STUDIES IN MODERN THERMODYNAMICS 2

PRINCIPLES OF THERMODYNAMICS

JAMES A. BEATTIE and IRWIN OPPENHEIM

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PREFACE

The main purpose of this book is to present a rigorous and logical discussion of the fundamentals of thermodynamics. We have been particularly careful to specify and discuss the postulates and laws which form the bases for the science of thermodynamics. We have attempted to give a clear and full account of the first, second and third laws of thermodynamics. Some applications of these laws are treated in detail; others are not considered here.

Partial molar properties are treated fully and emphasis has been placed on the importance of writing changes in state for thermodynamic calculations. The Gibbs criteria for equilibrium and stability are discussed in great detail.

The inspiration for this work comes from the classic work of Gibbs and from discussions with our teachers and colleagues.

In his lectures on thermodynamics, Professor Henry B. Phillips has given the clearest and most complete treatment of the second law which we have found anywhere. With his consent we have used some of these results in our Chapter 8.

Professor Louis J. Gillespie was always ready to give his time and knowledge to solve problems, especially those arising from the *Thermodynamics* of J. Willard Gibbs.

Professor Clark C. Stephenson has helped us to understand certain features of the third law of thermodynamics.

Professor John G. Kirkwood introduced one of us (I.O.) to the beauty and logical structure of thermodynamics.

This book would not have appeared without the aid and superb typing abilities of Doris L. Currier, Frances M. Doherty, Virginia Prescott and Vera M. Spanos who have participated in its preparation at various stages in its development.

James A. Beattie
Irwin Oppenheim

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Chapter 1

DEFINITIONS

Thermodynamics is a phenomenological discipline dealing with the interactions of systems with their surroundings, and with the description of and the relations among the macroscopic properties of systems. The values of these interactions and gross properties are determined by macroscopic measuring devices, all of which have the following properties: (1) their spacial resolution is such that they make measurements over regions of space which are very large compared to molecular dimensions (10^{-10} m) and therefore contain many molecules; (2) their time constants are such that they make measurements over time intervals that are very long compared to molecular times (10^{-12} sec); and (3) their inherent errors are very large compared to the contribution of individual molecules to the property under consideration.

Thermodynamics is a logical deductive science based on a small number of postulates called laws. These laws summarize accurately our knowledge of the macroscopic behavior of systems in certain respects, but make no explicit reference to the structure of matter. The final results of thermodynamics are equations of great generality. The actual magnitudes of the quantities appearing in these equations are not predicted; they must be derived from direct measurement, or from the results of statistical thermodynamics which involves molecular theory explicitly.

1.1. System, boundary, surroundings, medium. A thermodynamic system is the part of the physical universe under investigation. It usually contains one or more chemical substances, but it may consist only of one or more of the following: radiation, an electric field, a magnetic field.

The system is confined by a boundary that separates it from the rest of the physical universe, called the surroundings. The boundary usually consists of the inner walls of the vessel containing the system. However, it may be composed entirely or in part of mathematical surfaces. For example, the boundary of a fixed mass of fluid flowing in a horizontal pipe is, in part, the inner surface of the pipe and, in part, two imaginary vertical planes that separate the mass under consideration from the fluid ahead of and that behind it. The description of a thermodynamic system necessarily includes certain information concerning its boundary. The precise location of the boundary and the constraints imposed by the boundary on the interactions of the system with its surroundings are matters of great importance and must be given. Unless otherwise stated we shall always suppose that the boundary does not react chemically with any of the substances composing the system.

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The part of the surroundings in the immediate neighborhood of a system is sometimes called the medium. It is large when compared with the system but small compared with the surroundings. The system and medium constitute a composite system which is usually considered to be enclosed in an exterior boundary.

1.2. Closed and open systems. A system is called closed when no mass crosses its boundary, and open when mass flows across its boundary.

1.3. Isolated system. An isolated system has no observable interaction with its surroundings. The boundary of an isolated system shields it from all external influences so that events occurring in the system are not affected by changes taking place in the surroundings. Such a boundary is an abstraction. However, real boundaries approaching this ideal behavior more or less closely are known for all types of interaction except gravitation.

1.4. Thermodynamic properties of a system. The properties of a system that are of interest in thermodynamic discussions are those physical attributes that are perceived directly by the senses, or are made perceptible by certain macroscopic experimental methods of investigation. Thus, thermodynamics deals with macroscopic rather than microscopic properties. We recognize two classes of properties: (1) numerical properties, such as pressure and volume, to which a numerical value can be assigned by direct or indirect comparison with a standard, or by combining certain measurements in accordance with definite rules; and (2) non-numerical properties, such as the kinds of substances composing a system and the states of aggregation of its parts.

1.5. State of thermodynamic equilibrium. A system is in a state of thermodynamic equilibrium, or more simply in an equilibrium state, when each of its thermodynamic properties is time independent and when there are no fluxes within the system or across its boundary. For example, there must not be any transfer of matter or electricity from one place to another, within or across the boundary.

In an equilibrium state "caused by the balance of the active tendencies" [1] of a system, all agents tending to produce change in the properties of the system are so balanced that an infinitesimal variation in the value of each agent, either in the positive or negative direction, is sufficient to produce a corresponding change in the state of the system; and restoration of this agent to its former value causes the system to return to its initial state. Hence, such a state of thermodynamic equilibrium can be reached from the two opposite sides with respect to each agent tending to produce change in the system. Of course, it is possible to pass from one equilibrium state to another by changing the external constraints on the system. We shall call this condition a state of dynamic equilibrium.

In a system as initially constituted several different processes may be taking place simultaneously at quite different rates. After a while the system may apparently have reached a state of equilibrium, at least with respect to variations in the values of the properties being studied. However, processes leading to entirely different equilibrium states may be occurring so slowly that they do not produce a detectable displacement in the supposed equilibrium state because (1) the investigator cannot observe the system for an indefinitely long time, and (2) all of his measuring instruments are subject to inherent errors that may mask the effect of a small change in the properties of the system. Examples of processes which may take place quite slowly are: (1) the sliding of one solid over another when they are in contact; (2) the diffusion of a constituent of a solid or of a viscous liquid solution; (3) a chemical or nuclear reaction; (4) the transformation of a solid from one crystalline form to another; (5) the relief of strains in a solid; and (6) the growth of crystal size in a solid.

Insistence on a strict interpretation of the definition of equilibrium would rule out the application of thermodynamics to practically all states of real systems. Fortunately thermodynamic results can be applied to measurements on systems that are not in equilibrium with respect to all processes occurring therein. Of course, we must know from an experimental study of the given system, or from experience with similar systems, which processes occur so slowly that their effects on the given state may safely be ignored. In the study of the properties of a system in a supposed equilibrium state, the experimental investigator considers the effects of all processes which, he believes, have a perceptible effect on the properties under investigation; and he proves experimentally that this state can be approached from the two opposite sides by each such process. He neglects the effects of very slow processes on the state of the system. The success, or failure, of this procedure when applied to a particular equilibrium state is determined by the agreement, or lack of agreement, between thermodynamic deduction and experiment.

In his discussion of equilibrium states of a system, Gibbs invoked passive forces that prevent certain changes in state no matter how the initial state or external conditions are varied, within limits which, however, allow finite variations in the values of these forces [1]. Hence we can apply the definition of an equilibrium state to a system without regard to very slow processes by associating a passive force with each such agent tending to produce change.

In the study of the properties of systems in equilibrium states the careful experimental investigator specifies: (1) the system and the values of a sufficient number of its properties to fix its state with the requisite accuracy for the proposed study; (2) the location of the boundary and its effect on the interactions between the system and its surroundings; and (3) the variations in state with respect to which the equilibrium is being discussed. Furthermore, he proves that the given state can be approached from the two opposite sides with respect to each agent tending to produce the variations in state mentioned in (3) above; and he checks his measurements by means of equations derived from thermodynamics.

The measured pressure of a closed system composed of liquid nitric oxide (NO) and its vapor, enclosed in a rigid, thermally conducting boundary, attains a constant value shortly after it has been immersed in a thermostat maintained at a fixed temperature. The same value of pressure is observed whether we approach the given temperature from a higher or from a lower value. Yet we have reason to believe from the extrapolation of other data that nitric oxide is decomposing into nitrogen and oxygen, but at an exceedingly small rate. We can either consider that the decomposition of NO is prevented by a passive force, or that the properties of NO are idealized to the extent that no decomposition takes place in the temperature range under consideration. Under either assumption the system attains an equilibrium state with respect to the transfer of NO from one phase to the other and to the establishment of uniform pressure and temperature throughout the system shortly after it has been placed in the thermostat. Measurements of vapor pressures over a range of temperatures can be correlated with other equilibrium measurements on this system by a thermodynamic equation not involving the dissociation of NO.

In contrast to the example just cited, the equilibrium between nitrogen tetroxide (N_2O_4) and nitrogen dioxide (NO_2) is established rapidly from each side. We could not correlate measurements of vapor pressures in this system by means of thermodynamic equations if we supposed it to be composed of an idealized N_2O_4 which did not dissociate under conditions where appreciable quantities of each species are actually present.

Usually we can easily distinguish between a process whose effect on the state of a system must be taken into account and one whose effect can be ignored. Occasionally the rate of a process lies so near the limit at which its effect can be neglected that a more detailed study of the system is required. Such is the case for the two systems now to be considered. Each is used to define a fixed temperature on the International Practical Temperature Scale [2] of 1948, which will be discussed in Chapter 2. Originally it was believed that the temperatures of equilibrium of ice, liquid water, and water vapor, 0.01°C (Int.), and that of liquid sulfur and its vapor under a pressure of one standard atmosphere, 444.6°C (Int.), were established rather quickly, in a matter of several hours or, at most, in a day. And so they were, within the accuracy of measurement of temperature at that time. Later investigations made under more carefully controlled conditions with more sensitive thermometers showed [3] that: (1) the triple point of water increased on the average by 1.7×10^{-4} °C the first day, 0.3×10^{-4} °C the second day, and 0.1×10^{-4} °C per day for about seven more days, thereafter remaining constant to within 0.1×10^{-4} °C; and (2) the sulfur point usually dropped by a total of 10×10^{-3} °C over a period of one to ten days (depending on the amount of trace impurities in the sample), after which it remained constant to 1×10^{-3} °C. The change of the triple point of water has been attributed to the growth in crystal size of ice (thereby reducing the effect of capillarity) and to the relief of strains in the crystal; and the change in the boiling point of sulfur has been attributed to the slowness of the attainment of equilibrium among the polymorphs of sulfur in the liquid and perhaps in the vapor. Further study of these systems would be necessary if we should desire to define the temperature scale more accurately than 0.1×10^{-4} °C at the triple point of water, and 1×10^{-3} °C at the sulfur point.

1.6. State variables, extensive and intensive properties, independent and dependent variables. Each numerical property of a system is called a state variable.

Consider a group of λ identical systems B. The numerical value of an extensive property F of the composite system λB is λ times the corresponding value of F for each system B

$$F(\lambda \mathrm{B}) = \lambda F(\mathrm{B}) \tag{1.1}$$

The numerical value of an intensive property f of the system (λB) is equal to the value of f for each system B

$$f(\lambda \mathrm{B}) = f(\mathrm{B}) \tag{1.2}$$

Volume and mass are extensive properties of a system; pressure and temperature are intensive properties.

Any set of state variables, all of whose numerical values must be specified to determine the state of a system, constitutes a set of independent variables. The remaining state variables are called dependent variables.

1.7. Specification of the state of a simple system. The state of a system is determined with sufficient accuracy for most thermodynamic studies by the specification of the values of a relatively small number of properties. A simple system is defined as one whose state is uninfluenced by the following effects: (1) external gravitational, electric, and magnetic field intensities; (2) shape (capillary tensions); (3) distortion of solid crystals [4]; and (4) variations of the isotopic compositions of the constituent substances from their normal values. Fortunately, most of the systems of thermodynamic interest may be regarded as simple systems for all ordinary laboratory conditions and procedures.

In general, we fix the state of a homogeneous simple system composed of one substance by specifying the substance, mass, aggregation state, pressure, and temperature, for example, $2\mathrm{H}_2$(g, 1 atm, 25°C). Here the symbol H_2 designates not only the substance hydrogen, but also one formula weight expressed in some unit of mass, such as the gram or the pound.

If the system is a homogeneous mixture of two or more substances (a solution) we must give the composition in addition to the quantities specified above. For example, $\mathrm{HCl} \cdot 5.551\mathrm{H}_2\mathrm{O}$ (l, 1 atm, 25°C) designates a solution of one formula weight of HCl in 5.551 formula weights of H_2O at a given pressure and temperature. In many thermodynamic studies we are interested in only one of the constituents of a solution, for example the HCl in the above system. In this case we would write HCl (0.1 wf, 1 atm, 25°C). This designates the substance HCl in the dissolved state, in a sufficient amount of solution of HCl in water of 0.1 weight formal concentration (0.1 formula weights of HCl in 1 kg of water) to contain one formula weight of HCl. The solvent is always understood to be liquid water unless otherwise stated.

We cannot apply thermodynamics to a system in an equilibrium state unless we have specified the state with sufficient exactness to fix the properties of interest with the required accuracy.

The following proposition has been amply confirmed by experiment. We shall call it a thermodynamic postulate. A simple homogeneous system can exist in only a very small number of equilibrium states when its pressure, density, and composition (expressed in units of mass) are fixed. In general, this number of states is unity. There are a few exceptions where two states can exist over limited ranges of pressure and density. For example, liquid water under a pressure of one atmosphere has a maximum density at about 4°C, so that in the neighborhood of this temperature there are two states having the same pressure, density, and mass: one at a temperature above and one at a temperature below 4°C.

1.8. Change in state, chemical reaction. Let the external constraints acting on a system in a fixed initial state be varied so that the system undergoes a change in its state to some final fixed value. The change in state of the system is completely defined when its initial and its final states are specified. For example, we write

$$H_2O\ (l,\ 1\ \text{atm},\ 100^\circ\text{C}) = H_2O\ (g,\ 2\ \text{atm},\ 150^\circ\text{C}) \tag{1.3}$$

to indicate that the initial state of the system is one formula weight of liquid H_2O at 1 atm and 100°C, and its final state is one formula weight of gaseous H_2O at 2 atm and 150°C. The method of accomplishing this result does not appear in the change in state. If we desire to impart this additional information, we must describe the process, which is defined in Section 1.9.

The importance of the change in state arises from the fact that all thermodynamic quantities concerned with any change in a system depend in part on the change in state; and the increments of many of these quantities depend only on the change in state, not on the process. We have called the latter quantities state variables. The first step in the solution of any problem in thermodynamics concerned with change is to write the change in state. Unless this can be done, the results of thermodynamics cannot be applied to the change under investigation.

We frequently associate with the notation H_2O (l, 1 atm, 100°C) of eqn. (1.3) any extensive property of this system, for example, its volume. We can then specify, next to the right-hand side of the equation, the increase in this property accompanying the change in state; for example $\Delta V = a\ \mathrm{m}^3$, where a is the volume of the system in its final state minus its volume in its initial state.

Changes in state may be added and subtracted in the same manner as the accompanying changes in volume. For example, the change in state in eqn. (1.3) may be regarded as the sum of the following three changes:

$$H_2O\,(l) = H_2O\,(g)\ (1\ \text{atm},\ 100°\text{C}) \tag{1.4}$$

$$H_2O\,(g,\ 100°\text{C}) = H_2O\,(g,\ 150°\text{C})\ (1\ \text{atm}) \tag{1.5}$$

$$H_2O\,(g,\ 1\ \text{atm}) = H_2O\,(g,\ 2\ \text{atm})\ (150°\text{C}) \tag{1.6}$$

Here a property written to the right of an equation applies to each term, but does not imply that this property is constant during the change.

When writing a change in state involving a chemical reaction, we must have clearly in mind the distinction between a chemical equation and a change in state. A chemical equation expresses only the relative amounts of the substances taking part in the reaction. For example, the equation

$$3H_2 + N_2 = 2NH_3 \tag{1.7}$$

says that whenever NH_3 is produced from H_2 and N_2, the relative numbers of formula weights of these substances involved are in the proportion

$$H_2 : N_2 : NH_3 = 3:1:2 \tag{1.8}$$

Equation (1.7) does not imply a particular experiment in which two formula weights of NH_3 are formed. In theoretical thermodynamic discussions, we frequently write eqn. (1.7) in the form

$$-3H_2 - 1N_2 + 2NH_3 = 0 \tag{1.9}$$

and represent it by the notation

$$\sum_{1\ i}^{3} \nu_i B_i = 0 \tag{1.10}$$

Here ν_i is the stoichiometric coefficient of B_i in the chemical equation; it has a negative value for a reactant and a positive value for a product. Thus, if we identify B_1, B_2, and B_3 with H_2, N_2, and NH_3, respectively, we find

$$\nu_1 = -3,\ \nu_2 = -1,\ \nu_3 = +2 \tag{1.11}$$

In writing chemical equations, we enter the correct molecular formula (see Section 1.17) of the substances involved, and we frequently indicate the aggregation state (see Section 1.14) of each substance, but we do not give all of the information necessary to fix the state of each.

For comparison purposes we shall now write a chemical change in state involving the chemical equation (1.7):

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