THERMODYNAMICS

BY

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Preface

THIS book originated in a course of lectures held at Columbia University, New York, during the summer session of 1936.

It is an elementary treatise throughout, based entirely on pure thermodynamics; however, it is assumed that the reader is familiar with the fundamental facts of thermometry and calorimetry. Here and there will be found short references to the statistical interpretation of thermodynamics.

As a guide in writing this book, the author used notes of his lectures that were taken by Dr. Lloyd Motz, of Columbia University, who also revised the final manuscript critically. Thanks are due him for his willing and intelligent collaboration.

<div align="right">E. FERMI</div>

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Introduction

THERMODYNAMICS is mainly concerned with the transformations of heat into mechanical work and the opposite transformations of mechanical work into heat.

Only in comparatively recent times have physicists recognized that heat is a form of energy that can be changed into other forms of energy. Formerly, scientists had thought that heat was some sort of fluid whose total amount was invariable, and had simply interpreted the heating of a body and analogous processes as consisting of the transfer of this fluid from one body to another. It is, therefore, noteworthy that on the basis of this heat-fluid theory Carnot was able, in the year 1824, to arrive at a comparatively clear understanding of the limitations involved in the transformation of heat into work, that is, of essentially what is now called the second law of thermodynamics (see Chapter III).

In 1842, only eighteen years later, R. J. Mayer discovered the equivalence of heat and mechanical work, and made the first announcement of the principle of the conservation of energy (the first law of thermodynamics).

We know today that the actual basis for the equivalence of heat and dynamical energy is to be sought in the kinetic interpretation, which reduces all thermal phenomena to the disordered motions of atoms and molecules. From this point of view, the study of heat must be considered as a special branch of mechanics: the mechanics of an ensemble of such an enormous number of particles (atoms or molecules) that the detailed description of the state and the motion loses importance and only average properties of large numbers of particles are to be considered. This branch of mechanics, called *statistical mechanics*, which has been developed mainly through the work of Maxwell, Boltzmann, and Gibbs, has led to a very satisfactory understanding of the fundamental thermodynamical laws.

But the approach in pure thermodynamics is different. Here the fundamental laws are assumed as postulates based on experimental evidence, and conclusions are drawn from them without entering into the kinetic mechanism of the phenomena. This procedure has the advantage of being independent, to a great extent, of the simplifying assumptions that are often made in statistical mechanical considerations. Thus, thermodynamical results are generally highly accurate. On the other hand, it is sometimes rather unsatisfactory to obtain results without being able to see in detail how things really work, so that in many respects it is very often convenient to complete a thermodynamical result with at least a rough kinetic interpretation.

The first and second laws of thermodynamics have their statistical foundation in classical mechanics. In recent years Nernst has added a third law which can be interpreted statistically only in terms of quantum mechanical concepts. The last chapter of this book will concern itself with the consequences of the third law.

CHAPTER I

Thermodynamic Systems

1. The state of a system and its transformations. The state of a system in mechanics is completely specified at a given instant of time if the position and velocity of each mass-point of the system are given. For a system composed of a number N of mass-points, this requires the knowledge of $6N$ variables.

In thermodynamics a different and much simpler concept of the state of a system is introduced. Indeed, to use the dynamical definition of *state* would be inconvenient, because all the systems which are dealt with in thermodynamics contain a very large number of mass-points (the atoms or molecules), so that it would be practically impossible to specify the $6N$ variables. Moreover, it would be unnecessary to do so, because the quantities that are dealt with in thermodynamics are average properties of the system; consequently, a detailed knowledge of the motion of each mass-point would be superfluous.

In order to explain the thermodynamic concept of the state of a system, we shall first discuss a few simple examples.

A system composed of a chemically defined homogeneous fluid. We can make the following measurements on such a system: the temperature t, the volume V, and the pressure p. The temperature can be measured by placing a thermometer in contact with the system for an interval of time sufficient for thermal equilibrium to set in. As is well known, the temperature defined by any special thermometer (for example, a mercury thermometer) depends on the particular properties of the thermometric substance used. For the time being, we shall agree to use the same kind of thermometer for all temperature measurements in order that these may all be comparable.

The geometry of our system is obviously characterized not only by its volume, but also by its shape. However, most thermodynamical properties are largely independent of the shape, and, therefore, the volume is the only geometrical datum that is ordinarily given. It is only in the cases for which the ratio of surface to volume is very large (for example, a finely grained substance) that the surface must also be considered.

For a given amount of the substance contained in the system, the temperature, volume, and pressure are not independent quantities; they are connected by a relationship of the general form:

$$f(p, V, t) = 0, \tag{1}$$

which is called the *equation of state*. Its form depends on the special properties of the substance. Any one of the three variables in the above relationship can be expressed as a function of the other two by solving equation (1) with respect to the given variable. Therefore, the state of the system is completely determined by any two of the three quantities, p, V, and t.

It is very often convenient to represent these two quantities graphically in a rectangular system of co-ordinates. For example, we may use a (V, p) representation, plotting V along the abscissae axis and p along the ordinates axis. A point on the (V, p) plane thus defines a state of the system. The points representing states of equal temperature lie on a curve which is called an *isothermal*.

A system composed of a chemically defined homogeneous solid. In this case, besides the temperature t and volume V, we may introduce the pressures acting in different directions in order to define the state. In most cases, however, the assumption is made that the solid is subjected to an isotropic pressure, so that only one value for the pressure need be considered, as in the case of a fluid.

A system composed of a homogeneous mixture of several chemical compounds. In this case the variables defining the state of the system are not only temperature, volume, and

pressure, but also the concentrations of the different chemical compounds composing the mixture.

Nonhomogeneous systems. In order to define the state of a nonhomogeneous system, one must be able to divide it into a number of homogeneous parts. This number may be finite in some cases and infinite in others. The latter possibility, which is only seldom considered in thermodynamics, arises when the properties of the system, or at least of some of its parts, vary continuously from point to point. The state of the system is then defined by giving the mass, the chemical composition, the state of aggregation, the pressure, the volume, and the temperature of each homogeneous part.

It is obvious that these variables are not all independent. Thus, for example, the sum of the amounts of each chemical element present in the different homogeneous parts must be constant and equal to the total amount of that element present in the system. Moreover, the volume, the pressure, and the temperature of each homogeneous part having a given mass and chemical composition are connected by an equation of state.

A system containing moving parts. In almost every system that is dealt with in thermodynamics, one assumes that the different parts of the system either are at rest or are moving so slowly that their kinetic energies may be neglected. If this is not the case, one must also specify the velocities of the various parts of the system in order to define the state of the system completely.

It is evident from what we have said that the knowledge of the thermodynamical state alone is by no means sufficient for the determination of the dynamical state. Studying the thermodynamical state of a homogeneous fluid of given volume at a given temperature (the pressure is then defined by the equation of state), we observe that there is an infinite number of states of molecular motion that correspond to it. With increasing time, the system exists successively in all these dynamical states that correspond to the given thermodynamical state. From this point of view we may say that a thermodynamical state is the ensemble of all the

dynamical states through which, as a result of the molecular motion, the system is rapidly passing. This definition of state is rather abstract and not quite unique; therefore, we shall indicate in each particular case what the state variables are.

Particularly important among the thermodynamical states of a system are the *states of equilibrium*. These states have the property of not varying so long as the external conditions remain unchanged. Thus, for instance, a gas enclosed in a container of constant volume is in equilibrium when its pressure is constant throughout and its temperature is equal to that of the environment.

Very often we shall have to consider *transformations* of a system from an initial state to a final state through a continuous succession of intermediate states. If the state of the system can be represented on a (V, p) diagram, such a transformation will be represented by a curve connecting the two points that represent the initial and final states.

A transformation is said to be *reversible* when the successive states of the transformation differ by infinitesimals from *equilibrium states*. A reversible transformation can therefore connect only those initial and final states which are states of equilibrium. A reversible transformation can be realized in practice by changing the external conditions so slowly that the system has time to adjust itself gradually to the altered conditions. For example, we can produce a reversible expansion of a gas by enclosing it in a cylinder with a movable piston and shifting the piston outward very slowly. If we were to shift the piston rapidly, currents would be set up in the expanding gaseous mass, and the intermediate states would no longer be states of equilibrium.

If we transform a system reversibly from an initial state A to a final state B, we can then take the system by means of the reverse transformation from B to A through the same succession of intermediate states but in the reverse order. To do this, we need simply change the conditions of the environment very slowly in a sense opposite to that in the original transformation. Thus, in the case of the gas

discussed in the preceding paragraph, we may compress it again to its original volume and bring it back to its initial state by shifting the piston inward very slowly. The compression occurs reversibly, and the gas passes through the same intermediate states as it did during the expansion.

During a transformation, the system can perform positive or negative external *work*; that is, the system can do work on its surroundings or the surroundings can do work on the system. As an example of this, we consider a body enclosed in a cylinder having a movable piston of area S at one end (Figure 1). If p is the pressure of the body against the walls of the cylinder, then pS is the force exerted by the body on the piston. If the piston is shifted an infinitesimal distance dh, an infinitesimal amount of work,

$$dL = pSdh, \tag{2}$$

is performed, since the displacement is parallel to the force. But Sdh is equal to the increase, dV, in volume of the system. Thus, we may write[1]:

$$dL = pdV. \tag{3}$$
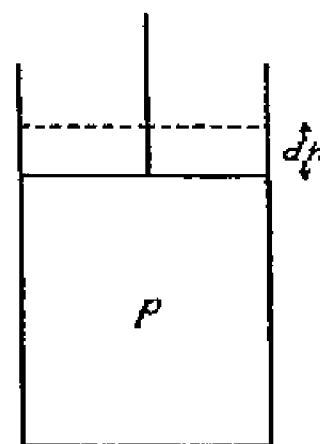
Fig. 1.

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[1] It is obvious that (3) is generally valid no matter what the shape of the container may be. Consider a body at the uniform pressure p, enclosed in an irregularly shaped container A (Figure 2). Consider now an infinitesimal transformation of our system during which the walls of the container move from the initial position A to the final position B, thus permitting the body inside the container to expand. Let $d\sigma$ be a surface element of the container, and let dn be the displacement of this element in the direction normal to the surface of the container. The work performed on the surface element $d\sigma$ by the pressure p during the displacement of the container from the situation A to the situation B is obviously $p\ d\sigma\ dn$. The total amount of work performed during the infinitesimal transformation is obtained by integrating the above expression over all the surface σ of the container; since p is a constant, we obtain:

$$dL = p \int d\sigma\ dn.$$

It is now evident from the figure that the variation dV of the volume of the container is given by the surface integral,

$$dV = \int d\sigma\ dn.$$

Comparing these two equations, we obtain (3).

For a finite transformation, the work done by the system is obtained by integrating equation (3):

$$L = \int_A^B p\,dV, \qquad (4)$$

where the integral is taken over the entire transformation.

When the state of the system can be represented on a

Fig. 2.

(V, p) diagram, the work performed during a transformation has a simple geometrical representation. We consider a transformation from an initial state indicated by the point A to a final state indicated by the point B (Figure 3). This transformation will be represented by a curve connecting A and B the shape of which depends on the type of transformation considered. The work done during this transformation is given by the integral
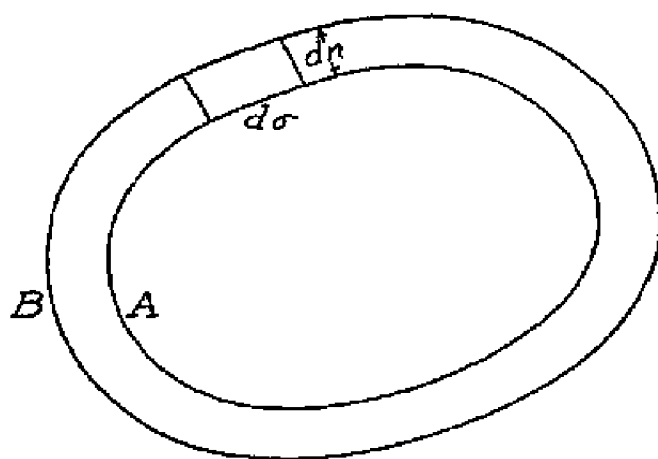
$$L = \int_{V_A}^{V_B} p\,dV, \qquad (5)$$

where V_A and V_B are the volumes corresponding to the states A and B. This integral, and hence the work done, can

Fig. 3.

be represented geometrically by the shaded area in the figure.
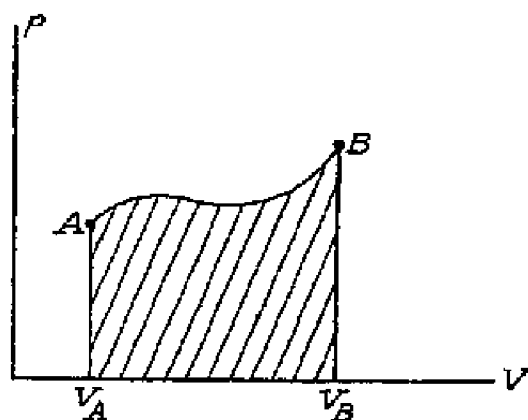
Transformations which are especially important are those for which the initial and final states are the same. These are called *cyclical transformations* or *cycles*. A cycle, therefore, is a transformation which brings the system back to its initial state. If the state of the system can be represented on a (V, p) diagram, then a cycle can be represented on

this diagram by a closed curve, such as the curve $ABCD$ (Figure 4).

The work, L, performed by the system during the cyclical transformation is given geometrically by the area enclosed by the curve representing the cycle. Let A and C be the points of minimum and maximum abscissa of our cycle, and let their projections on the V-axis be A' and C', respectively. The work performed during the part ABC of the transformation is positive and equal to the area $ABCC'A'A$. The work performed during the rest of the transformation, CDA, is negative and equal in amount to the area $CC'A'ADC$. The total amount of positive work done is equal to the difference between these two areas, and hence is equal to the area bounded by the cycle.

It should be noted that the total work done is positive because we performed the cycle in a clockwise direction. If the same cycle is performed in a counterclockwise direction, the work will again be given by the area bounded by the cycle, but this time it will be negative.
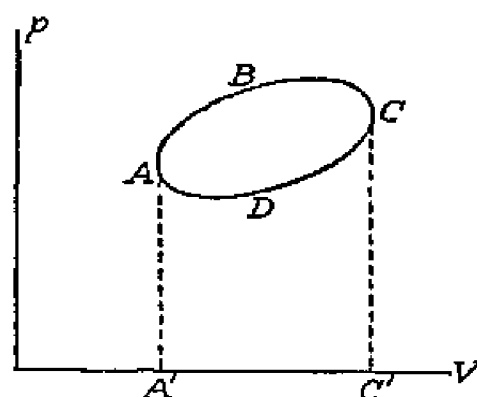
A transformation during which the system performs no external work is called an *isochore transformation*. If we assume

Fig. 4.

that the work dL performed during an infinitesimal element of the transformation is given, according to equation (3), by pdV, we find for an isochore transformation $dV = 0$, or, by integration, $V = $ a constant. Thus, an isochore transformation in this case is a transformation at constant volume. This fact justifies the name *isochore*. It should be noticed, however, that the concept of isochore transformation is more general, since it requires that $dL = 0$ for the given transformation, even when the work dL cannot be represented by equation (3).

Transformations during which the pressure or the temperature of the system remains constant are called *isobaric* and *isothermal* transformations, respectively.

2. Ideal or perfect gases. The equation of state of a system composed of a certain quantity of gas occupying a volume V at the temperature t and pressure p can be approximately expressed by a very simple analytical law. We obtain the equation of state of a gas in its simplest form by changing from the empirical scale of temperatures, t, used so far to a new temperature scale T.

We define T provisionally as the temperature indicated by a gas thermometer in which the thermometric gas is kept at a very low constant pressure. T is then taken proportional to the volume occupied by the gas. It is well known that the readings of different gas thermometers under these conditions are largely independent of the nature of the thermometric gas, provided that this gas is far enough from condensation. We shall see later, however (section 9), that it is possible to define this same scale of temperatures T by general thermodynamic considerations quite independently of the special properties of gases.

The temperature T is called the *absolute temperature*. Its unit is usually chosen in such a way that the temperature difference between the boiling and the freezing points of water at one atmosphere of pressure is equal to 100. The freezing point of water corresponds then, as is well known, to the absolute temperature 273.1.

The equation of state of a system composed of m grams of a gas whose molecular weight is M is given approximately by:

$$pV = \frac{m}{M} RT. \tag{6}$$

R is a universal constant (that is, it has the same value for all gases: $R = 8.314 \times 10^7$ erg/degrees, or (see section 3) $R = 1.986$ cal/degrees). Equation (6) is called *the equation of state of an ideal or a perfect gas*; it includes the laws of Boyle, Gay-Lussac, and Avogadro.

No real gas obeys equation (6) exactly. An ideal substance that obeys equation (6) exactly is called an ideal or a perfect gas.

For a gram-molecule (or mole) of a gas (that is, for a number of grams of a gas equal numerically to its molecular weight), we have $m = M$, so that (6) reduces to:

$$pV = RT. \tag{7}$$

From (6) or (7) we can obtain the density ρ of the gas in terms of the pressure and the temperature:

$$\rho = \frac{m}{V} = \frac{Mp}{RT}. \tag{8}$$

For an isothermal transformation of an ideal gas (transformation at constant temperature), we have:

$$pV = constant.$$

On the (V, p) diagram the isothermal transformations of an ideal gas are thus represented by equilateral hyperbolas having the V- and p-axes as asymptotes.

We can easily calculate the work performed by the gas during an isothermal expansion from an initial volume V_1 to a final volume V_2. This is given (making use of (5) and (6)) by:

$$L = \int_{V_1}^{V_2} p dV = \frac{m}{M} RT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= \frac{m}{M} RT \log \frac{V_2}{V_1}$$

$$= \frac{m}{M} RT \log \frac{p_1}{p_2}, \tag{9}$$

where p_1 and p_2 are the initial and final pressures, respectively. For one mole of gas, we have:

$$L = RT \log \frac{V_2}{V_1} = RT \log \frac{p_1}{p_2}. \tag{10}$$

A mixture of several gases is governed by laws very similar to those which are obeyed by a chemically homogeneous gas. We shall call the *partial pressure* of a component of a mixture of gases the pressure which this component would exert if it alone filled the volume occupied by the mixture

at the same temperature as that of the mixture. We can now state Dalton's law for gas mixtures in the following form:

The pressure exerted by a mixture of gases is equal to the sum of the partial pressures of all the components present in the mixture.

This law is only approximately obeyed by real gases, but it is assumed to hold exactly for ideal gases.

Problems

1. Calculate the work performed by a body expanding from an initial volume of 3.12 liters to a final volume of 4.01 liters at the pressure of 2.34 atmospheres.

2. Calculate the pressure of 30 grams of hydrogen inside a container of 1 cubic meter at the temperature of 18°C.

3. Calculate the density and specific volume of nitrogen at the temperature of 0°C.

4. Calculate the work performed by 10 grams of oxygen expanding isothermally at 20°C from 1 to .3 atmospheres of pressure.

CHAPTER II

The First Law of Thermodynamics

3. The statement of the first law of thermodynamics.
The first law of thermodynamics is essentially the statement of the principle of the conservation of energy for thermodynamical systems. As such, it may be expressed by stating that the variation in energy of a system during any transformation is equal to the amount of energy that the system receives from its environment. In order to give a precise meaning to this statement, it is necessary to define the phrases "energy of the system" and "energy that the system receives from its environment during a transformation."

In purely mechanical conservative systems, the energy is equal to the sum of the potential and the kinetic energies, and hence is a function of the dynamical state of the system; because to know the dynamical state of the system is equivalent to knowing the positions and velocities of all the mass-points contained in the system. If no external forces are acting on the system, the energy remains constant. Thus, if A and B are two successive states of an isolated system, and U_A and U_B are the corresponding energies, then

$$U_A = U_B.$$

When external forces act on the system, U_A need no longer be equal to U_B. If $-L$ is the work performed by the external forces during a transformation from the initial state A to the final state B ($+L$ is the work performed by the system), then the dynamical principle of the conservation of energy takes the form:

$$U_B - U_A = -L. \tag{11}$$

From this equation it follows that the work, L, performed during the transformation depends only on the extreme

states A and B of the transformation and not on the particular way in which the transformation from A to B is performed.

Let us assume now that we do not know the laws of interaction among the various mass-points of our dynamical system. Then we cannot calculate the energy of the system when it is in a given dynamical state. By making use of equation (11), however, we can nevertheless obtain an empirical definition of the energy of our system in the following way:

We consider an arbitrarily chosen state O of our system and, by definition, take its energy to be zero:

$$U_o = 0. \tag{12}$$

We shall henceforth refer to this state as the *standard* state of our system. Consider now any other state A; by applying suitable external forces to our system, we can transform it from the standard state (in which we assume it to be initially) to the state A. Let L_A be the work performed by the system during this transformation ($-L_A$ is, as before, the work performed by the external forces on the system). Applying (11) to this transformation, and remembering (12), we find that

$$U_A = -L_A. \tag{13}$$

This equation can be used as the empirical definition of the energy U_A of our system in the state A.

It is obviously necessary, if definition (13) is to have a meaning, that the work L_A depend only on the states O and A and not on the special way in which the transformation from O to A is performed. We have already noticed that this property follows from (11). If one found experimentally that this property did not hold, it would mean either that energy is not conserved in our system, or that, besides mechanical work, other means of transfer of energy must be taken into account.

We shall assume for the present that the work performed by our mechanical system during any transformation depends only on the initial and final states of the transformation, so that we can use (13) as the definition of the energy.

We can immediately obtain (11) from (13) as follows: A transformation between any two states A and B can always be performed as a succession of two transformations: first a transformation from A to the standard state O, and then a transformation from O to B. Since the system performs the amounts of work $-L_A$ and $+L_B$ during these two transformations, the total amount of work performed during the transformation from A to B (which is independent of the particular way in which the transformation is performed) is:

$$L = -L_A + L_B.$$

From (13) and the analogous equation,

$$U_B = -L_B,$$

we obtain now:

$$U_B - U_A = -L,$$

which is identical with (11).

We notice, finally, that the definition (13) of the energy is not quite unique, since it depends on the particular choice of the standard state O. If instead of O we had chosen a different standard state, O', we should have obtained a different value, U'_A, for the energy of the state A. It can be easily shown, however, that U'_A and U_A differ only by an additive constant. Indeed, the transformation from O' to A can be put equal to the sum of two transformations: one going from O' to O and the other going from O to A. The work L'_A performed by the system in passing from O' to A is thus equal to:

$$L'_A = L_{O'O} + L_A,$$

where $L_{O'O}$ is the work performed by the system in going from O' to O. We have now:

$$U_A = -L_A; \qquad U'_A = -L'_A,$$

so that

$$U_A - U'_A = L_{O'O},$$

which shows that the values of the energy based on the two definitions differ only by the constant $L_{O'O}$.

This indeterminate additive constant which appears in the definition of the energy is, as is well known, an essential feature of the concept of energy. Since, however, only differences of energy are considered in practice, the additive constant does not appear in the final results.

The only assumption underlying the above empirical definition of the energy is that the total amount of work performed by the system during any transformation depends only on the initial and final states of the transformation. We have already noticed that if this assumption is contradicted by experiment, and if we still do not wish to discard the principle of the conservation of energy, then we must admit the existence of other methods, besides mechanical work, by means of which energy can be exchanged between the system and its environment.

Let us take, for example, a system composed of a quantity of water. We consider two states A and B of this system at atmospheric pressure; let the temperatures of the system in these two states be t_A and t_B, respectively, with $t_A < t_B$. We can take our system from A to B in two different ways.

First way: We heat the water by placing it over a flame and raise its temperature from the initial value t_A to the final value t_B. The external work performed by the system during this transformation is practically zero. It would be exactly zero if the change in temperature were not accompanied by a change in volume of the water. Actually, however, the volume of the water changes slightly

during the transformation, so that a small amount of work is performed (see equation (3)). We shall neglect this small amount of work in our considerations.

Second way: We raise the temperature of the water from t_A to t_B by heating it by means of friction. To this end, we immerse a small set of paddles attached to a central axle in the water, and churn the water by rotating the paddles. We observe that the temperature of the water increases continuously as long as the paddles continue to rotate. Since the water offers resistance to the motion of the paddles, however, we must perform mechanical work in order to keep the paddles moving until the final temperature t_B is reached. Corresponding to this considerable amount of positive work performed by the paddles on the water, there is an equal amount of negative work performed by the water in resisting the motion of the paddles.

We thus see that the work performed by the system in going from the state A to the state B depends on whether we go by means of the first way or by means of the second way.

If we assume that the principle of the conservation of energy holds for our system, then we must admit that the energy that is transmitted to the water in the form of the mechanical work of the rotating paddles in the second way is transmitted to the water in the first way in a nonmechanical form called *heat*. We are thus led to the fact that heat and mechanical work are equivalent; they are two different aspects of the same thing, namely, energy. In what follows we shall group under the name of work electrical and magnetic work as well as mechanical work. The first two types of work, however, are only seldom considered in thermodynamics.

In order to express in a more precise form the fact that heat and work are equivalent, we proceed as follows.

We first enclose our system in a container with non-heat-conducting walls in order to prevent exchange of heat with

the environment.[1] We assume, however, that work can be exchanged between the system and its environment (for example, by enclosing the system in a cylinder with non-conducting walls but with a movable piston at one end). The exchange of energy between the inside and the outside of the container can now occur only in the form of work, and from the principle of the conservation of energy it follows that the amount of work performed by the system during any transformation depends only on the initial and the final states of the transformation.[2]

We can now use the empirical definition (13) of the energy and define the energy U as a function of the state of the system only.[3] Denoting by $\Delta U = U_B - U_A$ the variation in the energy of our system that occurs during a transformation from the state A to the state B, we can write equation (11), which is applicable to our thermally insulated system, in the form:

$$\Delta U + L = 0. \tag{14}$$

If our system is not thermally insulated, the left-hand side of (14) will in general be different from zero because there can then take place an exchange of energy in the form of

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[1] We need only mention here that no perfect thermal insulators exist. Thermal insulation can be obtained approximately, however, by means of the well-known methods of Calorimetry.

[2] It would be formally more exact, although rather abstract, to state the content of the preceding sentences as follows:

Experiments show that there exist certain substances called *thermal insulators* having the following properties: when a system is completely enclosed in a thermal insulator in such a way that work can be exchanged between the inside and the outside, the amount of work performed by the system during a given transformation depends only on the initial and final states of the transformation.

[3] It should be noticed here that if definition (13) of the energy of a state A of our system is to be applicable, it must be possible to transform the system from the standard state O to the state A while the system is thermally insulated. We shall show later (see section 13) that such a transformation is not always possible without an exchange of heat. In such cases, however, the opposite transformation $A \rightarrow O$ can always be performed. The work performed by the system during this reverse transformation is $-L_A$; we can therefore apply (13) to such cases also.

heat. We shall therefore replace (14) by the more general equation:

$$\Delta U + L = Q, \qquad (15)$$

where Q is equal to zero for transformations performed on thermally insulated systems and otherwise, in general, is different from zero.

Q can be interpreted physically as the amount of energy that is received by the system in forms other than work. This follows immediately from the fact that the variation in energy, ΔU, of the system must be equal to the total amount of energy received by the system from its environment. But from (15)

$$\Delta U = -L + Q,$$

and $-L$ is the energy received in the form of work. Hence, Q stands for the energy received in all other forms.

By definition, we shall now call Q the amount of heat received by the system during the transformation.

For a cyclic transformation, equation (15) takes on a very simple form. Since the initial and final states of a cycle are the same, the variation in energy is zero: $\Delta U = 0$. Thus, (15) becomes:

$$L = Q. \qquad (16)$$

That is, the work performed by a system during a cyclic transformation is equal to the heat absorbed by the system.

It is important at this point to establish the connection between this abstract definition of heat and its elementary calorimetric definition. The calorimetric unit of heat, the *calorie*, is defined as the quantity of heat required to raise the temperature of one gram of water at atmospheric pressure from 14°C to 15°C. Thus, to raise the temperature of m grams of water from 14°C to 15°C at atmospheric pressure, we require m calories of heat. Let Δu_a denote the variation in energy of one gram of water, and l_c the work done as a result of its expansion when its temperature is

raised from 14°C to 15°C at atmospheric pressure. For m grams of water, the variation in energy and the work done are:

$$\Delta U_c = m \Delta u_c; \qquad L_a = m l_a. \tag{17}$$

We now consider a system S which undergoes a transformation. In order to measure the heat exchanged between the system and the surrounding bodies, we place the system in contact with a calorimeter containing m grams of water, initially at 14°C. We choose the mass of the water in such a way that after the transformation has been completed, the temperature of the water is 15°C.

Since an ideal calorimeter is perfectly insulated thermally, the complex system composed of the system S and the calorimetric water is thermally insulated during the transformation. We may therefore apply equation (14) to this transformation. The total variation in energy is equal to the sum:

$$\Delta U = \Delta U_S + \Delta U_c,$$

where ΔU_S is the variation in energy of the system S, and ΔU_c is the variation in energy of the calorimetric water. Similarly, for the total work done, we have:

$$L = L_S + L_c.$$

From (14) we have, then,

$$\Delta U_S + \Delta U_c + L_S + L_c = 0;$$

or, by (17),

$$\Delta U_S + L_S = -(\Delta U_c + L_c)$$

$$= -m(\Delta u_c + l_c).$$

But from the definition (15), $\Delta U_S + L_S$ is the amount of heat Q_S received by the system S. Thus, we have:

$$Q_S = -m(\Delta u_c + l_c). \tag{18}$$

We see from this that the amount of heat is proportional to m.

On the other hand, in calorimetry the fact that m grams of calorimetric water have been heated from 14°C to 15°C means that m calories of heat have been transferred from the system S to the calorimeter; that is, that the system S has received $-m$ calories, or that Q_s, expressed in calories, is equal to $-m$. We see also, by comparison with (18), that the amount of heat, as given by the definition (15), is proportional to the amount when it is expressed in calories; the constant of proportionality is $(\Delta u_c + l_c)$.

According to (15), heat is measured in energy units (ergs). The constant ratio between ergs and calories has been measured by many investigators, who have found that

$$1 \text{ calorie} = 4.185 \times 10^7 \text{ ergs.} \qquad (19)$$

In what follows we shall generally express heat measurements in energy units.

Equation (15), which is a precise formulation of the equivalence of heat and work, expresses the *first law of thermodynamics*.

4. The application of the first law to systems whose states can be represented on a (V, p) diagram. We shall now apply the first law of thermodynamics to a system, such as a homogeneous fluid, whose state can be defined in terms of any two of the three variables V, p, and T. Any function of the state of the system, as, for example, its energy, U, will then be a function of the two variables which have been chosen to represent the state.

In order to avoid any misunderstanding as to which are the independent variables when it is necessary to differentiate partially, we shall enclose the partial derivative symbol in a parenthesis and place the variable that is to be held constant in the partial differentiation at the foot of the parenthesis. Thus, $\left(\dfrac{\partial U}{\partial T}\right)_V$ means the derivative of

U with respect to T, keeping V constant, when T and V are taken as the independent variables. Notice that the above expression is in general different from $\left(\dfrac{\partial U}{\partial T}\right)_p$, because in the first case the volume is kept constant while in the second case the pressure is kept constant.

We now consider an infinitesimal transformation of our system, that is, a transformation for which the independent variables change only by infinitesimal amounts. We apply to this transformation the first law of thermodynamics as expressed by equation (15). Instead of ΔU, L, and Q, we must now write dU, dL, and dQ, in order to point out the infinitesimal nature of these quantities. We obtain, then,

$$dU + dL = dQ. \tag{20}$$

Since for our system, dL is given by (3), we have:

$$dU + pdV = dQ. \tag{21}$$

If we choose T and V as our independent variables, U becomes a function of these variables, so that:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV,$$

and (21) becomes:

$$\left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]dV = dQ. \tag{22}$$

Similarly, taking T and p as independent variables, we have:

$$\left[\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right]dT + \left[\left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T\right]dp = dQ. \tag{23}$$

Finally, taking V and p as independent variables, we obtain:

$$\left(\frac{\partial U}{\partial p}\right)_V dp + \left[\left(\frac{\partial U}{\partial V}\right)_p + p\right]dV = dQ. \tag{24}$$

The *thermal capacity* of a body is, by definition, the ratio, dQ/dT, of the infinitesimal amount of heat dQ absorbed by the body to the infinitesimal increase in temperature dT

produced by this heat.   In general, the thermal capacity of a body will be different according as to whether the body is heated at constant volume or at constant pressure. Let C_V and C_p be the thermal capacities at constant volume and at constant pressure, respectively.

A simple expression for C_V can be obtained from (22). For an infinitesimal transformation at constant volume, $dV = 0$; hence,

$$C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V. \tag{25}$$

Similarly, using (23), we obtain the following expression for C_p :

$$C_p = \left(\frac{dQ}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p. \tag{26}$$

The second term on the right-hand side represents the effect on the thermal capacity of the work performed during the expansion.   An analogous term is not present in (25), because in that case the volume is kept constant so that no expansion occurs.

The thermal capacity of one gram of a substance is called the *specific heat* of that substance; and the thermal capacity of one mole is called the *molecular heat*.   The specific and molecular heats at constant volume and at constant pressure are given by the formulae (25) and (26) if, instead of taking an arbitrary amount of substance, we take one gram or one mole of the substance, respectively.

5. **The application of the first law to gases.**   In the case of a gas, we can express the dependence of the energy on the state variables explicitly.   We choose T and V as the independent variables, and prove first that the energy is a function of the temperature T only and does not depend on the volume V.   This, like many other properties of gases, is only approximately true for real gases and is assumed to hold exactly for ideal gases.   In section 14 we shall deduce from the second law of thermodynamics the

result that the energy of any body which obeys the equation of state, (7), of an ideal gas must be independent of the volume V. At this point, however, we shall give an experimental proof of this proposition for a gas; the experiment was performed by Joule.

Into a calorimeter Joule placed a container having two chambers, A and B, connected by a tube (Figure 5). He filled the chamber A with a gas and evacuated B, the two chambers having first been shut off from each other by a stopcock in the connecting tube. After thermal equilibrium had set in, as indicated by a thermometer placed within the calorimeter, Joule opened the stopcock, thus permitting the gas to flow from A into B until the pressure everywhere
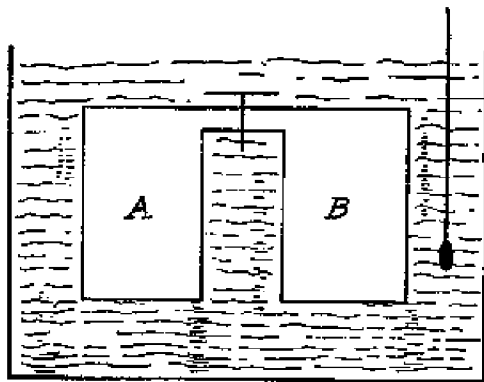

Fig. 5.

in the container was the same. He then observed that there was only a very slight change in the reading of the thermometer. This meant that there had been practically no transfer of heat from the calorimeter to the chamber or vice versa. It is assumed that if this experiment could be performed with an ideal gas, there would be no temperature change at all.

We now apply the first law to the above transformation. Since $Q = 0$, we have from equation (15) for the system composed of the two chambers and the enclosed gas:

$$\Delta U + L = 0,$$

where L is the work performed by the system and ΔU is the variation in energy of the system. Since the volumes of the two chambers A and B composing our system do not change during the experiment, our system can perform no external work, that is, $L = 0$. Therefore,

$$\Delta U = 0;$$

the energy of the system, and, hence, the energy of the gas, do not change.

Let us now consider the process as a whole. Initially the gas occupied the volume A, and at the end of the process it filled the two chambers A and B; that is, the transformation resulted in a change in volume of the gas. The experiment showed, however, that there was no resultant change in the temperature of the gas. Since there was no variation in energy during the process, we must conclude that a variation in volume at constant temperature produces no variation in energy. In other words, *the energy of an ideal gas is a function of the temperature only and not a function of the volume*. We may therefore write for the energy of an ideal gas:

$$U = U(T). \tag{27}$$

In order to determine the form of this function, we make use of the experimental result that the specific heat at constant volume of a gas depends only slightly on the temperature; we shall assume that for an ideal gas the specific heat is exactly constant. In this section we shall always refer to one mole of gas; C_V and C_p will therefore denote the molecular heats at constant volume and at constant pressure, respectively.

Since U depends only on T, it is not necessary to specify that the volume is to be kept constant in the derivative in (25); so that, for an ideal gas, we may write:

$$C_V = \frac{dU}{dT}. \tag{28}$$

Since C_V is assumed to be constant, we can integrate at once, and we get:

$$U = C_V T + W, \tag{29}$$

where W is a constant of integration which represents the energy left in the gas at absolute zero temperature.[4]

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[4] This additive constant affects the final results of the calculations only when chemical transformations or changes of the states of aggregation of the substances are involved. (See, for example, Chapter VI.) In all other cases, one may place the additive constant equal to zero.

For an ideal gas, equation (21), which expresses the first law of thermodynamics for infinitesimal transformations, takes on the form:

$$C_V dT + p dV = dQ. \tag{30}$$

Differentiating the characteristic equation (7) for one mole of an ideal gas, we obtain:

$$p dV + V dp = R dT. \tag{31}$$

Substituting this in (30), we find:

$$(C_V + R)dT - V dp = dQ. \tag{32}$$

Since $dp = 0$ for a transformation at constant pressure, this equation gives us:

$$C_p = \left(\frac{dQ}{dT}\right)_p = C_V + R. \tag{33}$$

That is, the difference between the molecular heats of a gas at constant pressure and at constant volume is equal to the gas constant R.

The same result may also be obtained from (26), (29), and (7). Indeed, for an ideal gas we have from (29) and (7):

$$\left(\frac{\partial U}{\partial T}\right)_p = \frac{dU}{dT} = C_V; \qquad \left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial}{\partial T}\frac{RT}{p}\right)_p = \frac{R}{p}.$$

Substituting these expressions in (26), we again obtain (33).

It can be shown by an application of kinetic theory that:

$$C_V = \tfrac{3}{2} R \text{ for a monatomic gas; and}$$
$$C_V = \tfrac{5}{2} R \text{ for a diatomic gas.} \tag{34}$$

Assuming these values, which are in good agreement with experiment, we deduce from (33) that:

$$C_p = \tfrac{5}{2} R \text{ for a monatomic gas; and}$$
$$C_p = \tfrac{7}{2} R \text{ for a diatomic gas.} \tag{35}$$

If we place

$$K = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}, \tag{36}$$

we also obtain:

$$K = \tfrac{5}{3} \text{ for a monatomic gas; and}$$

$$K = \tfrac{7}{5} \text{ for a diatomic gas.} \qquad (37)$$

6. Adiabatic transformations of a gas. A transformation of a thermodynamical system is said to be *adiabatic* if it is reversible and if the system is thermally insulated so that no heat can be exchanged between it and its environment during the transformation.

We can expand or compress a gas adiabatically by enclosing it in a cylinder with non-heat-conducting walls and piston, and shifting the piston outward or inward very slowly. If we permit a gas to expand adiabatically, it does external work, so that L in equation (15) is positive. Since the gas is thermally insulated, $Q = 0$, and, hence, ΔU must be negative. That is, the energy of a gas decreases during an adiabatic expansion. Since the energy is related to the temperature through equation (29), a decrease in energy means a decrease in the temperature of the gas also.

In order to obtain a quantitative relationship between the change in temperature and the change in volume resulting from an adiabatic expansion of a gas, we observe that, since $dQ = 0$, equation (30) becomes:

$$C_v dT + p \, dV = 0.$$

Using the equation of state, $pV = RT$, we can eliminate p from the above equation and obtain:

$$C_v dT + \frac{RT}{V} dV = 0,$$

or

$$\frac{dT}{T} + \frac{R}{C_v} \frac{dV}{V} = 0.$$

Integration yields:

$$\log T + \frac{R}{C_v} \log V = \text{constant.}$$

Changing from logarithims to numbers, we get:

$$TV^{\frac{R}{C_V}} = \text{constant}.$$

Making use of (36), we can write the preceding equation in the form:

$$TV^{K-1} = \text{constant}. \tag{38}$$

This equation tells us quantitatively how an adiabatic change in the volume of an ideal gas determines the change in its temperature. If, for example, we expand a diatomic gas adiabatically to twice its initial volume, we find from (38) (assuming, according to (37), that $K = \frac{7}{5}$) that the temperature is reduced in the ratio $1:2^{0.4} = 1: 1.32$.

Using the equation of state, $pV = RT$, we can put equation (38) of an adiabatic transformation in the following forms:

$$pV^{K} = \text{constant}. \tag{39}$$

$$\frac{T}{p^{\frac{K-1}{K}}} = \text{constant}. \tag{40}$$

Equation (39) is to be compared with the equation,

$$pV = \text{constant},$$

of an isothermal transformation. On the (V, p) diagram, the isothermals are a family of equilateral hyperbolae; the adiabatic lines represented by equation (39), are qualitatively similar to hyperbolae, but they are steeper because $K > 1$.

Isothermal and adiabatic curves are represented in Figure 6, the former by the solid lines and the latter by the dotted lines.

An interesting and simple application of the adiabatic expansion of a gas is the calculation of the dependence of the temperature of the atmosphere on the height above sea level. The principal reason for this variation of tempera-