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MME 6106, Lecture 01

Basic Concepts and Definitions

Ref: J W Tester and M Modell, Thermodynamics and Its Applications.

1. The System and Its Environment

The subject of any thermodynamic experiment or study is known as the *system*, which refers to a region that is clearly defined in terms of spatial coordinates that can be in a fixed or moving frame of reference.

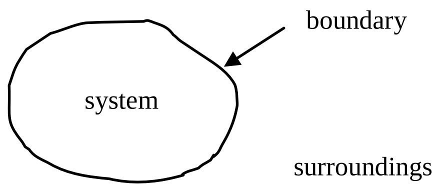

Figure 1: Subset of universe showing the system and its surroundings, separated by a boundary.

The surface enclosing this region is called the *boundary*, Figure 1. It may be an actual wall or it may be an imaginary surface whose position is defined during the experiment. The choice of boundary is often dictated by the kind of information desired. In any given situation, there are often many different system boundaries one can choose, each having some advantages and disadvantages. Developing a means for choosing those system boundaries that will result in the most tractable path to the desired information is essential.

The experiment itself may be a complete or partial process; it may be cyclic or non-cyclic. But in most cases, the initial and the final conditions will be specified in some manner. The region of space external to the system and sharing a common boundary with the system is referred to as the *environment* or *surroundings*. The system and its surroundings are jointly called the *universe*.

2. Primitive Properties and Derived Properties

Primitive properties refer to the characteristics of the system that can be determined or measured by performing a standardised experiment on the system. To ensure that the measurement is a characteristic of only the system, we require that the experiment must not disturb the system. Some of the primitive properties of a system include thermometric temperature, volume, mass, and pressure.

These properties are important because they are directly associated with the system at a particular time, and the observer need not know the history of the system to ascertain the value of the property. Thus, primitive properties are not restricted to stable equilibrium states.

Primitive properties are also useful in defining a system and in recording the occurrence of events in a system. In an *event*, at least one primitive property changes. An *interaction* is defined as events occurring simultaneously in the system and surroundings.

There are other properties of the system that are not measurable by any method but could be used to characterize the system. We will find that we can define such properties only in terms of changes in the system between initial and final stable equilibrium states. (Note that the path need not be *quasi-static*). To distinguish these properties from the primitive type, we will call them *derived properties*.

As defined, derived properties exist only for stable equilibrium states and, as such, may be used as variables to define a system as required in Postulate I.

Since derived properties are functions of state, and since any stable equilibrium state of simple systems can be characterized by the values of two independently variable properties plus the masses, any derived property can be expressed mathematically as a function of two other independently variable properties, derived or primitive.

3. Classification of Boundaries

The interactions between a system and its surroundings are governed by the nature of their common boundary. If the boundary is impermeable to mass flow, the system is called a *closed system*. An *open system* has a boundary that permits a mass flux of at least one component of the system through at least one point. In either case, the boundary may be rigid or movable.

There is one other set of conjugates needed to complete the classification of boundaries: *adiabatic* and *diathermal* walls. These boundaries represent extremes in the rate of heat exchange between the system and its surroundings. The adiabatic boundary or wall is one of the key concepts in thermodynamics, and we use it to define work and heat interactions.

The concept of the adiabatic wall evolves from our experience; it can be illustrated by conducting a series of simple experiments. Consider a closed, rigid system in which a device to measure the thermometric temperature has been placed. Surround this system with a system having a higher thermometric temperature. If the initial system were constructed from copper, the variation of the thermometric temperature with time would look like curve 1 of Figure 2. Curves 2, 3, and 4 would result if the initial system were constructed from steel, glass, and asbestos, respectively. These results are, of course, based on our intuitive understanding of the effect of declining values of thermal conductivity in going from copper to asbestos. Finally, if the container were made of a double-walled, insulated Dewar flask, the variation of temperature over the time of the experiment would be quite small (curve 5). The adiabatic wall is an idealized concept representing the limiting case of curve A in Figure 2. In practice, adiabatic boundaries are approached in many situations, especially those in which events occur rapidly in relation to the time scale of the experiment.

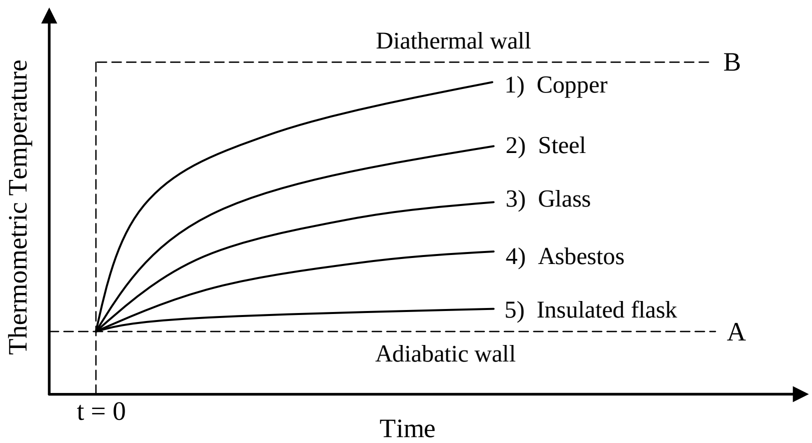

Figure 2: Temperature-time behaviour for different materials.
Limiting diathermal and adiabatic boundary behaviour shown.

The case diametric to that of adiabatic is the diathermal wall (curve B), in which the change in thermometric temperature is very rapid in relation to the time scale of the experiment (i.e., the thermometric temperature of the two systems is always identical).

In the absence of external force fields, specification of one of each of the three conjugate sets of boundaries (i.e., permeable and impermeable, rigid and movable, adiabatic and diathermal) is necessary to describe completely the external constraints placed on the system. Of the eight combinations there is one that is of particular importance. This is the system enclosed by impermeable, rigid, and adiabatic walls, called an *isolated* system. This system can have no interactions and any events occurring within this system are independent of events in the environment.

4. Simple and Composite Systems

There is a special class of systems that plays a central role in the developments to follow. These systems, referred to as *simple systems*, are devoid of any internal boundaries (adiabatic, rigid, or impermeable) and *are not acted upon* by external force fields or inertial forces.

A stable *phase* is defined as a region within a simple system throughout which all of the properties are uniform. A single-phase, well-mixed, homogeneous system is the simplest of simple systems. A system containing multiple phases is also a simple system provided that no adiabatic, rigid, or impermeable boundary exists between any two phases.

Composite systems are systems composed of two or more simple subsystems. There are no restrictions on the kinds of boundaries separating the subsystems of the composite. For example, a volume of pure water separated from a volume of salt water by a semi-permeable membrane used for reverse osmosis or hyperfiltration would be considered a composite system.

Restraints are defined as barriers within a system that prevent some changes from occurring within the time span of interest. In simple systems, restraints of interest are barriers to chemical reaction or barriers to phase change. For example, the room temperature action of hydrogen and oxygen to form water can be made to occur within milliseconds if a proper catalyst is incorporated in the system. In the absence of a catalyst, no noticeable reaction occurs within months or years. In the latter case, there is an internal restraint (the activation energy barrier) which, for all intents and purposes, prevents the occurrence of the reaction. For composite systems, internal boundaries that are adiabatic, rigid, or impermeable are also considered restraints.

Thermodynamics does not dictate the restraints that may be present in a given system. In any given situation, one must decide which restraints are present. Two factors that must be considered in making this decision are the laws of matter and the rates of the various conceivable processes. The laws of matter are comprised of three parts: (1) the continuity of matter (matter cannot move from one position to another without appearing at some time in the intervening space), (2) the conservation of electrical charge (net electrical charge must be conserved in all processes), and (3) the conservation of chemical elements (in the absence of nuclear transformations and relativistic effects, mass must be conserved). Even though process rates cannot be determined directly from thermodynamics, their magnitudes relative to time scales of interest are important in specifying tractable solution methodologies for many problems in thermodynamics.

Example 1

A closed vessel contains water, oil, and air at room temperature. If the system is synthesized by first adding the water and then layering the oil on the water, is this system a simple or composite system? If composite, define each simple subsystem and the internal restraints. If the vessel is shaken vigorously, is the system then a simple or composite system?

Solution

There are clearly no adiabatic or rigid walls within the vessel. Thus, it is only necessary to decide if there are impermeable walls. At room temperature, a system containing water and air should have appreciable water vapour present in the air. If the system is formed by layering the oil on the water without shaking, the law of continuity of matter requires that the water pass through the oil layer. This process is slow and will not occur to any appreciable extent even after several hours. If our interest in this system did not extend beyond this time scale, the oil layer would have to be considered as an impermeable barrier to the water. In this case, the vessel would be considered a composite system of two simple subsystems: air + oil (assuming oil evaporates into the air within the time scale of the experiment), and water. If the system is shaken vigorously, water droplets will contact the air directly. Thus, the entire contents of the vessel would be considered a simple system.

5. States of a System

We can characterise or identify the condition or *state* of the system by the values of those properties that are required to reproduce the system in experiments. Although this definition is functional, it is not very practical because we do not always know the number of properties that are required to specify the state of the system. We are fortunate, however, to have available a large body of experimental data, accumulated over several hundred years, which indicates that there are particular types of states that can be specified by delineating only a certain number of properties. These states are called *stable equilibrium states*. In general, non-equilibrium states can also be specified (for the purpose of reproducing them) from a finite number of properties; the number of such properties, however, is not given by the principles of classical thermodynamics.

To characterise stable equilibrium states, the following two postulates are used.

> **Postulate I:** For closed simple systems with given internal restraints, there exist stable equilibrium states which can be characterized completely by two independently variable properties in addition to the masses of the particular chemical species initially charged.
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> **Postulate II:** In processes for which there is no net effect on the environment, all systems (simple and composite) with given internal restraints will change in such a way as to approach one and only one stable equilibrium state for each simple subsystem. In the limiting condition, the entire system is said to be at equilibrium.

Postulate I, sometimes referred to as *Duhem's Theorem*, indicates that the stable equilibrium state can be characterised by two independently variable properties. By "two independently variable properties" it is meant that each property could be varied (by at least a small amount) in at least one experiment during which the other property is held constant. Since the stable equilibrium state is defined as a limiting condition toward which any simple system tends to change, it follows that no property of this state varies with time. Then, from Postulate I, once a simple system has reached a stable equilibrium state, only two independently variable properties and the masses initially charged need to be specified to determine this state completely. Since all other properties are fixed in the stable equilibrium state, it follows that all other properties of the simple system are dependent variables that are determined by the two independently variable properties and the masses of the initial chemical species. Note that this conclusion is valid for each simple system at equilibrium, even if the simple systems are part of a composite system. The conclusion, however, does not apply to the composite system at equilibrium; that is, the state of a composite system at equilibrium cannot be specified by two independently variable properties plus the masses initially charged. The difficulty arises from the fact that all properties may vary from one subsystem to another within a composite system at equilibrium. For example, the thermometric temperature of a composite system has little significance if the subsystems of the composite are separated by adiabatic, impermeable walls. Postulate I has been restricted to simple systems in order to avoid such difficulties.

Postulate II indicates that, for an isolated system, there exists one and only one set of stable equilibrium states (toward which the subsystems tend) *for a given set of internal restraints*. There will be different sets of stable equilibrium states for different sets of internal restraints. For example, with reference to Example 1.1, there will be a unique equilibrium state if we assume that there is an impermeable barrier preventing water from reaching the air space; there will also be a unique equilibrium state if we assume that no such barrier exists. Although each of these states is unique, the properties of each will be different. Thus, before the equilibrium state can be completely defined, the internal restraints must be identified. Specification of internal restraints is clearly an important part of specifying the system.

This connection between Postulates I and II will later be shown to provide the basis for deriving fundamental relationships for phase and chemical equilibria.

6. Thermodynamic Processes

A *change of state* of a system is identified by a change in the value of at least one property. For systems initially in stable equilibrium states, changes of state will occur only when the system has an interaction with the environment or when internal restraints are altered. "Change of state" is usually applied to systems that are initially in one stable equilibrium state and are found after some event to be in another equilibrium state. The change of state is then fully described by the values of the properties in the two end states.

The *path* refers to the description of all the states that the system traverses during a change of state. Thus, the path is described in terms of the primitive properties that define the intermediate states. Paths for which all the intermediate states are equilibrium states are termed *quasi-static paths*. From Postulate I, quasi-static paths of closed simple systems can be completely described in terms of successive values of only two independent properties.

It also follows from Postulate II that if a system progressing along a quasi-static path is isolated at some point (e.g., by temporarily altering a boundary condition), the values of all the properties will remain constant at the values observed just prior to isolation. It may, however, take more than two properties to describe a non-quasi-static path. If the system is isolated during such a path, some primitive properties will change after isolation as the system approaches a stable equilibrium state. For example, consider the system of a gas initially at two atmospheres which is contained in a cylinder fitted with a piston and stops. The stop holding the piston is removed, and the gas expands until the piston reaches a second stop. If the piston is lubricated, the expansion process will be rapid. At any instant during the process, there will be a finite and measurable pressure gradient within the gas phase. To describe such an intermediate state, it will be necessary to determine the pressure (in addition to other properties) at all points within the cylinder. The intermediate states are not stable equilibrium states; if such a state were isolated (by stopping the piston at an intermediate point), the pressure gradient would be damped out as the system approached a stable equilibrium state. Clearly, this frictionless process is not quasi-static. Alternatively, if there were external forces acting against the piston so that the expansion was very slow, no appreciable pressure gradient would be found. If the system were then isolated at an intermediate point, no properties would change because the system was, at all times, in some stable equilibrium state. Thus, the latter process is quasi-static.

All reversible processes are quasi-static, but the reverse is not necessarily true. A system undergoing an internally reversible process must traverse a quasi-static path. Nevertheless, an entire process is not necessarily reversible even if all subsystems traverse quasi-static paths because there may be irreversibilities occurring at the boundaries between the subsystems.

The thermodynamic process involved in a change of state usually refers to a description of the end states, the phenomena occurring at the system boundaries (i.e., heat and work interactions), and the path (which is usually described only for quasi-static processes). In many instances, however, the term "process" is loosely applied to describe the path without explicitly specifying the boundary conditions. Thus, an isothermal, isobaric, or isochoric process is one in which the temperature, pressure, or volume is constant. In such cases the boundary conditions are usually implied by the nature of the process or may be immaterial to the problem in question.