THERMODYNAMICS

BY

ENRICO FERMI

16·3·79

DOVER PUBLICATIONS, INC.
NEW YORK

IIA Lib.,

Copyright © 1936 by Enrico Fermi.
Laura Fermi, Copyright Owner.
All rights reserved under Pan American and International Copyright Conventions.

Published in Canada by General Publishing Company, Ltd., 30 Lesmill Road, Don Mills, Toronto, Ontario.
Published in the United Kingdom by Constable and Company, Ltd., 10 Orange Street, London WC 2.

This Dover edition, first published in 1956, is an unabridged and unaltered republication of the work originally published by Prentice-Hall Company in 1937.

Library of Congress Catalog Card Number: 57-14599

Manufactured in the United States of America
Dover Publications, Inc.
180 Varick Street
New York, N. Y. 10014

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.

E. FERMI

Contents

PAGE
PREFACE v
INTRODUCTION ix
CHAPTER
I. THERMODYNAMIC SYSTEMS 1
  1. The state of a system and its transformations . . 1
  2. Ideal or perfect gases 8

II. THE FIRST LAW OF THERMODYNAMICS 11
  3. The statement of the first law of thermodynamics . 11
  4. The application of the first law to systems whose states can be represented on a (V, p) diagram. . . 19
  5. The application of the first law to gases 21
  6. Adiabatic transformations of a gas 25

III. THE SECOND LAW OF THERMODYNAMICS 29
  7. The statement of the second law of thermodynamics. 29
  8. The Carnot cycle 31
  9. The absolute thermodynamic temperature 35
  10. Thermal engines 44

IV. THE ENTROPY 46
  11. Some properties of cycles 46
  12. The entropy 48
  13. Some further properties of the entropy 54
  14. The entropy of a system whose states can be represented on a (V, p) diagram 59
  15. The Clapeyron equation 63
  16. The Van der Waals equation 69

V. THERMODYNAMIC POTENTIALS 77
  17. The free energy 77
  18. The thermodynamic potential at constant pressure . 82
  19. The phase rule 86
  20. Thermodynamics of the reversible electric cell . . . 94

VI. GASEOUS REACTIONS 98
  21. Chemical equilibria in gases 98
  22. The Van't Hoff reaction box. 101
  23. Another proof of the equation of gaseous equilibria . 106
  24. Discussion of gaseous equilibria; the principle of Le Chatelier 109

CHAPTER PAGE
VII. THE THERMODYNAMICS OF DILUTE SOLUTIONS . . . 113
  25. Dilute solutions 113
  26. Osmotic pressure 118
  27. Chemical equilibria in solutions 123
  28. The distribution of a solute between two phases . . 127
  29. The vapor pressure, the boiling point, and the freezing point of a solution 130

VIII. THE ENTROPY CONSTANT 139
  30. The Nernst theorem 139
  31. Nernst's theorem applied to solids. 142
  32. The entropy constant of gases 147
  33. Thermal ionization of a gas; the thermionic effect . 151

INDEX 157

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]:

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

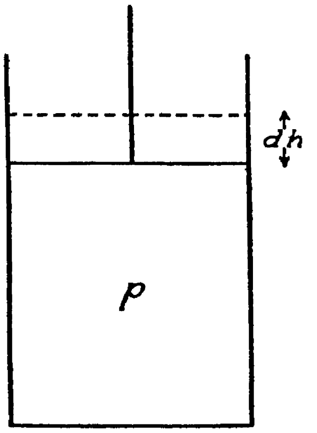

Fig. 1.

---

[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):

$$L = \int_A^B p\,dV, \tag{4}$$

where the integral is taken over the entire transformation.

When the state of the system can be represented on a (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

$$L = \int_{V_A}^{V_B} p\,dV, \tag{5}$$

where V_A and V_B are the volumes corresponding to the states A and B. This integral, and hence the work done, can be represented geometrically by the shaded area in the figure.

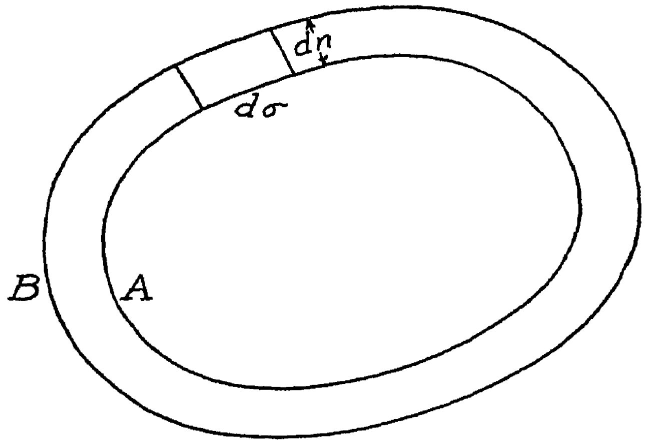

Fig. 2.

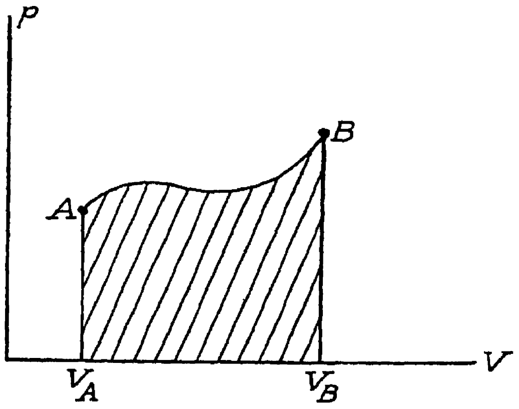

Fig. 3.

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.

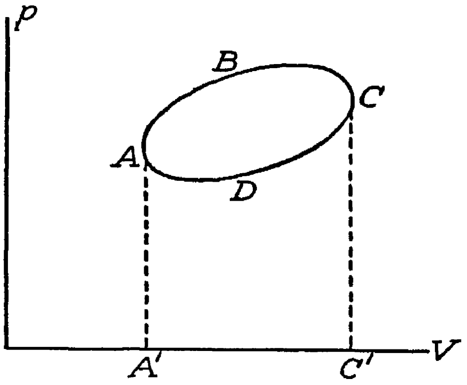

Fig. 4.

A transformation during which the system performs no external work is called an *isochore transformation.* If we assume 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:

$$\begin{aligned} L = \int_{V_1}^{V_2} pdV &= \frac{m}{M} RT \int_{V_1}^{V_2} \frac{dV}{V} \\ &= \frac{m}{M} RT \log \frac{V_2}{V_1} \\ &= \frac{m}{M} RT \log \frac{p_1}{p_2}, \end{aligned} \tag{9}$$

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.