EXPERIMENTAL THERMOCHEMISTRY

VOLUME 2

Edited by
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Foreword

Following the appearance in 1956 of its first volume entitled 'Experimental Thermochemistry', the Subcommission on Experimental Thermochemistry of the Commission on Chemical Thermodynamics of the International Union of Pure and Applied Chemistry proceeded with plans for a second volume under the same title, with Dr. H. A. Skinner serving as Editor.

The first volume aimed to place before the scientific and technical world the then best existing knowledge relating to experimental thermochemistry and the measurement of heats of chemical reactions. At the time of the completion of the first volume, several topics could be dealt with only in a more or less cursory way and, in addition, a number of new experimental developments in the field of thermochemistry were in the making. Accordingly, it was most appropriate that a second volume would present the aforementioned several topics in a more complete and authoritative fashion and would describe the new experimental developments in detail.

In modern science, the two most important thermodynamic properties of substances are entropy and energy. Appropriately combined, values of these properties yield quantitative information on the thermodynamic stability of chemical substances. Important needs of science are therefore served by reliable values of entropy and energy (measured with respect to an appropriate reference). About 25 years ago, the writer pointed out that theoretical developments in physics and chemistry were making it possible to calculate values of entropy with an accuracy quite adequate for modern day science, simply from a knowledge of the geometry and architecture of molecules of interest. Therefore, the need to make experimental measurements of entropy would become less and less. On the other hand, the situation with respect to needed values of energy presented quite a different picture, and it was predicted that experimental thermochemistry would

become an increasingly important part of science. Even today, with our high-speed computors, calculations of energy with adequate accuracy can be made only for a few of the simpler molecules. In general, recourse must be had to experimental measurement of the heats of chemical reactions, appropriately selected.

In this second volume, we have the following presentations by some of the world's leading investigators in experimental thermochemistry: Waddington, with an introductory chapter on rotating bomb combustion calorimetry; Good and Scott, on combustion of organic fluorine compounds with a rotating bomb calorimeter; Bjellerup, on combustion of organic bromine compounds with a rotating bomb calorimeter; Good and Scott again, on combustion of organometallic compounds with a rotating bomb calorimeter; Huber and Holley, on combustion of metals in a bomb; Hubbard, on calorimetry involving reactions with fluorine in a bomb; Armstrong, on calorimetry involving reactions with fluorine in a flame; Skinner, with an introductory chapter on the calorimetry of reactions other than those of 'combustion'; Skinner, Sturtevant, and Sunner, on the design and operation of calorimeters for reactions other than those of 'combustion'; Lacher, on the calorimetric measurement of heats of hydrogenation and of halogenation; Sunner and Wadsö, on the measurement of heats of hydrolysis; Dainton and Ivin, on the measurement of heats of polymerization; Evans, on calorimetry at high temperatures; Coughlin, on calorimetry involving solutions and on the thermochemistry of silicates; McGlashan, on the measurement of heats of mixing; Kubaschewski and Hultgren, on the thermochemistry of alloys and metallurgically important substances; Calvet, on recent progress in microcalorimetry; Prat, on calorimetry involving biochemical and zoological thermogenesis; and Sturtevant, on calorimetry involving biochemical reactions.

The modern advances in experimental thermochemistry are exemplified by the subjects which are discussed authoritatively in this second volume. It is seen that the calorimetry proper of thermochemical investigations today is in general very well under control, whereas the accuracy of the thermochemical results is largely limited by knowledge of the analytical chemistry of the reaction being measured, consisting essentially in knowing the identity and amount of the reaction actually taking place.

The Editor and authors of the chapters in this book are to be complimented on their fine work. The writer is confident that all scientists interested in the measurement of the heats of any chemical reactions will find this volume most fruitful of study.

FREDERICK D. ROSSINI
President
Commission on Chemical Thermodynamics
International Union of Pure and Applied Chemistry

May, 1961
University of Notre Dame
Notre Dame, Indiana, U.S.A.

Preface

During the IUPAC Conference in Paris in the summer of 1957, the Subcommission on Experimental Thermochemistry proposed that they should prepare a second volume on the subject of Experimental Thermochemistry, thus to carry a stage further the project initiated by the then Commission on Thermochemistry at Amsterdam in 1947, which led to the publication of Volume I by Interscience Publishers, Inc., in 1956. This proposal was endorsed by the IUPAC Commission on Chemical Thermodynamics, and a provisional list of authors and contents was subsequently drafted. The Subcommission on Experimental Thermochemistry at the time of the Paris meetings was composed of the following:

President: J. Coops, Free University of Amsterdam, Amsterdam, Holland.

Secretary: H. A. Skinner, The University, Manchester, England.

Members: E. Calvet, Faculty of Science, University of Aix-Marseilles, Marseilles, France; E. J. Prosen, National Bureau of Standards, Washington, D.C.; F. D. Rossini, Carnegie Institute of Technology, Pittsburgh, Pennsylvania; M. Beckers, Faculty of Science, Brussels, Belgium; W. Swietoslawski, University of Warsaw, Poland; G. Waddington, Bureau of Mines, Bartlesville, Oklahoma.

Expert Advisers: A. R. Meetham, National Physical Laboratory, Teddington, England; M. Colomina, Rocasolano Institute, Madrid, Spain; S. Sunner, University of Lund, Sweden; K. Schafer, University of Heidelberg, Germany.

By the time of the next meeting of the Subcommission of Experimental Thermochemistry during the 1959 Conference of IUPAC at Munich, a large part of the present volume was well on the way to completion. The Subcommission carefully examined the progress made, and proposed a number of amendments, including the addition of further chapters in order to cover some important new developments in the field. The scope of the present

Volume was thus finalized at the Munich meetings of the Subcommission, attended by the following:

President: J. Coops, Amsterdam.

Secretary: H. A. Skinner, Manchester.

Members: E. Calvet, Marseilles; E. J. Prosen, Washington; G. Waddington, National Research Council, Washington, D.C.; S. Sunner, Lund.

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The Editor was in receipt of the majority of the contributions, in final form, from the authors early this year, and the task of editing the scripts proved to be a light one. He wishes to express his thanks to all the authors of this book for their enthusiastic cooperation, and to acknowledge the continued encouragement given by Frederick D. Rossini, President of the Commission on Chemical Thermodynamics, by W. Kuhn, President of the Section on Physical Chemistry, and by R. Morf, Secretary General of the International Union of Pure and Applied Chemistry. He is also indebted to his colleague at Manchester University, G. Pilcher, for many useful discussions, and to Interscience Publishers for their help throughout the preparation of this book.

H. A. Skinner,
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Subcommission on Experimental Thermochemistry
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June, 1961
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