

specifying four quantities: composition, volume, pressure, and temperature. These quantities refer to the gross characteristics, or large-scale properties, of the system and provide a *macroscopic description*. They are therefore called *macroscopic coordinates*. The quantities that must be specified to provide a macroscopic description of other systems are, of course, different; but macroscopic coordinates in general have the following characteristics in common:

- 1 They involve no special assumptions concerning the structure of matter.
- 2 Only a few coordinates are needed for a macroscopic description.
- 3 They are suggested more or less directly by our sense perceptions.
- 4 They can in general be directly measured.

In short, a macroscopic description of a system involves the specification of a *few fundamental measurable properties* of a system.

1-2 Microscopic Point of View

From the viewpoint of *statistical mechanics*—or, as it is often called, *statistical thermodynamics*—a system is considered to consist of an enormous number N of molecules, each of which is capable of existing in a set of states whose energies are $\epsilon_1, \epsilon_2, \dots$. The molecules are assumed to interact with one another by means of collisions or by forces at a distance. The system of molecules may be imagined to be isolated or, in some cases, may be considered to be embedded in a set of similar systems, or *ensemble* of systems. Concepts of probability are applied, and the equilibrium state of the system is assumed to be the state of highest probability. The fundamental problem is to find the number of molecules in each of the molecular energy states (known as the *populations* of the states) when equilibrium is reached.

Since statistical thermodynamics will be treated at some length in Chap. 10, it is not necessary to pursue the matter further at this point. It is evident, however, that a microscopic description of a system involves the following characteristics:

- 1 Assumptions are made concerning the structure of matter; e.g., the existence of molecules is assumed.
- 2 Many quantities must be specified.
- 3 The quantities specified are not suggested by our sense perceptions.
- 4 These quantities cannot be measured.

1-3 Macroscopic vs. Microscopic

Although it might seem that the two points of view are hopelessly different and incompatible, there is nevertheless a relation between them; and when

both points of view are applied to the same system, they must lead to the same conclusion. The relation between the two points of view lies in the fact that the few directly measurable properties whose specification constitutes the macroscopic description are really averages over a period of time of a large number of microscopic characteristics. For example, the macroscopic quantity, pressure, is the average rate of change of momentum due to all the molecular collisions made on a unit of area. Pressure, however, is a property that is perceived by our senses. We feel the effects of pressure. Pressure was experienced, measured, and used long before physicists had reason to believe in the existence of molecular impacts. If the molecular theory is changed or even discarded at some time in the future, the concept of pressure will still remain and will still mean the same thing to all normal human beings. Herein lies an important distinction between the macroscopic and microscopic points of view. The few measurable macroscopic properties are as sure as our senses. They will remain unchanged as long as our senses remain the same. The microscopic point of view, however, goes much further than our senses. It postulates the existence of molecules, their motion, their energy states, their interactions, etc. It is constantly being changed, and we can never be sure that the assumptions are justified until we have compared some deduction made on the basis of these assumptions with a similar deduction based on the macroscopic point of view.

1-4 Scope of Thermodynamics

It has been emphasized that a description of the gross characteristics of a system by means of a few of its measurable properties, suggested more or less directly by our sense perceptions, constitutes a macroscopic description. Such descriptions are the starting point of all investigations in all branches of physics. For example, in dealing with the mechanics of a rigid body, the macroscopic point of view is adopted in that only the external aspects of the rigid body are considered. The position of its center of mass is specified with reference to coordinate axes at a particular time. Position and time and a combination of both, such as velocity, constitute some of the macroscopic quantities used in mechanics and are called *mechanical coordinates*. The mechanical coordinates serve to determine the potential and the kinetic energy of the rigid body with reference to the coordinate axes, i.e., the kinetic and the potential energy of the body as a whole. These two types of energy constitute the *external, or mechanical, energy* of the rigid body. It is the purpose of mechanics to find such relations between the position coordinates and the time as are consistent with Newton's laws of motion.

In thermodynamics, however, the attention is directed to the *interior* of a system. A macroscopic point of view is adopted, but only those macroscopic quantities are considered which have a bearing on the internal state of a system. It is the function of experiment to determine the quantities that are necessary and sufficient for such a purpose. Macroscopic quantities having a bearing on the internal state of a system are called *thermodynamic coordinates*. Such coordinates serve to determine the *internal energy* of a system. It is the purpose of thermodynamics to find general relations among the thermodynamic coordinates that are consistent with the fundamental laws of thermodynamics.

A system that may be described in terms of thermodynamic coordinates is called a *thermodynamic system*. In engineering, the important thermodynamic systems are a gas, such as air; a vapor, such as steam; a mixture, such as gasoline vapor and air; and a vapor in contact with its liquid, such as liquid and vaporized ammonia. Chemical thermodynamics deals with the above systems and, in addition, with solids, surface films, and electric cells. Physical thermodynamics includes, in addition to the above, such systems as stretched wires, electric capacitors, thermocouples, and magnetic substances.

1-5 Thermal Equilibrium

We have seen that a macroscopic description of a gaseous mixture may be given by specifying such quantities as the composition, the mass, the pressure, and the volume. Experiment shows that, for a given composition and for a constant mass, many different values of pressure and volume are possible. If the pressure is kept constant, the volume may vary over a wide range of values, and vice versa. In other words, the pressure and the volume are independent coordinates. Similarly, experiment shows that, for a wire of constant mass, the tension and the length are independent coordinates, whereas, in the case of a surface film, the surface tension and the area may be varied independently. Some systems that, at first sight, seem quite complicated, such as an electric cell with two different electrodes and an electrolyte, may still be described with the aid of only two independent coordinates. On the other hand, some systems composed of a number of homogeneous parts require the specification of two independent coordinates for each homogeneous part. Details of various thermodynamic systems and their thermodynamic coordinates will be given in Chap. 2. For the present, to simplify our discussion, we shall deal only with systems of constant mass and composition, each requiring *only one pair* of independent coordinates for its description. This involves no essential loss of generality and results in a considerable saving of words. In referring to any nonspecified system, we shall use the symbols Y and X for the pair of independent coordinates.

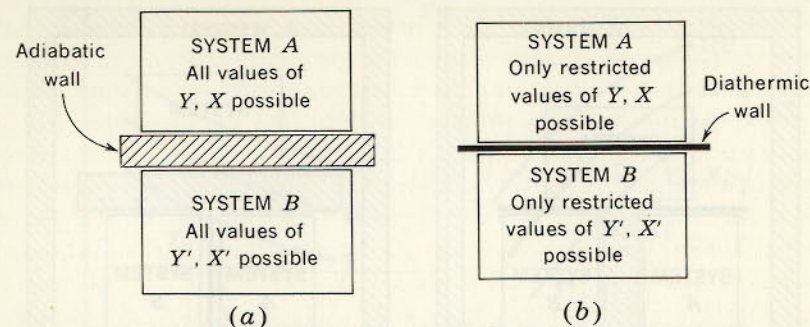


Fig. 1-1 Properties of adiabatic and diathermic walls.

A state of a system in which Y and X have definite values that remain constant so long as the external conditions are unchanged is called an *equilibrium state*. Experiment shows that the existence of an equilibrium state in one system depends on the proximity of other systems and on the nature of the wall separating them. Walls are said to be either adiabatic or diathermic. If a wall is *adiabatic* (see Fig. 1-1a), a state Y, X for system A and Y', X' for system B may coexist as equilibrium states for *any* attainable values of the four quantities, provided only that the wall is able to withstand the stress associated with the difference between the two sets of coordinates. Thick layers of wood, concrete, asbestos, felt, etc., are good experimental approximations to adiabatic walls. If the two systems are separated by a *diathermic wall* (see Fig. 1-1b), the values of Y, X and Y', X' will change spontaneously until an equilibrium state of the combined system is attained. The two systems are then said to be in *thermal equilibrium* with each other. The most common diathermic wall is a thin metallic sheet. *Thermal equilibrium is the state achieved by two (or more) systems, characterized by restricted values of the coordinates of the systems, after they have been in communication with each other through a diathermic wall.*

Imagine two systems A and B separated from each other by an adiabatic wall but each in contact with a third system C through diathermic walls, the whole assembly being surrounded by an adiabatic wall as shown in Fig. 1-2a. Experiment shows that the two systems will come to thermal equilibrium with the third and that no further change will occur if the adiabatic wall separating A and B is then replaced by a diathermic wall (Fig. 1-2b). If, instead of allowing both systems A and B to come to equilibrium with C at the same time, we first have equilibrium between A and C and then equilibrium between B and C (the state of system C being the same in both cases), then, when A and B are brought into communication through a diathermic wall, they will be found to be in thermal equilibrium. We shall use the expression "two systems are in thermal equilibrium" to mean that the two systems

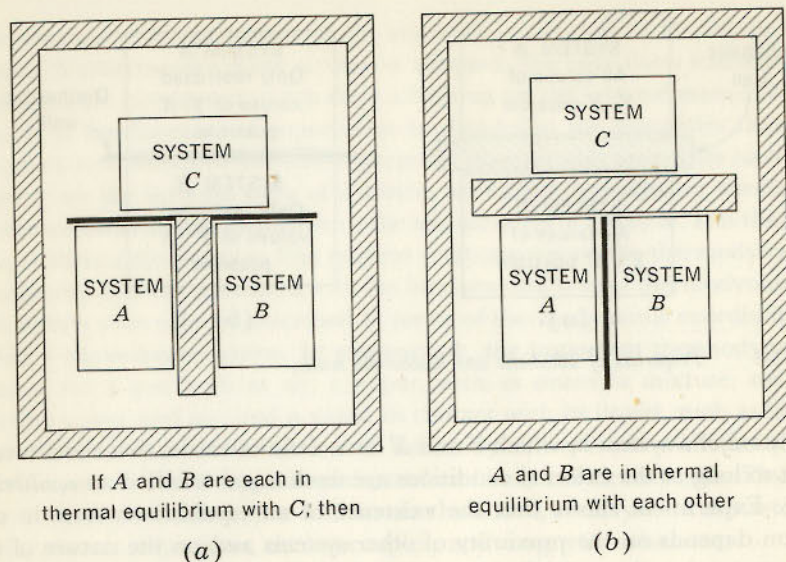


Fig. 1-2 The zeroth law of thermodynamics. (Adiabatic walls are designated by cross shading; diathermic walls, by heavy lines.)

are in states such that, if the two *were* connected through a diathermic wall, the combined system *would be* in thermal equilibrium.

These experimental facts may then be stated concisely in the following form: *Two systems in thermal equilibrium with a third are in thermal equilibrium with each other.* Following R. H. Fowler, we shall call this postulate the *zeroth law of thermodynamics*.

1-6 Temperature Concept

Consider a system *A* in the state Y_1, X_1 in thermal equilibrium with a system *B* in the state Y'_1, X'_1 . If system *A* is removed and its state changed, there will be found another state Y_2, X_2 in which it is in thermal equilibrium with the *original* state Y'_1, X'_1 of system *B*. Experiment shows that there exists a whole set of states $Y_1, X_1; Y_2, X_2; Y_3, X_3; \text{etc.}$, every one of which is in thermal equilibrium with this *same* state Y'_1, X'_1 of system *B* and which, by the zeroth law, are in thermal equilibrium with one another. We shall suppose that *all* such states, when plotted on a YX diagram, lie on a curve such as I in Fig. 1-3, which we shall call an *isotherm*. An *isotherm* is the locus of all points representing states at which a system is in thermal equilibrium with one state of another system. We make no assumption as to the continuity of the isotherm, although experi-

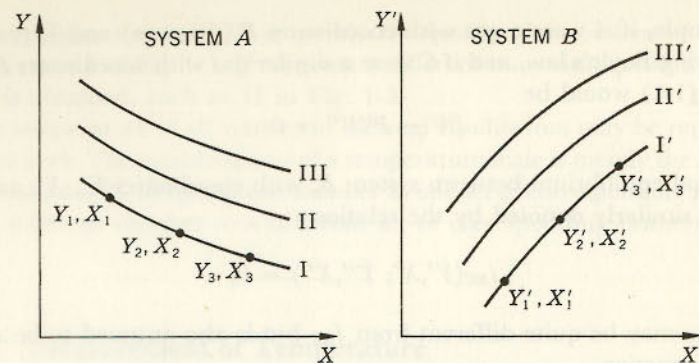


Fig. 1-3 Isotherms of two different systems.

ments on simple systems indicate usually that at least a portion of an isotherm is a continuous curve.

Similarly, with regard to system *B*, we find a set of states $Y'_1, X'_1; Y'_2, X'_2; \text{etc.}$, all of which are in thermal equilibrium with one state (Y_1, X_1) of system *A*, and therefore in thermal equilibrium with one another. These states are plotted on the $Y'X'$ diagram of Fig. 1-3 and lie on the isotherm *I'*. From the zeroth law, it follows that all the states on isotherm *I* of system *A* are in thermal equilibrium with all the states on isotherm *I'* of system *B*. We shall call curves *I* and *I'* *corresponding isotherms* of the two systems.

If the experiments outlined above are repeated with different starting conditions, another set of states of system *A* lying on curve *II* may be found, every one of which is in thermal equilibrium with every state of system *B* lying on curve *II'*. In this way, a family of isotherms, *I, II, III, etc.*, of system *A* and a corresponding family *I', II', III', etc.*, of system *B* may be found. Furthermore, by repeated applications of the zeroth law, corresponding isotherms of still other systems *C, D, etc.*, may be obtained.

All states of corresponding isotherms of all systems have something in common, namely, that they are in thermal equilibrium with one another. The systems themselves, in these states, may be said to possess a property that ensures their being in thermal equilibrium with one another. We call this property *temperature*. The temperature of a system is a property that determines whether or not a system is in thermal equilibrium with other systems.

The concept of temperature may be arrived at in a more sophisticated manner. When a system *A* with coordinates Y, X is separated from a system *C* with coordinates Y'', X'' , the approach to thermal equilibrium is indicated by changes in the four coordinates. The final state of thermal equilibrium is denoted by a relation among these coordinates which may be written in the general functional form

$$f_{AC}(Y, X; Y'', X'') = 0. \quad (1-1)$$

For example, if A were a gas with coordinates P (pressure) and V (volume) and obeying Boyle's law, and if C were a similar gas with coordinates P'' and V'' , Eq. (1-1) would be

$$PV - P''V'' = 0.$$

Thermal equilibrium between system B , with coordinates Y' , X' , and system C is similarly denoted by the relation

$$f_{BC}(Y', X'; Y'', X'') = 0, \quad (1-2)$$

where f_{BC} may be quite different from f_{AC} but is also assumed to be a well-behaved function.

Suppose Eqs. (1-1) and (1-2) are solved for Y'' ; then

$$Y'' = g_{AC}(Y, X, X''),$$

and

$$Y'' = g_{BC}(Y', X', X''),$$

or

$$g_{AC}(Y, X, X'') = g_{BC}(Y', X', X''). \quad (1-3)$$

Now, according to the zeroth law, thermal equilibrium between A and C and between B and C implies thermal equilibrium between A and B , which is denoted by a relation among *coordinates of systems A and B only*; thus,

$$f_{AB}(Y, X; Y', X') = 0. \quad (1-4)$$

Since Eq. (1-3) also expresses the same two equilibrium situations, it must agree with Eq. (1-4): that is, it must reduce to a relation among Y , X ; Y' , X' only. The extraneous coordinate X'' in Eq. (1-3) must therefore drop out, and the equation must reduce to

$$h_A(Y, X) = h_B(Y', X').$$

Applying the same argument a second time with systems A and C in equilibrium with B , we get finally, when the three systems are in thermal equilibrium,

$$h_A(Y, X) = h_B(Y', X') = h_C(Y'', X''). \quad (1-5)$$

In other words, *a function of each set of coordinates exists, and these functions are all equal when the systems are in thermal equilibrium with one another*. The common value t of these functions is the *empirical temperature* common to all the systems.

$$t = h_A(Y, X) = h_B(Y', X') = h_C(Y'', X''). \quad (1-6)$$

The relation $t = h_A(Y, X)$ is merely *the equation of an isotherm of system A*, such as curve I of Fig. 1-3. If t is given a different numerical value, a different curve is obtained, such as II in Fig. 1-3.

The temperature of all systems in thermal equilibrium may be represented by a number. The establishment of a temperature scale is merely the adoption of a set of rules for assigning one number to one set of corresponding isotherms and a different number to a different set of corresponding isotherms.

1-7 Measurement of Temperature

To establish an empirical temperature scale, we select some system with coordinates Y and X as a standard, which we call a *thermometer*, and adopt a set of rules for assigning a numerical value to the temperature associated with each of its isotherms. To every other system in thermal equilibrium with the thermometer, we assign the same number for the temperature. The simplest procedure is to choose any convenient path in the YX plane, such as that shown in Fig. 1-4 by the dashed line $Y = Y_1$ which intersects the isotherms at points each of which has the same Y coordinate but a different X coordinate. The temperature associated with each isotherm is then taken to be a convenient function of the X at this intersection point. The coordinate X is called the *thermometric property*, and the form of the *thermometric function* $\theta(X)$ determines the temperature scale. There are six important kinds of thermometer, each with its own thermometric property, as shown in Table 1-1.

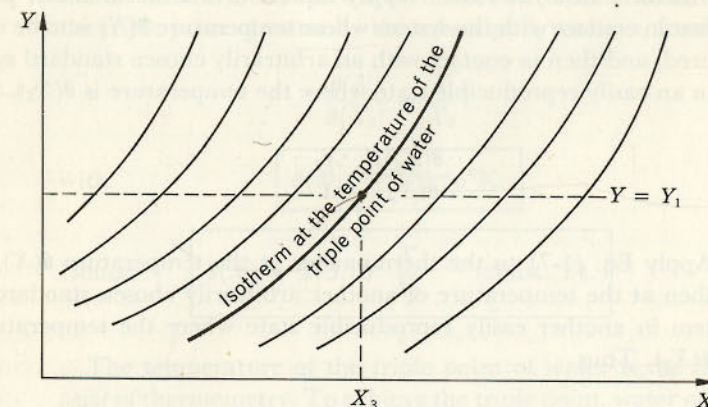


Fig. 1-4 Setting up a temperature scale involves assignment of numerical values to the isotherms of an arbitrarily chosen standard system, or thermometer.