2. Fundamental Concepts

The concepts and definitions in these lecture notes[1] are indispensable. Definitions that follow are the basic building blocks of thermodynamics. One cannot learn to read or write without knowing the alphabet; similarly, one cannot learn to practice engineering without knowing the basics, no matter how simplistic or redundant. For this reason, the material should be memorized (like the alphabet) and reviewed habitually by the student so that the full significance of each definition or concept can be thoroughly understood.

2-1. The System. Thermodynamics (and most engineering studies) involve the study and understanding of change or transformation on a device or body which may be a component or subsystem of a larger, more complex entity. Before a change can be analyzed, it is essential that the participants - mass and energy - be known and included in the analysis; therefore, the region under study must be defined:

The system is a specified region, not necessarily of constant volume, where transfers of energy and/or mass are to be studied.

Since both mass and energy may be added to or removed from the system, an especially important concept is the boundary, or limits, of the system:

The boundary is the actual or hypothetical envelope enclosing the system.

This logically leads to the thermodynamic definition of the surroundings:

The surroundings is the region outside the system.

All mass and energy transfers are evaluated at the boundary. The boundary may be either fixed or elastic if the system is allowed to expand or contract.

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[1] These notes are taken from Obert, E., G. Gaggioli, Thermodynamics, McGraw Hill Book Company, New York (1963); Wylen, G., R. Sonntag, Fundamentals of Classical Thermodynamics, Wiley Book Company, New York (1976); Obert, E., Thermodynamics and Heat Transfer, McGraw Hill Book Company, New York (1962), and modified to reflect currency, SI units, etc.

Systems may exist with or without the transfer of mass. Thus:

A closed system is a specified region where transfers of energy without the transfer of mass are to be studied.

A closed system is a region of constant mass. The closed system may be at rest or else moving relative to the observer. A closed system may be isolated from the surroundings, thus the system is considered isolated:

An isolated system cannot transfer either energy or mass to or from the surroundings.

The isolated system is therefore constrained to a fixed volume since the boundary cannot move and perfectly insulated having fixed energy content.

In a more general sense mass often crosses the system boundary. Most engineering systems are open:

An open system is a specified region where both transfers of mass and energy are to be studied.

The mass within an open system may or may not be constant. In some texts the open system is called a "control volume".

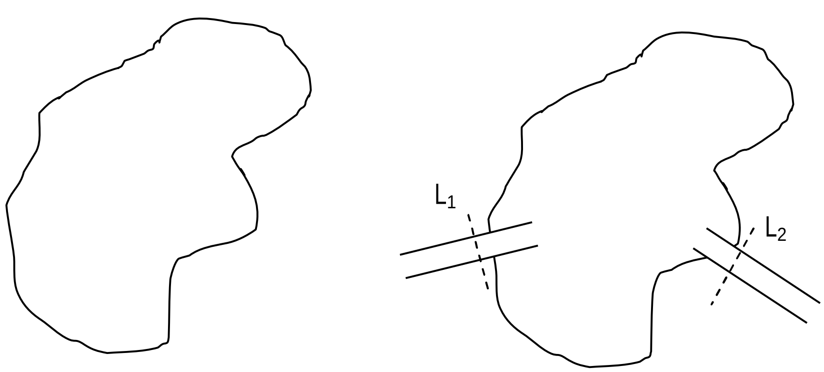

Figure 2-1. (a) Closed and (b) open systems.

In the open system of Fig. 2-1ib, note that the boundaries where mass (and the energy accompanying mass) enters or leaves the open system are fixed relative to one another and denoted by L_1 and L_2. Nothing restricts the number of entrances or exits. Other fixed-position coordinates L can also be located, if desired. The enclosing walls between L_1 and L_2 are not necessarily stationary, and through this enclosing surface energy (but not mass) can pass by conduction or radiation, or by expansion of the walls, or by a rotating shaft, or by flow of electrical energy, etc. Through the entrance flow boundary at L_1 (or L_2) energy enters (or leaves) the system in direct proportion to the mass which crosses the boundary.

The Independent Variables of Time and Position. Time and position are independent variables chosen at discretion and are not direct functions of other thermodynamic variables. In the analysis of a closed system the variable time is of essence. The initial and end states are of critical importance. Position within the system is irrelevant because analysis is of the system as a whole. This simplistic but essential fact means that what happens within the system is not important. What happens during the time interval from t1 to t2 is essential.

In the analysis of an open system however, both time and position are of essence however the only position of interest is at the system boundary. The question "What happens at the system boundary?" is critical. What happens within the system is irrelevant. Thus judiciously selecting the boundary is important. When an open system is at steady state (mass entering the system equals mass leaving the system and the change in energy within the system is not a function of time) then position is the only independent variable. In the most general case, when the change in mass or energy within a system is not constant but a function of time then both time and position become independent variables. Still, what happens within the system in any case is not important; what happens at the system boundaries (a function of both time and position) is of essence.

2-2. Homogeneous and Heterogeneous Systems. A quantity of matter, homogeneous throughout in chemical composition and in physical structure, is called a phase. Homogeneity in chemical composition does not imply a single chemical species, for a mixture of gases or a solution is a phase. Homogeneity in physical structure specifies that the material is all gas, all liquid, or all solid. A system of water and its vapor (steam) contains two phases: a gas and a liquid phase. In all instances, phase signifies no abrupt change in either chemical or physical characteristics. A system comprising a single phase is called a homogeneous system, while a heterogeneous system consists of more than one phase.

2-3. Components, Constituents, and Pure Substances. The chemical species making up a phase or a system are called either components or constituents. The names are synonymous when chemical changes are not present.

In these notes, the name pure substance describes a substance with essentially one chemical structure (and, in general, molecular structures will be studied). Note that a heterogeneous system of one or more phases of a pure substance will be uniform throughout in chemical composition:

A pure substance is a particular chemical species.
(One-component system of one or more phases)

The elements O_2, N_2, He, Ar, etc are obviously pure substances. No change in temperature will change the chemical composition (except at very high temperatures when they may become plasmas, but this is beyond the discussion here). Air can also be considered pure *at reasonable temperatures and pressures* since the constituents of air (primarily N_2 and O_2) are mixed thoroughly and behave as a homogeneous pure substance. At low temperatures however the gases begin to condense thus changing the chemical composition. This is also true at extremely low pressures where single molecules of N_2 or O_2 affect the behavior of the component gas.

2-4. Equilibrium. The equilibrium of a mechanical system is a condition of balance maintained by an equality of opposing forces. Thermodynamic equilibrium, however, is a broader concept since it includes not only mechanical forces but also "forces" arising from thermal, electrical, chemical, and other influences. Each kind of influence on the system dictates a particular aspect of thermodynamic equilibrium: thermal equilibrium requires an equality of temperature; mechanical equilibrium requires an equality of stresses (including pressure); electrical equilibrium requires an equality of electric potentials; phase and chemical-reaction equilibria require an equality of chemical potentials. Thus thermodynamic equilibrium is complete equilibrium:

A system in thermodynamic equilibrium is incapable of spontaneous change even after being subjected to catalysts or to disturbances; it is in complete balance with the restraints of the surroundings.

Consider again the examples presented earlier. The gasoline -air mixture in the cylinder is in mechanical equilibrium when its pressure is constant throughout and balanced by an opposing force in the surroundings. Similarly, the mixture is in thermal equilibrium when its temperature is constant throughout and balanced by an equal temperature of the surroundings. On the other hand, the gasoline -air mixture is not in stable chemical equilibrium since a small spark may cause combustion or a violent explosion. Here it seems logical to conclude that, since latent chemical energy was released by a small disturbance (the spark), a chemical "force" must also have been lying dormant in the mixture.

The absence of chemical equilibrium may be an unimportant detail of a particular problem. For example, suppose the problem is to find the variation of pressure with temperature (at constant volume) of a specified mixture of CO, CO_2, and O_2. If this system of fixed constituents is said to be in equilibrium, it is implicitly understood that only pressure and temperature equilibria are designated. Alternatively, such systems can be specified to be in unstable or metastable equilibrium to warn that complete equilibrium is not present—to warn that the system could change spontaneously:

A system in balance with the restraints offered by the surroundings may be in stable or unstable equilibrium. The equilibrium is unstable if the system could change spontaneously, after being subjected to an appropriate disturbance.

2-5. Property, State, and Process.

Consider an isolated system in equilibrium. Here energy or mass transfers with the surroundings are absent, since the system is isolated, and gradients in temperature, pressure, composition, etc., are, in general, absent, since the system is in equilibrium. The system, however, would have many other characteristics, more or less observable, such as its mass, physical composition, pressure, temperature, volume, surface area, electrical potential, etc. In addition, a host of other characteristics could be defined[2] or else indirectly measured[3]. All these characteristics have different dimensions and are the variables called internal, or thermostatic, properties:

An internal, or thermostatic, property is a characteristic of the matter within the equilibrium system.

Thus, the class of variables called internal, or thermostatic, properties is restricted, arbitrarily, to those characteristics of the physical and chemical structures of matter exhibited in equilibrium systems; gradients in these properties and energy or mass transfers with the surroundings are therefore not properties.

Intensive properties are independent of the mass of the system.

Examples of intensive properties are pressure, temperature, viscosity, velocity, height, etc.

Extensive properties are related to the mass of the system.

Examples of extensive properties are volume, energies of all kinds, surface area, etc. Specific[4] values of extensive properties, that is, values per unit mass, can also be called intensive properties.

The system can be described or measured at each instant of time by its properties. Each unique condition of the system is called a state:

State is the condition of the system at an instant of time as described or measured by its properties.

Thus, state denotes not a change but particular values of the properties at one instant of time.

The system can pass from one state to another state or undergo energy or mass transfers at a steady state by a process:

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[2] For example, the temperature divided by the pressure is a characteristic.

[3] Chemical composition, internal energy, electrical and thermal conductivity, etc.

[4] Specific volume, specific internal energy, etc. In the following pages, specific values are most often implied, although the prefix specific will not always be shown (except, invariably, for specific volume).

A process occurs whenever the system undergoes either a change in state or an energy or mass transfer at a steady state.

Experimental observations show that functional relationships exist among all thermostatic properties; this postulate is the rightful Zeroth Law of Thermodynamics:

A thermostatic property is a function of other thermostatic properties: it is not necessary to specify the value of all thermostatic properties to fix the internal, or thermostatic, state of an equilibrium system.

On the other hand, the mechanical properties are not functionally related to each other or to the thermostatic properties. No function can be proposed, for example, that would enable the kinetic energy to be calculated from specified values of potential and internal energies. This difference between the external and internal properties of a system arises because the mechanical properties of velocity and elevation have been arbitrarily superimposed upon the system and declared to be independent by definition.

An independent property, as the name implies, is one that can be arbitrarily assigned a value. For example, water at constant pressure can be heated from the freezing point to the boiling point. Within this range, both temperature and pressure can be assigned values at will— each is an independent property. When the water boils and two phases are present then only one of these two properties can be an independent variable (and the other is called a dependent variable), because the value of one fixes the value of the other. Also, some properties are dependent on other properties by definition. For instance, the specific volume v is defined as the reciprocal of the density ρ hence specific volume and density are not independent.

It follows from the definition of state that each thermostatic property can have but one value at each state (since state fixes the physical and chemical structure). The mechanical properties have this same quality (since state fixes specific values to both kinetic and potential energies). Therefore, all properties are state functions:

A property has a single value at each equilibrium state - it is a function of the state.

To recognize that a variable is a property, one of the following tests can be applied:

1. *A variable is a property if, and only if, it has a single value at each equilibrium state.*

2. *A variable is a property if, and only if, its change in value between two equilibrium states is independent of the process (is single-valued).*

3. *A variable is a thermostatic property if, and only if, it is a function of other thermostatic properties.*

Examples of thermostatic properties include temperature T, pressure p, volume V, specific volume v, and yet to be defined internal energy U. To illustrate the concept of property, a number of new properties will be defined (and their usages left for future development) that are combinations of other properties . Enthalpy is defined as

$$H = U + pV$$

or, per unit mass,

$$h = u + pv$$

The properties c_p and c_v are defined only for chemically inert systems,

$$c_p \equiv \left.\frac{\partial h}{\partial T}\right|_p$$

$$c_v \equiv \left.\frac{\partial u}{\partial T}\right|_v$$

The property k is simply the ratio

$$k = \frac{c_p}{c_v}$$

These examples are properties because they are single valued, their values are independent on the process, and they are functions of other thermostatic properties.

Properties fix the state and a process occurs when the system undergoes a change of state. When a sequence of processes occurs that produce a desirable (or otherwise) result and these processes can be repeated continuously then the system is said to have undergone a cycle.

A cycle occurs when the system undergoes a sequence of processes that return the system to its original state.

Thermodynamic cycles are a major component of engineering and touch every human soul on the planet Earth. Thermodynamic cycles produce work from heat (or heat from work in the case of refrigeration and air conditioning). Automobile, truck, train, and ship engines operate on the basis of thermodynamic cycles (Otto, Diesel, Brayton cycles). Electrical power generation is based upon thermodynamic cycles (Rankine cycle). In the chapters that follow, the engineering student will begin to understand that the conversion of heat to work was the forefather of the industrial revolution and now is the crux of modern civilization.

2-6. The Zeroth Law of Thermodynamics. A fundamental postulate, in the modern world, now appearing overly simplistic, but having significance in the development of eighteenth century science, is the Zeroth Law. This postulate is of importance today as students of thermodynamics strive to learn and understand the basics. Early scientists were deeply concerned about the constituent of energy and the driving force behind energy transfer. Eventually the transfer of energy was found to be driven by a fundamental property common to two bodies exchanging energy. This fundamental dimension was and still is called *temperature:*

Temperature is the property which gauges the ability of matter to transfer energy by conduction or radiation.

Two bodies at the same temperature cannot change each other by the processes of either radiation or conduction. Since *equilibrium* means *balance* and *temperature* implies *thermal,* two bodies at the same temperature are said to be in *thermal equilibrium.* It logically follows that:

Two bodies, each in thermal equilibrium with a third body, are in thermal equilibrium with each other.

This statement is one primary component of the Zeroth Law of Thermodynamics; here it has been *deduced* from the observation that temperature is a fundamental dimension - a fundamental property.

From a broader viewpoint, the Zeroth Law implies that functional relationships tie together the properties of matter:

The properties of matter are functionally related.

This then, forms the basis of thermodynamics. Thermodynamic properties are functionally related and this relationship is represented by various analytical expressions, algorithms, graphs, figures, and data sets. Further, this interdependence is a gift that allows the scientists and engineers the ability to analyze, predict, and model real world behavior to create, invent, and improve on devices and systems that improve the existence of humankind.

2-7. Fixing and Identifying the State.

The Zeroth Law proclaims functional relationships among the thermostatic properties of equilibrium systems; such a relationship is called an equation of state. It still remains, however, to determine how many properties must be specified to fix the state and which properties, if any, serve as the preferable variables for an equation of state. The number of properties required to fix the state - the number of independent variables in an equation of state – is referred to as the State Postulate. The number of independent properties required to fix the state is a function of the number of work modes. In classical thermodynamics only one work mode is considered, that of simple compression (or moving boundary work). The State Postulate declares:

The equilibrium states of a simple system[5] are fixed by two intensive properties. For the homogeneous system, any two independent properties will suffice. For the heterogeneous system, two selected independent properties are required.

Then an equation of state can be employed involving two independent variables.

$f(p, v, T) = 0$

In its various forms, the equation above is called the pvT equation of state for liquids, gases, and solids. Observe that the number of independent thermostatic properties has been arbitrarily reduced to two, for convenience.

The ideal gas equation of state is an example of the above relationship.

$pv = RT$

where R is the specific gas constant (discussed later).

Despite its name, the relationship above is an incomplete description of the state since no knowledge of other properties is given. The internal energy, for example, must be experimentally determined and expressed in terms of two of the variables.

Also, for an overall description, a mechanical property (position, velocity, etc.) is required for each external effect superimposed on the internal, or thermostatic, state.

Consider, next, the number of variables required to identify a thermostatic system. For the equilibrium states (extensive) of a simple system, at least four properties are required:

Chemical composition
Mass
Two thermostatic properties which fix the state

This along with a physical description of the system describes the system thermodynamically along with the independent variables of time and position.

[5] In the absence of gravitational, kinetic, surface, shear strain, electrical, or magnetic effects and with constant components.