THE CHEMICAL THERMODYNAMICS OF ORGANIC COMPOUNDS

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FOREWORD

The critical evaluation of published data, culminating in the compilation of tables of selected values of physical and thermodynamic properties of chemical substances, constitutes the viable end product of experimental thermodynamics for practical and industrial purposes. Before 1939 most compilations in common use were the result of individual enterprise, as instanced by the extensive review of heats of combustion of organic substances by M. S. Kharasch in 1929 and by the book *Thermochemistry of Chemical Substances* by F. R. Bichowsky and F. D. Rossini, published in 1936. Even the well-known Landolt-Börnstein Tabellen, although produced as a result of organized collective effort, were based on individual contributions. Several scientific groups are currently engaged in the systematic compilation of thermodynamic tables, such as those at the National Bureau of Standards, at Texas A & M University, at The Dow Chemical Company (Midland, Michigan), at the Academy of Sciences, Moscow, and at Imperial College, London. Full-time data compilation by specialist groups is essentially a postwar development, necessitated by the increasing rate of output of new data in recent years and encouraged by the advent of computer aids.

American Chemical Society Monograph No. 60, by G. S. Parks and H. M. Huffman, *The Free Energies of Some Organic Compounds*, one of the most influential of earlier compilations, aimed at presenting thermodynamics and equilibria in a practical manner as well as providing the reader with a reference book on the thermodynamic properties of the more common organic chemicals. The monograph went out of print in 1938 and the authors subsequently began the task of revision, but the war intervened and little progress was made. Huffman, Parks, and Stull discussed the possibility of a complete rewrite in 1948 at the Portland, Oregon, A.C.S. meeting. All agreed that a new book was needed, but both original authors felt unable to give a sufficient amount of their time to it and suggested that Stull accept full responsibility for the updating of the original monograph.

In June 1952 Sinke joined the Thermal Laboratory of the Dow Chemical Company at Midland, and later he accepted an invitation from Stull to collaborate with him in the preparation of the book. The primary task was to collect and evaluate all relevant data and reduce them to convenient tabular form. Previously, toward the end of 1948, Stull had

developed machine computer techniques specifically for the compilation of thermodynamic properties, which he described at the 118th A.C.S. meeting in Chicago (reported in *Chemical and Engineering News*, September 25, 1950). These techniques were thereafter used and developed in the day-to-day operations of the Dow Thermal Laboratory and also served in the preparation of the book *Thermodynamic Properties of the Elements* by Stull and Sinke, published by the American Chemical Society in 1956 as No. 18 in the *Advances in Chemistry* series. In 1959 the Dow Thermal Laboratory was commissioned to prepare the Joint Army-Navy-Air Force Thermodynamic Tables (JANAF Tables), by which time Stull and Sinke had fully developed the computer techniques necessary for the preparation of such extensive tables and of the tables in this book. The reader is given complete tabular data, as opposed to generating equations.

In May 1961 Stull invited Westrum of the University of Michigan to collaborate in the preparation of the book, but completion of the task required six more years. Data compilation today is a frustrating occupation; all too often new data appear that demand instant reassessment of completed work, so that the end of the road is never reached.

The book follows the philosophy of A.C.S. Monograph 60. It goes further than its parent in appealing to the industrial chemist and is perhaps the clearest available exposition on *how* to apply thermodynamics to practical problems in the laboratory and in the plant. The Dow Thermal Laboratory for many years has served industrial needs of the company profitably, and, in an interesting manner, some of its experience and much of its enthusiasm happily have entered the pages of Stull, Westrum, and Sinke.

The authors are to be complimented on their fine work and for their perseverance over many years in developing comprehensive tables, despite the need for continual revisions. Acknowledgment is surely due to the Dow Chemical Company for its early and continuing support of the Thermal Laboratory in all its aspects. Thermodynamicists and thermochemists will welcome this publication, which will find its place in teaching and, as a reference book, in laboratories throughout the world.

University of Manchester
September 1967

HENRY A. SKINNER,
Chairman, Commission on Thermodynamics and Thermochemistry International Union of Pure and Applied Chemistry

PREFACE

The classical publication *Thermodynamics and the Free Energy of Substances*, written in 1923 by Lewis and Randall, is generally conceded to be the first complete mathematical formulation of chemical thermodynamics. A generation of students studied this famous text, and they are convinced of the usefulness of these relationships in technical applications. One of two significant developments since 1923 has been the experimental verification of the third law, spearheaded by W. F. Giauque and his students. The other is the development of statistical mechanical methods for computing the thermodynamic properties of an ideal gas from first principles. There is now no question that free energy values based on thermal data and statistical calculations can be used reliably to predict reaction equilibria.

Nevertheless, two factors have prevented full use of this powerful tool in the field of organic chemistry. Because of the employment of inaccurate information or failure to recognize the limitations of thermodynamics, some conclusions have been reached that are not in accord with experimental results and have led some to mistrust the predictions based on thermodynamics. The other factor that has impeded the application of thermodynamic reasoning to problems of organic chemistry is the lack of easily accessible numerical values of free energies. Moreover, the data of chemical thermodynamics are so widely scattered throughout the technical literature that compilations are an indispensable aid to the practicing thermochemist. The first authors to note this lack of data for organic compounds were G. S. Parks and H. M. Huffman, who introduced their pioneering monograph, *The Free Energies of Organic Compounds*, in 1932. This volume was received favorably by academic and industrial chemists alike and was used as seminar material in numerous universities. It struck resolutely at the two disparaging factors mentioned above and possessed a high degree of utility. About the time the book went out of print war clouds were gathering and the authors turned to other tasks.

A few limited attempts have been made to summarize the thermo-

dynamic and thermochemical data for organic substances. Rossini, Pitzer, Arnett, Braun, and Pimentel (1248) Rossini et al. (1250), and Zwolinski et al. (1653) have provided continuing attention to thermodynamic data on hydrocarbons. Ribaud (1222) has tabulated some Gibbs energy functions (based on degrees Kelvin) for saturated hydrocarbons and other organic substances. Westrum and McCullough (1598) have summarized work on the thermodynamics of the organic solid state; Scott and McCullough (1316) have tabulated data for gaseous organic sulfur compounds; Kharasch (744) has provided data on heats of combustion; and Auer (52) has compiled 25°C data on the enthalpies of combustion, heat capacities, and entropies of organic and metal organic compounds. Moreover, Chermin [cf. (223) et prec.] and Kobe (784) have treated the thermodynamics of certain classes of hydrocarbons and their derivatives. However, no broad review or tabulation covering the increasing wealth of thermodynamic data on organic compounds has appeared since the pioneer work of Parks and Huffman (1105) in 1932.

By contrast, chemical thermodynamic data have been tabulated for the elements by Stull and Sinke (1437), for metals and alloys by Hultgren, Orr, Anderson, and Kelley (660), supplemented by Hultgren, Orr, and Kelley (661), and for inorganic substances by Kelley (736, 737), Kelley and King (738), Bichowsky and Rossini (125), Coughlin (278), Kubaschewski and Evans (812), and, as "Circular 500," by Rossini, Wagman, Evans, Levine, and Jaffe (1249). "Circular 500" has been revised and extended in part by Technical Notes issued by Wagman, Evans, Halow, Parker, Bailey, and Schumm (1560, 1561). Other tabulations for more or less restricted groups of inorganic substances have been compiled by Wagman and Evans (1559), Zwolinski et al. (1654), Brewer, Bromley, Gilles, and Lofgren (167), Ribaud (1222), Zeise (1643), Margrave (930), Katz and Margrave (726), Stull et al. (1435), Auer (52), Hilsenrath et al. (604), Glushko, Gurvich, Khachkuruzov, Veits, and Medvedev (499, 500), Gerasimov, Krestovnikov, and Shakov (467–470), and Schick (1282, 1283). In addition, preliminary tabulations to meet specific and urgent needs have been issued by government agencies and other organizations.

Because progress in the scientific and technological aspects of organic chemistry is increasingly dependent on basic information on the properties of substances, the lack of a unifying treatment of organic chemical thermodynamics that is both comprehensive and systematic has unquestionably delayed more rapid advances. It is the purpose of this book to rectify this conspicuous neglect.

By 1940 research workers at the Dow Chemical Company had recognized the need for quantitative measurements of thermal properties

of chemical compounds. The laboratory established for this purpose has successfully dealt with many of the day-to-day problems by application of Gibbs energy data. Problems of organic compounds other than hydrocarbons required continual searching of the literature. Thus this book has been born of industrial necessity and is intended to provide the organic chemist with a single exhaustive survey of thermodynamic data pertinent to his concerns. Industrial organic chemists and chemical engineers outside the petroleum industry appear to have made too little application of thermodynamic data in solving their problems. This situation is changing, however, and many of the newer industrial organic chemists are beginning to seek those synthetic routes that are the most favorable energetically because the processes that require the least energy will probably be most economical and will therefore have long-term utility. Moreover, as energy is becoming more expensive daily, we are rapidly approaching the time when the chemical engineer must be as concerned about the energy balance in his process as he is about the mass balance.

We have therefore made a complete search of the literature up to January 1, 1966. For the ideal gas state we have tabulated the heat capacity, entropy, enthalpy, and Gibbs energy of formation for 741 pure organic compounds from 298 to 1000°K. The entropy, enthalpy, and Gibbs energy of formation are presented as fully as possible for approximately 4400 organic compounds in the ideal gaseous and condensed states at 298°K. Few organic compounds are stable above 1000°K (727°C), and so tabulations of organic compounds have been limited to the temperature range from 298.15 to 1000°K. We have pointed out some of the regularities existing between hydrocarbons and the other classes of organic compounds, which are useful in the estimation of thermodynamic properties of compounds that have not been experimentally measured.

We assume that users of this book have some knowledge of thermodynamics and mathematics. However, sufficient review of relevant elements of thermodynamics and discussion of calculational methods are included in Section I to assist the laboratory worker in utilizing the data tables provided herein in the solution of his problems. The organization is intended to provide ready reference to practical calculations of particular types and is meant to be for supplementary reading rather than for initial exposure. Although many troublesome matters are discussed, the brief scope of this review can hardly plumb the depths and subtle aspects of interest to thermodynamic specialists. Brief descriptions of calorimetric measurements are provided to acquaint the organic experimentalist with the measurement of thermal data, the primary source of the information tabulated in Sections II and III. Chapter 6 introduces the reader to the

methods used to estimate thermodynamic properties of compounds that have not yet been measured but are essential to his application.

Still more recently, academically oriented organic chemists have come to appreciate the significant contribution made by chemical thermodynamic data to the understanding of molecular structures, molecular freedom in crystals, stabilities of organic molecules, strain energies, and the manifold energetic restrictions on transitional and transformational perturbation in structures. Such applications also can be greatly facilitated by the compiled experimental values contained in this volume. Organic chemists in general will therefore find much of interest and relevance here.

Finally, it should be noted that many academic thermal studies involve molecules of no immediate or present direct industrial interest. It is hoped that a further dividend from the use of this book will be the recognition of extant serious gaps in chemical thermodynamic data and the stimulation of measurements of thermal and thermochemical properties of technically important compounds.

We have made an honest attempt to avoid errors, but in an effort of this magnitude some may have escaped our notice. Consequently we hope that errors of commission and omission will be reported to us. We solicit the patience and understanding of the reader.

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The following illustrations are based on diagrams in the sources named: Figure 5–7 from John Wiley & Sons, Inc.; Figures 2–6 and 2–7 from *The Journal of the American Chemical Society*; Figure 2–1 from *The Journal of Chemical Education*; Figure 2–5 from *The Journal of Chemical Physics*; Figures 7–13 and 7–14 from *The Journal of the Chemical*

Society; Figure 2–3 from *The Journal of Physical Chemistry*; Figures 7–3 through 7–9 from Reinhold Publishing Corporation; Figures 3–3 and 3–5 from *The Journal of Research of the National Bureau of Standards*; Figure 3–4 from the Parr Instrument Company; and Figure 2–13 from D. Van Nostrand Company, Inc.

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G.C.S.

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CONTENTS