

Lecture 1. Introduction

Thermodynamics is the science that is concerned with the study of the changes in “state” of a chosen system from one static equilibrium situation to another, due to its interactions with its surroundings.

Engineering thermodynamics studies energy transformations and interactions and the way that they can be employed in a useful manner by humankind.

There are several approaches to present and study thermodynamics, most of those approaches complement each other (statistical thermodynamics, rational thermodynamics, general thermodynamics, etc).

We will focus on Engineering Thermodynamics, which is basically a formulation of “Classical Thermodynamics” in engineering terms, and more exactly in Mechanical Engineering terms (there are Chemical Engineering presentations where the emphasis is on properties, relations among properties, reactions, etc.).

1 Basic Concepts and Definitions

1.1 Thermodynamics System

Thermodynamics deals with interactions and for an interaction to occur we need at least two entities (a system, and what is outside of the system (i.e. the rest)).

- A **System** is a collection of matter or region of space being subject to analysis.

The **environment** or **surroundings** of a system are collection of matter or region of space that resides outside the system.

The system and the environment are divided by a surface called system **boundary**, and it is through the boundary that interactions (of mass, work, heat) take place.

Remarks:

-System is simply a chunk of matter bounded by some surface. The matter can have solid, liquid or gaseous forms. The surface may be associated to a "real surface" or it may be imaginary, like the boundary of a certain mass of liquid as it flows along a pipe. The boundary surface does not need to be constant in shape or volume.

- The system (being the entity of study) is selected by the analyst! and such a selection can significantly influence the complexity of the problem in hands. (We will see this later with some examples).

- The system boundary is a **surface**, it does not have any mass, the system and its surroundings are in contact at the boundary. (We will explain why this is important when we study entropy transfer).

What do we mean by defining a system?

To define a **system** means to define the system **boundary**, its **environment** and the system itself.

Interactions:

Interactions may be of the nature of:

ENERGY:

1) Work interactions: Work done on the system by the surroundings or work done by the system on the surroundings.

2) Heat interactions: energy transferred from the system in the form of heat the surroundings or vice versa.

MASS:

Mass interactions: mass coming in and out of the system.

All other interactions: electromagnetic processes, chemical reactions, nuclear reactions, etc.

Classification of systems

- Isolated system: A system whose boundary is impermeable to all kind of interactions. No mass or energy cross the system boundary.
- Closed system: A system whose boundary is impermeable to mass. There are no mass interactions between the system and its environment. A closed system is also know as **control mass**.
- Open system: A system whose boundary allows interaction of both mass and energy. It is also know as **flow system** or **control volume**. When talking about **control volume** the system boundary is called **control surface** and the regions where the mass crosses the boundary are referred as **ports** (inlet and outlet ports).

Continuous or macroscopic description:

Matter (gas, liquid or solid) considered as continuously distributed (ignoring the discrete particle structure of matter) is known as a continuum or continuous medium. This implies that the measurable average properties such as density (mass per unit volume) can be defined satisfactorily and that they are uniform (have the same values) for each element under consideration. Such a description is usually know as macroscopic or bulk or continuum description (as opposed to a particle description).

Thermodynamics State and Thermodynamics Properties

When we study a system, we need to be able to define how the system is at particular time. The condition of the system is called **state**. The state of a system is described by a set of quantities called thermodynamic **properties**.

Think of a cartesian three dimensional space with x, y and z denoting its axis. Imagine that every point in that space defines a state. If at a particular time, we know where in the space we are located, we know the condition (the state) in which the system is at that particular time.

A point in the space can be defined by a set of quantities (3 in this case: (x,y,z)). The coordinates in this example are associated to properties.

REMARKS:

- Not every quantity we deal with in thermodynamics is a thermodynamic property and not every set of properties define a thermodynamic state.
- Thermodynamic properties are quantities whose numerical value does NOT depend upon the history of the system.
- Quantities that depend upon the history of the system (i.e. the way how the system arrived to its current state) do NOT qualify as properties.
- Examples of thermodynamic properties: pressure, temperature, energy, volume, enthalpy, entropy, Gibbs free energy.
- Examples of quantities that we deal with in thermodynamics that are NOT properties: heat transfer, work, entropy generation.
- If we know the value of all thermodynamic properties of a system we know the state of the system. Fortunately, not all properties are independent, and we don't need to measure all of them.

There are two classes of properties: extensive and intensive. Extensive properties depend on the size of the system; for example: mass, volume, energy. Intensive properties do not depend on the size of the system; examples are temperature, pressure, and specific properties. Specific properties are formed by dividing an extensive property by the mass of the system. Examples of specific properties are: Specific volume is equal to the volume of the system divided by its mass, similarly, specific energy is the total energy divided by its mass.

It is common practice to use lower case letters to denote intensive properties (with exception of the temperature, T), and upper case letters to denote extensive prop-

erties.

Phase (Solid, liquid, gas), do not confuse with state.

Process

Change undergone by a system from an initial state to a final state.

To know the process means to know the end states (initial and final) and the **interactions** experienced by the system.

The **Path** of the process is the history or the succession of states followed by the system from the initial to the final state.

Changes in quantities that are properties do not depend on the path.

- properties (not path dependent).

-Not properties (path dependent).

A **cycle** is a special process in which the initial and final states coincide.

Suggested readings and references:

1. Adrian Bejan (Duke University). Advanced Engineering Thermodynamics. Wiley, 1988. Used as textbook for graduate level Engineering Thermodynamics.
2. K. Karamcheti. Lecture notes.
3. Ernest G. Cravalho and Joseph L. Smith, Jr. (MIT) Engineering Thermodynamics. 1992. Used as textbook for undergraduate Thermodynamics.

Lecture 2

More on thermodynamic properties...

For a system consisting of a given mass of a **pure substance** the following variables are most often encountered in thermodynamics:

Pressure	P
Volume	V
Absolute temperature	T
Internal Energy	U
Enthalpy	H
Entropy	S
Helmholtz Function	A
Gibbs function	G

It is an experimental fact that the state of a homogeneous system is fixed when two properties are fixed. Thus, with exceptions of cases of change of phase, any two variables may be chosen as independent, leaving the other as dependent. The existence of a functional dependence is one of the postulates of thermodynamics. The particular function for a particular substance must be determined by experiment. In theoretical analysis, however, it is always possible (for example) to write $V(p,T)$ to indicate that the volume is to be considered as a function of pressure and temperature. The choice of independent variables is purely a matter of convenience, and transformation to other independent variables is often done.

Because of the ease in measuring them, pressure and temperature are frequently chosen as independent variables, so that experimental data may lead to tables or empirical expressions for such concepts as volume, internal energy, entropy, as functions of pressure and temperature. In other words, if the functions $V(p,T)$, $U(p,T)$, $S(p, T)$ are considered known, and if it is desired to compute for example the function $U(s,v)$, then

the mathematical procedure is to solve the two simultaneous equations

$$S = S(p, T)$$

$$V = V(p, T)$$

and obtain the p and T in terms of s and V . These values of p and T are then substituted into the given expression $U(p, T)$ to give $U(s, V)$ as required. The importance of mathematics in the study of thermodynamics cannot be overstressed.

References:

K. Karamcheti, lecture notes.