shown in Figure 3(b). Most of the engineering systems are open systems where in mass and energy both transfer the boundary. It is the dynamic nature of the work which creates the entire problem in the case of open systems.
- Isolated system In these kind of systems neither energy nor mass transfer the system as shown in 3(c). As the name suggests it is isolated from the external effects completely.

In analyzing the system the main interest is in identifying the properties of the system and use these properties for further energy analysis of the system.

2.3 Units and Measurements

SI units will be followed in this course, any conversions from MKS and FPS will be introduced for information sake but will not be used.

- Basic Quantities and their units
 - Mass, "M", "kg"
 - Length, "L","m"
 - Time, "t", "s"
 - Temperature, " θ ", " ^{o}C " or " ^{o}K "
- Derived Quantities
 - Force
 - Velocity
 - Stress
 - Pressure
 - Internal energy
 - Enthalpy
 - Entropy

2.4 View Points - Macroscopic and Microscopic

Any substance/matter is structured arrangement of number of molecules. The gross or over all behaviour shown by the substance is in one sense attributed the behaviour of each of the molecule taken by some average. For example the pressure exerted on any surface is the due to the force exerted (momentum exchange) by the molecules on the surface of interest per unit area. If we could measure the pressure and attribute a number to that measurement, then the number represents some kind of average value taken representing the cumulative effect of all the molecules. This average pressure is the quantity of interest in **Classical Thermodynamics**. This view point of the pressure is Macroscopic in nature. It gives the average picture sof the property of interest. The other view point which reflects the properties on statistical basis is Microscopic view point, and need statistical techniques to analyze the property.

2.5 Property, State and Process

Property:- A macroscopic or observable characteristic of the sytem is called a property of system. A property is any qunatity which depends upon the state. Hence, it is also called "**Point Function**". Mathematically it can be written as

$$\int_{1,A}^{2} d\phi = \int_{1,B}^{2} d\phi \text{ or } \oint d\Phi = 0 \tag{1}$$

Properties are further divided into a) Primitive - not defined in Thermodynamics or borrowed from other branches of science b) Thermodynamically defined - defined in Thermodynamics c) Mathematically derived properties. The following list will illustrate few properties of interest

- 1. Mass Defined in Mechanics
- 2. Pressure Basic Definition given in Mechanics
- 3. Temperature To be defined in Thermodyanamics
- 4. Viscosity- Defined in Fluid Mechanics
- 5. Thermal Conductivity -
- 6. Enthalpy- To be defined in Thermodynamics
- 7. Entropy To be defined in Thermodynamics
- 8. Velocity- Defined in Mechanics
- 9. Elevation Defined in Physics
- 10. Electric restivity Defined in Electrical science.

These properties are further classified into

- Intensive Properties Those properties which are independent of mass or expressing in other way, Let ϕ be any property of the system, if the system is divided into "N" sub-regions then if $\phi_i, i = 1, 2, 3 \cdots N$ is the property of the "N" subsystems then $\phi_1 = \phi_2 = \phi_3 = \cdots \phi_N$ if ϕ is an intensive property. Example:- Consider a hot body whose temperature (Though not defined yet) is say 60°C. The temperature of the body remains at 60°C even if the body is cut into number of parts.
- Extensive Properties Those properties which are dependent on mass of the system. Let ϕ be any property of the system, if the system is divided into "N" sub-regions then if $\phi_i, i = 1, 2, 3 \cdots N$ is the property of the "N" subsystems then $\phi = \phi_1 + \phi_2 + \phi_3 + \cdots + \phi_N$ if ϕ is an extensive property. Examples:-Mass,Volume,Energy etc,.



Figure 4:

- **Specific Properties:-** Extensive properties per unit mass are called specific properties. These properties are independent of mass hence are intensive but not in a true sense. The adjective specific generally denotes mass basis and Molar denotes mole basis. Ex:- Specific volume is Volume per unit mass. Molar Volume:- Volume per unit mole.
- State Space:- A geometric space constructed with independent properties as axis is known as state space. State:- It refers to the condition of the system as described by a point by the independent properties in a state space. At a given state all the properties of the system have constant vlaues.

In graphical sense, a point in the space denoted by properties is called a state as shown in Figure 4(a) where X1, X2, X3 be any property of the system under consideration. A state can be specified by few sub set of properties and all other properties are evaluated from the prescribed sub set. The number of properties required to fix a state is given by **State Postulate**.

A change in property of the system results in change in state of the system as shown in Figure 4(b). The values of the system at two different states are not dependent upon the process it has taken to arrive at that two systems. The change in property of the system between two systems is independent of the process it has followed to arrive at that state. Hence the change in property only depends upon the end states. Other wise if the value of the property changes and it is dependent upon the way it has been taken from one state to other then it is not called property of the system

Process :- The sequence of changes in the state of the system is known as process as shown in Figure 4(e). A particular case of process where in the initial and final states are same is known as **Thermodynamic cycle** or **cyclic process**. When a system executes a cyclic process then there is no change in state of the system.

• Equilibrium:- From physics or engineering mechanics point of view equilibrium is kind of balance of all the forces acting on the body under consideration. Mathematically represented by $\sum_i \vec{F_i} = 0$. We can consider two chemically reacting substances before and after the reaction process. The chemical compounds are individually in a certain state or different chemical substances before reaction taking place, once the reaction is complete there will be no change in chemical constituents and the final product will be in a different state. If we observe carefully in both the cases mechanical and chemical change occurs in the state if unbalance of some form is present.

Similarly if a system is at a state, it means that there are no changes that can take place in the system. In other words there are no driving forces whatever so may be, to modify the state of the system. Now we define the term "**Thermodyanamic equilibrium**" which is of much importance in the analysis of thermodynamic systems. A thermodynamic system or simply system is in equilibrium if and only if it is in mechanical, chemical and all other sorts of equilibrium. This means that if a system assumes a state means that the system is in thermodynamic equilibrium.

• Continuum:- The properties in thermodynamics are all functions of both space and time. Let $\phi(\vec{r},t)$ is a property under consideration, where $\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$ is position vector of the state and "t" is the time. The control mass and control volume or the region of interest is a continuus space. We now ask the question, "What would be the smallest amount of control volume or the region in space, that we consider so that the property $\phi(\vec{r},t)$ behaves as a continuus function?". Let us take up and example and define the process of continuum. Consider the definition of density



$$\rho = \frac{dm}{dv} = \lim_{\Delta v \to 0} \frac{\Delta m}{\Delta v} \tag{2}$$

where Δv is the elemental volume of the region under consideration and Δm is the mass inside that elemental volume. If we plot the variation of ρ w.r.t Δv , in the limiting process we can observe that with in certain range of values of Δv , the value of ρ remains constant and apart from this range the value is found to be either oscillating or it takes up a value but varies. This region where in ρ takes a constant value is called continuum.

• Pure Substance

• Quasi-Static Process Consider piston cylinder arrangement and its corresponding state space diagram as shown in Figure 5(a), several known weights are mounted on the piston and the force due to these weights is exactly balances by the pressure exerted by the gas inside the cylinder.



Figure 5: Quasi static process

The system is in equilibrium and is represented by the unique value of pressure and volume as represented in the state-space of Figure 5(a), consider this as state 1. If one of the weights is removed then the equilibrium gets disturbed, the piston moves up due to the force exerted by the pressure and finally reaches another equilibrium state 2 as shown in in Figure 5(b). The process by which it reaches state 2 from state 1 is not well defined because we can't measure properties during which the changes are taking place, hence it is represented as dotted line in Figure 5.

It can be observed that the initial state 1 and final state 6 can be acheived in two different ways

- by removing all the weights at once.
- by gradually removing the weights (each weight at a time).

In both the cases the initial and final states are the same. Carefully observing the second process it is clear that upon removal of each weight the system attains a new equilibrium state and gradually reaches state 6. All of the intermediate states are also in equilibrium in the second process. Comparing the two processes it can be observed that the second process is a gradual change between two states and can be visualized between any two processes, for example even between state 1 and state 2, it can be assumed to be consisting of a cylinder and piston arrangement with infinitesmal masses δm and this arrangement can be taken between two states and as each infinitesmal mass is removed a new state is attained.

2.6 Basic Conservation Laws

These are the basic conservation laws which are to be satisfied.

2.6.1 Mass Conservation

Mass is neither created nor destroyed. It is also known as control mass, because the mass inside the system is not changing with respect to time.

$$\dot{m} = \frac{dm}{dt} = 0 \tag{3}$$

$$m = (\rho dv) \text{ for an elemental control volume}$$
(4)

$$\dot{\rho}dv = \frac{d\left(\rho dv\right)}{dt} = \rho \frac{dv}{dt} + \frac{d\rho}{dt}dv = 0 \tag{5}$$

$$\Rightarrow \frac{d\rho}{dt}dv = 0 \tag{6}$$

for entire control volume
$$\int \frac{d\rho}{dt} dv = \frac{d}{dt} \int \rho dv = 0$$
 (7)

2.6.2 Momentum Conservation

Its is the Newton's second law of motion. "The rate of change of linear momentum is equal to the net force acting on the body".

2.6.3 Energy Conservation

"Energy is neither created nor destroyed".