Heat And Thermodynamics

First Course 2022-2023

BASIC CONCEPTS AND DEFINITIONS

1.1 SYSTEMS AND SURROUNDINGS

A system is part of the physical world in which one is interested. What is not the system is the environment or the surroundings. We distinguish between several types of systems:

1) An isolated system is a system that is totally uninfluenced by the surroundings. There is no possibility of exchange of energy or matter with surroundings.
2) A closed system is a system in which energy but not matter can exchange with the surroundings.
3) An open system is a system in which both energy and matter can exchange with the surroundings.
Isolated or closed systems are often referred to as bodies. Theorems will first be developed for isolated and closed systems and later generalized to open systems.

1.2 STATE VARIABLES AND THERMODYNAMIC PROPERTIES

For a complete description of a macroscopic body, it is not enough to specify the identity of the substance. The state of the system must also be specified. The state is completely defined by the values of the thermodynamic properties or thermodynamic variables of the system. Thermodynamic properties (such as temperature, pressure, amount of substance, energy, etc.) are properties that do not depend on the rate at which something happens. For example, electric current and thermal conduction are rates and not thermodynamic variables. State variables are fully determined by the values at present and do not depend on the previous history of the system. In general, not all variables need to be specified to define the state of the system because the variables are interdependent and only a small number can be varied independently. These are referred to as independent variables

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1.3 INTENSIVE AND EXTENSIVE VARIABLES

Intensive variables or properties are properties that are independent of the amount or mass of the material. Extensive properties depend on the mass. But there is more to it. If the system is divided into several parts, the value of the total extensive property must equal the sum of the values of the parts.

1.4 HOMOGENEOUS AND HETEROGENEOUS SYSTEMS, PHASES

If the intensive variables are uniform throughout the system or if the variables change continuously (as air in a gravitational field), the system is said to be homogeneous. If some of the intensive properties change discontinuously, the system is said to be heterogeneous. A phase is a homogeneous subsystem. It is not necessary that all parts of a phase be contiguous. Ice chunks floating in water, for example, represent a two-phase system. A system that consists of several phases is obviously heterogeneous.

1. 5 WORK

There are various kinds of work. All elements of work, dw, can be written as the product of a generalized force, X, and a generalized displacement, dx. That is, $dw = Xdx$. There is no general agreement regarding the sign of w. Some authors use the convention that w is positive if done by the system on the surroundings. Others prefer to take work to be positive if done by the surroundings on the system. W is regarded as positive if done on the system by the surrounding.

Examples of forms of work include the following.

1- Pressure-volume or P-V work: $dw = \_P_{ex} dV$, where Pex is the external pressure and V the volume.

2- Gravitational work: $dw = mgdh$, where m is the mass, g the gravitational constant, and h the height.

3- Electrical work: $dw=EdQ$, where E is the electric potential difference and Q the charge.

4- Wire or rubber stretching: $dw = fL$, where f is the tensile force and L the length.

5- Surface Enlargement: $dw = sdA$, where s is the surface tension and A the area.

In all these examples, the generalized force is the external one (i.e., the force acting on the system). Only in reversible processes are the external and internal forces equal to each other.

1.6 REVERSIBLE AND QUASI-STATIC PROCESSES

Consider a gas in a cylinder fitted with a piston. If the gas is in equilibrium, its state is determined by a small number of macroscopic variables, such as pressure, volume, and composition. However, if the piston is in motion, the pressure varies from point to point. A pressure tensor, rather than a scalar, is needed to describe the motion. A rigorous treatment of pressure-volume work is obviously a problem of great complexity. However, there is one type of process that can be described simply, namely, a process that changes extremely slowly so that, for all practical purposes, the internal pressure is infinitesimally less than the external pressure. The system will be effectively in equilibrium, and the internal pressure will be basically the same as the external pressure. The work can then be calculated by using the internal pressure, which is generally known (for example, from an equation of state). This type of transformation, introduced by Carathe´odory (1909), is referred to as quasi-static. It cannot be realized exactly, but it may approximately represent the real situation in practice. A concept closely related to the concept of quasi-static transformation is the concept of reversibility.

1.6.1 Quasi-Static Process

The most widely used definition of quasi-static process is the one due to Carathe´odory (Carathe´odory, 1909), which states that a ‘‘quasi-static processes one that proceeds infinitely slowly via a continuous succession of equilibrium states.’’ The restriction to a continuous sequence of internal equilibrium state ensures that, for example, in a compression of a gas, the internal pressure is infinitesimally smaller than the external pressure. Obviously, this can be true only if there is no friction. Furthermore, by an infinitesimal change of the forces, the process can be reversed along exactly the same path. This means that, on completion of the reverse process, the system is restored to its original values but so is the environment. Restoration of the system to its original state as well as of the environment is an essential requirement of a reversible process.

Another definition of quasi-static process stipulates that the change proceeds at an infinitesimally slow rate but not necessarily via a continuous succession of equilibrium states. Such a process cannot be reversed by an infinitesimal change of the forces. As an example, consider a system and its surroundings—initially at finite (not infinitesimally) different temperatures—to be connected by a poorly heat-conducting metal plate. The heat transfer will proceed infinitely slowly, and the process may be dubbed quasi-static—but it is not reversible. Once equilibrium has been established, it is impossible to restore both system and surroundings to their initial states without producing finite changes. Only if the initial temperature difference between system and surroundings is infinitesimally small, rather than finite,will the transformation be reversible or quasi-static in the Carathe´odory sense.

1.6.2 Reversible Process

One definition states that a reversible process proceeds along a continuous sequence of internal equilibrium states so it can return along exactly the same path. This implies that both system and surrounding can be restored to the initial values. From this point of view, reversible and quasi-static processes (a´ la Carathe´odory) are the same.

Another definition states that a reversible process is one in which the system is taken from state A to state B and returned to state A, not necessarily along the same path, but along a path such that there are changes in neither the system nor the surroundings. This definition makes no reference to intermediate equilibrium states. It has been suggested that the first definition of reversibility be called retraceable and the second recoverable

Note: When a transition is carried out under quasi-static conditions, the work done by the surroundings on the system is the maximum work because the internal pressure differs only infinitesimally from the external one. In an expansion, the work is negative and as low as possible;
that is, it is a minimum. Had we adopted the convention that work is positive when done on the surroundings, the reversible work would have been maximum in an expansion and minimum in compression. The absolute values of work are always maximum in a reversible change regardless of convention and regardless of whether the transition is an expansion or compression.

In an irreversible change, the external pressure in a compression has to be greater than the internal pressure by a finite amount, since not all work energy, $w = -\int P_{ext} dV$, is utilized to compress the gas but some is needed to overcome friction.

1.7 ADIABATIC AND DIATHERMAL WALLS

Adiabaic wall or adiabaic boundary is one in which the state of the system can be changed only by moving the boundaries (i.e., doing mechanical work) or by applying an external field.

Diathermal wall or diathermal boundary is one in which the state of the system can be changed by means other than moving the boundary or by applying a field.

1.8 THERMAL CONTACT AND THERMAL EQUILIBRIUM

Two other concepts that will be needed to discuss the laws of thermodynamics, in particular the Zeroth and the First Law, are the concepts of thermal contact and thermal equilibrium. Thermal contact refers to systems in contact via a diathermal wall. When objects are brought into thermal contact, the macroscopic properties may initially change but after some time no further changes will occur. Thermal equilibrium refers to systems in thermal contact that do not change with time.