Equilibrium Thermodynamics

for Engineers and Scientists

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Preface

Equilibrium thermodynamics is basically concerned with the *macroscopic* (gross) behaviour of systems that are subject to processes which take them from one state of stable equilibrium to another while the system may interact energy-wise with its environment. It treats the material within the system as a continuum by ignoring the particulate nature of matter and the quantitization of energy. These are the concern of *statistical thermodynamics* in its prediction of macroscopic behaviour through the study of events occurring at the *microscopic* level. Thus, equilibrium thermodynamics, with which this book is principally concerned, constitutes essentially a study of the relations between work, heat, and the properties of systems; it is this which makes it of great importance to the engineer, particularly in the field of energy conversion. Not only must the engineer devise *performance parameters* by which to express the actual performance of his work-producing and work-absorbing devices, but he must also be able to establish *performance criteria* against which to judge the actual measured performance. It is the science of thermodynamics which enables him to do this on a rational basis.

Through the action of effects which for the present we may loosely term 'frictional' or 'dissipative', all natural processes are in some degree thermodynamically imperfect, termed by the thermodynamicist 'irreversible'. Consequently, either less work is produced or more work absorbed in real-life plant than would be the case in that imaginary and idyllic land of the thermodynamicist which we may call 'Thermotopia'. Here all processes are, in his language, 'reversible', so that there are no such imperfections. In this context, it is worth making the point that, as do all other scientists, thermodynamicists construct a simplified *model* to describe the behaviour of the physical world, that behaviour being of too complicated a nature to allow every facet to be taken into account at a first encounter.

Because all natural processes are in some degree imperfect (irreversible), the engineer cannot use the results of experiments to enable him to set up his performance criteria by which to judge the degree of excellence of his plant. Instead, he is only able to call upon the resources of the human intellect through the rational application of scientific thought. In this, the science of thermodynamics provides an outstanding example of the power of abstract thought.

The work of the engineering thermodynamicist is not ended when he has devised expressions, in the shape of algebraic formulae, for the respective performance parameters and criteria appropriate to each of his devices. He will then need numerical data on the thermodynamic properties of the working substances which are either contained within or passing through these devices. Here he will need to call upon both experimental and mathematical expertise. From this activity may come empirical or semi-empirical correlating formulae to fit the great wealth of experimental data. However, the values of the many thermodynamic properties of a given substance are all theoretically interrelated and in the revelation of these interrelations lies one of the great achievements of the science of thermodynamics. The mathematical equations which have been devised to fit the experimental data will therefore have to be put together in a form that will maintain thermodynamic consistency between the numerical values computed therefrom by the engineer. This task will fall upon the thermodynamicist.

The considerations outlined above have been influential in shaping the layout of this book, making it a volume designed for the engineer rather than for the physicist or chemist, though the latter will also have much to learn from it. However, other influences have been equally strong in giving it a distinctive character. In spite of the fact that there have been important developments in recent years, the subject matter of thermodynamics is still largely taught along lines which follow closely those set out by the great pioneers of the last century, who were at the time exploring the unknown. This book takes advantage of recent developments to restructure the presentation into a more logically satisfying sequence.

The most important of the recent developments in equilibrium thermodynamics has been the *Single-Axiom Approach* of Hatsopoulos and Keenan,[1] in which the previously disparate 'Laws' of thermodynamics have been shown to follow logically from a single basic *Law of Stable Equilibrium*. The next most important development is associated with the topic of ***thermodynamic availability*** and the associated concept of *exergy*. The topic of thermodynamic availability deals essentially with the availability of energy for work production, a factor which has become of increasing importance in very recent times as a result of the emphasis on energy 'saving'. Despite the fact that this topic originated with Willard Gibbs and Clark Maxwell over a century ago and has been pursued with some vigour in Germany, it has in general suffered comparative neglect, although the respective theorems have recently been formulated concisely in a critical review[2] by the present author. This book takes advantage of both these advances in our understanding. The numerous concepts and theorems of equilibrium thermodynamics are thereby restructured and presented in a more logical sequence than hitherto.

It is the author's experience that the important advances made by Hatsopoulos and Keenan have not received the recognition which they deserve in academic circles because the material appears in a volume which is not only set at a level of sophistication beyond the normal capacity of the undergraduate but also goes well beyond the content appropriate to an undergraduate course. The basic ideas, however, are not of great difficulty and the present author has always believed that they could be presented in a form which, while remaining equally rigorous, was set at a level which would be readily digestible by an undergraduate of reasonable competence coming fresh to a study of the science of thermodynamics. He has been confirmed in this belief by giving a short course of undergraduate lectures in which,

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over a number of years, he has been able to develop a mode of presentation of the ideas of Hatsopoulos and Keenan in more readily assimilable form. The interest displayed by the undergraduates has been very rewarding and the present volume is the natural outcome of this venture.

An earlier book[3] published by Keenan alone in 1941 had a greatly beneficial influence on the teaching of thermodynamics in schools of engineering in the United States and the United Kingdom. However, because the book developed the concepts and theorems of classical thermodynamics from *cyclic* statements of the so-called First and Second Laws, it had the unfortunate effect of focusing undue attention on cyclic processes at the expense of non-cyclic processes, which are the more natural. By contrast, the Law of Stable Equilibrium of Hatsopoulos and Keenan, from which those 'Laws' follow as corollaries, relates essentially to *non-cyclic* processes, as also do the theorems of thermodynamic availability. The cyclic approach unfortunately conceals for too long the nature of the true source of irreversibility, but the non-cyclic approach brings this out very clearly right from the start. Moreover, cyclic processes are somewhat artificial constructs. The naturally occurring processes of the physical world are basically non-cyclic in character, a cyclic process merely constituting the special case in which, by a deliberately created succession of non-cyclic processes, the final thermodynamic state of a system is made to coincide with its initial state. Furthermore, if we start with unproven propositions relating to cyclic processes, we are not led naturally into the theorems of thermodynamic availability, which relate to systems that are carried by non-cyclic processes between specified end states in the presence of a specified environment. On the other hand, when we take advantage of the Single-Axiom Approach of Hatsopoulos and Keenan to develop the concepts and theorems of equilibrium thermodynamics in terms first of non-cyclic processes, these important availability theorems take an earlier and more natural place in the sequence of ideas. Not only is there no longer any need to introduce the troublesome *Clausius Inequality* as a preliminary to the establishment of the concept of entropy (that Inequality itself essentially constituting a theorem in thermodynamic availability), but the whole sequence of ideas then follows a more logical pattern. That pattern is followed herein.

As the concepts and theorems are developed, chapter by chapter, from the starting point of the basic Law of Stable Equilibrium, the reader will find that the propositions which have been given the titles of the First and Second Laws of Thermodynamics take on the nature of corollaries, so ceasing to be basic 'Laws' in their own right; moreover, no need is found for the so-called 'Zeroth Law'. In order to help the reader to follow the logical development of the long sequence of ideas that form the groundwork of the science of thermodynamics, a 'Family Tree of Thermodynamics' is constructed and developed in the earlier chapters, its step-by-step growth being shown at the end of each relevant chapter. By this means, the logical structure of this rather abstract branch of science is made clearly evident.

The Second Law of Thermodynamics is frequently, but quite undeservedly, endowed with a certain mystical aura, which should now be firmly dispelled by its relegation to a status subsidiary to that of the Law of Stable Equilibrium, of which it is merely a corollary. No other important branch of science has been so dependent on so many unproven postulates as are represented by the so-called Zeroth, First, and Second Laws. It must be a matter of satisfaction that the science of thermodynamics now needs no such underpinning.

Close on fifty years ago, Keenan described the steady-flow availability equation as promising to be as revolutionary in its effect on thermodynamic reasoning as had been the development of the steady-flow energy equation in its time. Both equations relate to non-cyclic processes. That the importance of the concepts and theorems of availability have not even yet taken the position of importance that is undoubtedly their due must almost certainly be attributable to the fashion of starting the presentation of thermodynamics in terms of cyclic statements of the First and Second Laws, rather than starting with the study of non-cyclic processes and proceeding therefrom to cyclic processes, as in this book.

Textbooks on thermodynamics come on the market in a steady stream, most of them little different from each other. There would consequently be little justification for writing yet another if it did not have something new and important to say. However, that something must be expressed in terms which are readily assimilable by the undergraduate if the new approach is to stand a chance of gaining widespread acceptance. It is considered that this book is set at such a level and that it will help to bring thermodynamics out of its nineteenth-century setting, in which it has remained for too long. It is, indeed, unthinkable to the author that the recent developments of which it has taken advantage should continue to be neglected. It is a matter of some concern that, in an age in which the great importance of energy 'saving' is increasingly being appreciated, important books and papers on energy 'conservation' are still appearing in which the concept of the availability of energy for work production is found not to merit even a mention.

The book is in two parts, the first dealing with basic concepts and the second with the development of those concepts. The last two chapters of Part II give a fairly extensive and considerably more careful treatment of chemical thermodynamics than is found in most texts. These should appeal particularly both to the power engineer concerned with combustion and other chemical processes and to the chemical engineer.

The author's *Thermodynamic Tables in SI (metric) Units*[4] have been used in calculating the answers to the extensive collections of Problems set at the end of Part I and the end of Part II.

This book is the product of many years of teaching experience and owes much to the help received from many people, not least from those whom the author has taught, and, indirectly by their writings, from the late Professor Joseph H. Keenan and his collaborators. The author is also particularly indebted to his colleague Dr Martin D. Cowley, of Trinity College, for reading through early drafts of the manuscript and for his many helpful and perceptive comments. Finally, a warm word of thanks is due to Miss Jill Stroud for her patience and skill in the typing of the manuscript.

Cambridge, England
March 1979

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Steady-flow Processes

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