Preface to the fifth edition

Since the First Edition the most significant change to the book has been the addition of a new chapter which provides a simple treatment of the molecular basis of thermodynamics. Though this chapter has been placed at the end of the book it has been written in such a way that it could be employed with advantage at an earlier stage of a first course in chemical thermodynamics. Indeed, a prompt introduction to the elements of statistical thermodynamics can be very helpful in reinforcing the fundamental concepts of classical thermodynamics.

For subsequent editions I have tried to compromise between accommodating the suggestions of teachers of the subject and those of their students, which more often than not appear to conflict. Most often I have favoured the views of the students who in general advocate less radical surgery. The result is a little more rigour in specifying the dimensions within logarithmic expressions, the addition of more worked examples in the text, a reference to Ellingham diagrams, and a number of minor revisions in each edition.

Over five editions of a book and several reprintings one becomes indebted to many for their advice and help. In addition to those named in the Preface to the first edition I would like to thank: Professor Sir John Rowlinson, Drs J. H. Dymond, M. L. Khan, Sandor Kristyan, G. P. Matthews, G. D. Meakins, M. Rigby, J. J. Rooney, M. Spiro, A. R. Tindell, and B. H. Wells, Miss Anne Buckley, Miss Emma Collingwood, and Mr C. D. Eley. I am indebted to Dr J. van Mourik and Bohn, Scheltema, and Holkema publishers for the use of problems from the Dutch edition.

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Preface to the first edition

The first time I heard about chemical thermodynamics was when a second-year undergraduate brought me the news early in my freshman year. He told a spine-chilling story of endless lectures with almost three hundred numbered equations, all of which, it appeared, had to be committed to memory and reproduced in exactly the same form in subsequent examinations. Not only did these equations contain all the normal algebraic symbols but in addition they were liberally sprinkled with stars, daggers, and circles so as to stretch even the most powerful of minds.

Few would wish to deny the mind-improving and indeed character-building qualities of such a subject! However, many young chemists have more urgent pressures on their time. Chemical thermodynamics need not be a particularly esoteric branch of algebra: only a handful of thermodynamic relations are important for the student when he first meets the subject. It is essentially a practical subject that interrelates quantities which can be measured in the laboratory (some more easily than others).

This book is not intended to be a formal textbook of thermodynamics. It is intended to give the beginner some familiarity with the concepts of thermodynamics and a knowledge of the thermodynamic relations he will use in the laboratory. At a recent conference on the teaching of thermodynamics it was concluded that there was 'no place for axiomatics for introductory students'.† The presentation in this book is certainly non-axiomatic and occasionally non-rigorous. There is often a direct conflict between rigour and clarity in the presentation of elementary thermodynamics, and this book strays from the path of rigour more than most. The analogies used to provide 'insight' are (like all analogies) capable of being misleading if they are examined too closely or pursued too far. Nevertheless teaching the subject over a number of years has convinced me that this approach is on the whole beneficial.

The book assumes that the reader will have taken a course in elementary physics and have some (passing) acquaintance with the concepts of potential and kinetic energy, work, heat, temperature, and the perfect-gas state. A knowledge of very elementary calculus is also assumed.

Chapters 1–3 outline the basic concepts of chemical thermodynamics: energy, entropy, and equilibrium. Chapter 4 introduces free energy and

† See H. A. Skinner (1971) *Chemistry in Britain*, 7, 438.

develops the thermodynamic approach to the understanding of equilibrium in chemical systems. The order of presentation of material differs from that most commonly employed in that the determination of thermodynamic quantities is deferred until Chapter 5. In this chapter the changes in free energy and entropy accompanying chemical reactions are treated together with enthalpy changes, which are more often tackled at an earlier stage. These five chapters would form the basis of a suitable introductory course in chemical thermodynamics. Chapter 6 develops the concept of the ideal solution and applies it to colligative properties. Much of this chapter could also be included in a first approach to the subject. Chapter 8 and much of Chapter 7, on the other hand, are essentially notes intended to serve as a bridge between the elementary thermodynamics of the earlier chapters and more complete treatments.

The notation is consistent with the IUPAC recommendations of 1969 and SI units are employed. Not a great deal of thermodynamic reference data is available in SI units and therefore a reasonable quantity of such data is provided in Appendices 1 and 2. Stress has been laid throughout on the physical principles underlying the subject, and extensive mathematical manipulation of equations has, so far as is possible, been avoided. In order to emphasize that chemical thermodynamics is not an exercise in elementary algebra the individual equations have not been numbered. The more important relations have been identified in the text. When a reference to the origin of an equation is necessary the section of the book in which it is introduced is given.

I am indebted to many teachers and colleagues, not least to Professor J. H. Hildebrand who at 90 is still contributing to my education in thermodynamics. I hope other writers on the subject from whom I have drawn ideas or analogies will interpret this as a compliment. I would like to thank Dr G. C. Maitland, Dr R. P. H. Gasser, Mr P. Scott, and Dr L. A. K. Staveley who contributed numerous ideas for improving the manuscript and Dr P. W. Atkins for his editorial and scientific advice.

There will be, no doubt, all too many errors and weak arguments left for the reader to discover. I shall be very grateful to be informed of them.

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