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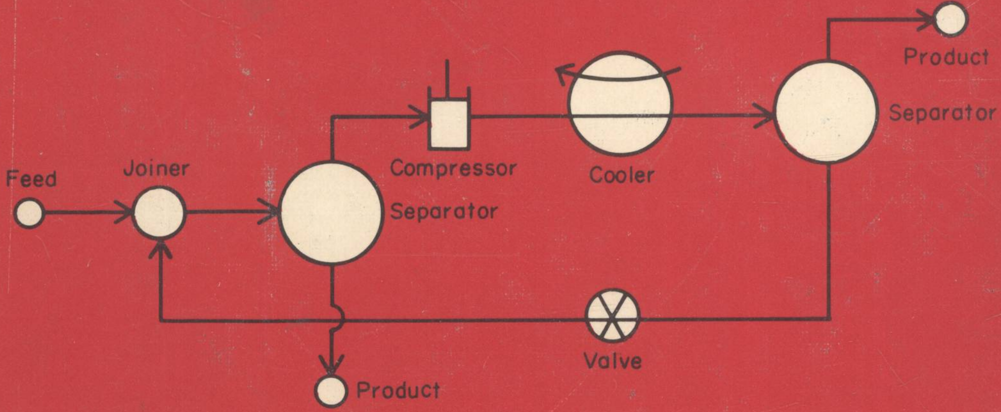
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THERMODYNAMICS OF FLUIDS

An Introduction to Equilibrium Theory

K. C. CHAO • R. A. GREENKORN

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Thermodynamics of Fluids

AN INTRODUCTION TO EQUILIBRIUM THEORY

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To our parents

Juipu and Chungpu Chao
and
Sophie and Frederick Greenkorn

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PREFACE

Equilibrium models play a major part in the engineering analysis of chemical processes. The main purpose of this book is to present tools that are needed for the construction of these models for real systems. The usefulness of equilibrium properties is, however, not limited to the construction of models. The task of making mass and energy balances requires a knowledge of the volumetric behavior and of the energy functions of the materials in question. The study of chemical reactors, of transport operations, and of the dynamic response of real systems presupposes that the equilibrium properties of the fluids involved are known.

The diversity of substances encountered in chemical processes precludes a compiler's approach, such as employed by heat power engineers in the preparation of the steam tables. Even when extensive experimental data are available on a system of interest, the data are hardly ever adequate without interpretation to account for effects of variation of compositions, temperature, and pressure. Direct experimental data for most real systems of practical interest are usually either unavailable or fragmentary. A large body of literature has been developed to answer the need for the correlation, prediction, and estimation of physical properties. The theory of equilibrium properties provides the basis for the judicious use of this literature.

The development of equilibrium theory has been rapid during the last two decades. The developments rest on the foundation of Gibbs' general theory of equilibrium, for which practical measures were invented by Lewis and co-workers in the 1920s and 1930s. The complexity of real fluid behavior nevertheless defeated all efforts at reducing the theory to meaningful practice except for ideal gases and ideal solutions until the principle of corresponding states was established on a molecular basis and exploited for the description of pure fluid behavior. Following this major achievement, the last two decades witnessed rapid advances in the study of nonideal mixtures in both the gas and liquid states. As a result of these advances more and more process systems are amenable to quantitative description and analysis. It is our intention to give a comprehensive account of theory to include the basic principles, some significant developments, and interesting applications.

The material contained in this book is meant to introduce the reader to the frontiers of application starting with the fundamental principles. The introductory nature of this work does not imply the exclusive use of elementary subject matter even though only elementary principles of classical and statistical thermodynamics are included. The applications are illustrated with examples chosen to cover a wi variety of subjects and from diverse sources in our effo to present a broad view of the area, although we must ad to an unavoidable predilection toward subjects that are familiar to us.

This book is designed primarily as a textbook f graduate students in chemical engineering. However, t troductory nature of the work should make it equally o to practicing engineers who wish to learn the subject m but have had no prior training in it. The example appli tions and quantitative correlations presented should als of interest to experienced practitioners.

At Purdue University, we use the book as the text a course entitled "Thermodynamics" for the entering gra students. With judicious selection of text material w the major part of the contents in one semester with th hour classes per week. There is enough material in th to offer some degree of flexibility in the selection of topics for use in a semester course to suit the interest of a particular institution or instructor.

We are indebted to many individuals directly and indirectly for their contribution and assistance. Both of us were introduced to the subject area by Professor O. A. Hougen. Dr. J. A. Ellis read parts of the manuscript and made many helpful comments. We owe a debt of thanks to several graduate students at Purdue who read the manuscript and offered suggestions. Particular mention is due to P. R. Bienkowski, D. K. Foster, A. R. Middleton, S. J. Swanson, D. J. Tassin, and M. G. White for contributions with calculations and other materials. Mrs. Mary Dobrasko, Susie O'Dore, and Nancy Smith typed and retyped parts of the manuscript.

K. C. Chao
R. A. Greenkorn

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Chapter 1

THERMODYNAMIC PRINCIPLES AND FUNCTIONS

1.1 INTRODUCTION

The subject matter of this chapter is classical thermodynamics. Our purpose is to present a concise recapitulation of the fundamental concepts and functions used in classical thermodynamics. The emphasis is to show the structure and to develop the relations that are needed for the study of physicochemical equilibrium.

We begin with several definitions and then discuss exact and inexact differentials. Thermodynamic laws are presented on the basis of this discussion as statements regarding state functions. The zeroth, first, and second laws are stated in terms of the state functions they introduce: temperature, internal energy, and entropy, respectively. The ideal gas and absolute temperatures are defined in the course of discussion of the laws. (The statement and discussion of the third law will be postponed until Chapter 5.)

The usefulness of the thermodynamic laws is greatly extended with the introduction of the energy functions. The concept of their association with certain natural variables is basic to this usefulness. Since these functions are related to reversible shaft work under various conditions of constraint, they provide the basis for the development of criteria of equilibrium and stability.

The quantity of central importance in all studies of equilibrium is the Gibbs chemical potential, which is introduced through considerations of open systems. The usefulness of the chemical potential is indicated, but not developed, because the development is one of the central themes of several chapters to follow.

We close this chapter with a discussion of Jacobians as the mathematical tool for manipulating thermodynamic identities and include a collection of such identities of common occurrence.

1.2 SYSTEMS, PROCESSES, AND PROPERTIES

In thermodynamic analysis, we study a portion of the universe. This portion is called a *system*. The rest of the universe is the *surroundings*. If a system is separated from its surroundings so as to preclude exchange of mass and energy between the system and its surroundings, the system is called *isolated*. An *open* system is free to exchange mass and energy with its surroundings; the exchange can take place through a porous wall, a phase-boundary surface, or just an imaginary geometrical surface. A *closed* system cannot exchange mass with the surroundings.

A *phase* is a homogeneous part of a system. Homogeneity must be defined in terms of an appropriate scale, since, with a sufficiently fine scale, all matter is heterogeneous in view of its atomic and molecular constitution. With a coarse scale, an emulsion could be considered homogeneous. All homogeneous phases have *extensive* properties that are directly proportional to the mass of the phase. For example, volume, internal energy, and entropy are extensive properties. An extensive property of a system is the sum of the extensive property values for all the phases in the system. The properties of a phase that are independent of mass, such as density, temperature, and pressure, are called *intensive* properties.

An extensive property E is a homogeneous function of degree 1 in mass m of the components and is expressed by

$$\lambda E(T,p,\rho,m_1,m_2,\ldots) = E(T,p,\rho,\lambda m_1,\lambda m_2,\ldots) \tag{1.1}$$

where λ is a positive number that is not necessarily equal to 1 and the subscripts refer to components. An intensive property I is a homogeneous function of degree zero in m,

$$I(T,p,\rho,m_1,m_2,\ldots) = I(T,p,\rho,\lambda m_1,\lambda m_2,\ldots) \tag{1.2}$$

The ratio of two extensive properties is an intensive property.

The *state* of a phase is specified by its composition and a relatively few intensive properties; usually two intensive properties (e.g., temperature and pressure) are enough. The exact number or kind of intensive properties required are determined by experience. Additional intensive properties such as specific surface area, gravitational acceleration, and magnetic or electric fields may be required to specify state of a phase for some systems.

State properties assume the same value at the same state regardless of the previous history of the system; that is, state properties are reproducible and have no memory. The hardness of a specimen of steel is not reproducible inasmuch as it depends on its heat treatment. Liquids of high polymers likewise have nonreproducible properties.

A system is at *equilibrium* if the net fluxes of mass, energy, and chemical reactions in the system are all zero. Temperature and chemical potentials are uniform in equilibrium systems. An equilibrium state is a *steady state*; that is, it does not change with time. Not all steady states, however, are equilibrium states, because there may be net flow of mass or energy.

A change of state is called a *process*. An *adiabatic* process takes place when the system is insulated from its surroundings; an *isothermal* process takes place at a constant temperature; and an *isobaric* process takes place at constant pressure.

A process is *reversible* when caused by an infinitesimal net driving force and when proceeding at infinitesimal speed. All the states that a system assumes during a reversible process are equilibrium states. The reversible process is an ideal zero-speed limit for actual processes, which must take place with finite speed; all actual processes are irreversible.

1.3 EXACT AND INEXACT DIFFERENTIALS

The quantities of interest in thermodynamics can be divided into two broad classes. One class contains quantities that are associated with the state of a system, such as density, isothermal compressibility, and heat capacity. These quantities are called state properties or state functions and assume definite values depending only on the state of the system. They are represented by exact differentials. The other class of quantities such as heat and work are associated with processes and are represented by inexact differentials.

The first and the second laws are statements regarding certain functions being state functions, which are independent of path. Since the values of state properties are independent of path, only the initial and final states must be determined, either by direct observations or by indirect derivations. The results become applicable to the myriad of possible processes that can take place in between the initial and final states. In this section we address ourselves to the mathematical considerations regarding exact and inexact differentials.

Consider the mechanical work done by a fluid at pressure p undergoing an infinitesimal change in volume dV; the mechanical work is p dV. The total work associated with a change from state 1 to state 2 is the integral $\int_1^2$ p dV and is represented by an area between V_1 and V_2 on the p-V diagram (Fig. 1.1). The value of the integral representing work depends on the path taken between 1 and 2. Without specifying the path, we could not meaningfully talk about the work. Another way of stating this is to say that work is not an exact differential.

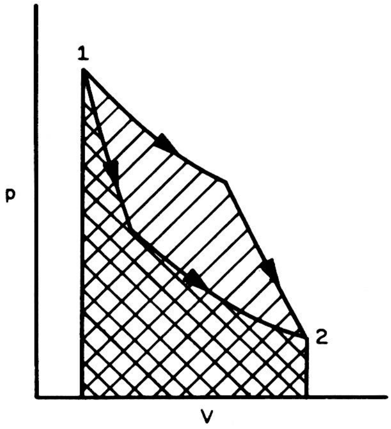

FIG. 1.1. p-V work.

An infinitesimal quantity of work is expressed by $\delta W = p\,dV$. By this equation we do not mean that W is a function of p or V, nor that δW is the differential of this function. On the other hand, take the ideal-gas equation,

$$T = \frac{p\tilde{V}}{R} \tag{1.3}$$

which says T is a function of p and $\tilde{V}$. A differential change of T, expressed by $dT = (p/R)\,d\tilde{V} + (\tilde{V}/R)\,dp$, is an exact differential.

We recall that a differential expression

$$M(x,y)\,dx + N(x,y)\,dy$$

is exact if

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \tag{1.4}$$

Equation (1.4) is a necessary and sufficient condition for a function f(x,y) to exist such that

$$df = M\,dx + N\,dy \tag{1.5}$$

It is easily seen that Eq. (1.4) is a necessary condition for Eq. (1.5) to be valid, because $M = \partial f/\partial x$ and $N = \partial f/\partial y$, and upon differentiating

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