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SECOND EDITION

J.B. Pedley, R.D. Naylor and S.P. Kirby

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Preface

The purpose of the material in this book is to enable users of thermochemical data to predict values for standard enthalpies of reactions involving organic compounds ranging in complexity from simple alkanes to biologically important compounds such as amino acids.

Chapter 1 contains tables of values for standard enthalpies of formation derived from experimental data for approximately 3000 organic compounds of the elements C, H, O, N, S and halogens; Chapters 2 to 4 describe a simple scheme for predicting unknown values of standard enthalpies of formation. Data presented in the book are stored in a data base at the University of Sussex and with associated software provides a simple but efficient method for dealing with thermochemical problems in organic chemistry.

The experimental data used in the computer calculation of the values for standard enthalpies of formation are clearly indicated in Table 1.2. Where alternative values for a given standard enthalpy of formation may be derived, from independent measurements, we have clearly indicated those which are regarded by the assessors as definitive and which are therefore used to derive the value for the compound concerned. We do not, however, give reasons for the assessors choice nor are details given of experimental techniques. The literature search for suitable references was discontinued in 1983 to allow development of the predictive scheme and the computer techniques for handling the data.

The predictive scheme has so far been tested on experimental values for the standard enthalpies of formation in the gaseous phase of all acyclic compounds in the data system. The method of calculation differs significantly from previous predictive schemes, particularly in the treatment of data for complex polyfunctional compounds. We have therefore not attempted to compare the procedure with previous methods; the value of the approach is determined solely by the comparison between calculated and experimental values for approximately 500 compounds in tables containing specific types of compound.

This book presents only a section of the total body of thermochemical data for organic compounds and at present contains no data on radicals, ions, organometallic compounds or multicomponent systems. Properties other than standard enthalpy of formation at 298.15 K are also not yet included. However, the system has been set up in such a way that it may readily be extended to incorporate a wider range of compounds and properties. It may also be updated readily, the necessary calculations being carried out automatically.

The problems associated with the assessment of thermochemical data depend strongly on the type of compound and the technique used in the measurement. It would therefore be advantageous if experts in various fields could pool their resources to form a single internally inconsistent data system. In this respect, data for organophosphorus compounds has already been provided by Dr E. O. Domalski (of the National Bureau of Standard, USA) but slightly too late to be incorporated in this volume; it will appear as a supplement in the near future. Similarly, Professor V. I. Kolesov (of Moscow State University) has promised to provide recent data obtained in the Soviet Union and Dr V. Mayer (of the Prague Institute of Chemical Technology) will be contributing his recent assessments of standard enthalpies of vaporization. In relation to the predictive scheme Dr H. A. Clark (of Dow Chemical, USA) has offered to carry out theoretical calculations on compounds of particular importance to the

further development of the theory thus allowing extension of the method to a much wider range of compounds.

University of Sussex
October 1985

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We are indebted to the National Physical Laboratory for the financial support given in the first stages of this project during the period 1974–76, and particularly to Dr John Cox, Dr Arthur Head and Dr Geoff Pilcher for their advice during this initial development phase which led to the publication of the predecessor of this book [77PED/RYL].

From 1978 to 1982 the data was set up as a computer search and retrieval system and work on the predictive schemes was started. During this period financial support was provided by the Science and Engineering Research Council. Our thanks go to Dr Mike Elder and his colleagues at the Daresbury Laboratory for their help in correcting the names and structures of compounds in the data base.

The National Bureau of Standards in Washington has given us material and moral support for a number of years and, in this respect we are particularly grateful to Dr Gene Domalski, Dr David Garvin, Dr Lew Gevantman, Dr David Lide and Dr Howard White.

We are also grateful to the University of Sussex for contributing to the cost of production of this book. The publishers and specifically Dr Jane Macintyre and Dr John Buckingham have been very patient in dealing with the many technical problems which have arisen and with our many failures to meet deadlines.

Members of staff of the University's computing centre, especially Dr David Joslin and Chris Wimlett, have given invaluable help in the development of the data base from which this book is derived. Our thanks are also due to the computer operators Pat Corbett, Mark Foster, Richard Shanahan and Tony Smith, who have dealt efficiently with our demands for non-standard output.

Over the period of development of the project many undergraduate and postgraduate students have been involved in setting up the data files and the predictive scheme. The extent of their contributions has varied considerably but we are very grateful to all of them for their efforts; they are listed in alphabetical order which gives no indication of the extent to which they have been involved in the project: Ken Barnes, Mark Baynham, Dr Philip Burkinshaw, Helen De Lemos, Julia Dickinson, Anne Pedley, John Pedley, Dr John Rylance and Bridget Wooldridge.

We are also grateful to colleagues in the School of Chemistry and Molecular Sciences, particularly Dr Peter Simpson who was actively involved in the early stages of the development of computer codes for chemical substructure search and retrieval, and to Professor Tony McCaffery and Professor John Murrell for their support. Our sincere gratitude is due to Dr Elizabeth Marshall who has generously given moral support over a number of years.

The manuscript copies of the book have been thoroughly checked at various stages in its development by the publishers and by Dr David Garvin, Dr Gene Domalski, Dr Malcolm Chase, Dr Alan Syverud, Dr John Cox and Dr Geoff Pilcher. Our appreciation is extended to these people for the personal effort involved in identifying errors and omissions.

It is a particular pleasure to record again our thanks to Dr John Cox and Dr Geoff Pilcher whose book [70COX/PIL] provided the basis for all our work. Their data tables still form a very large percentage of our data system and they have actively encouraged our work from its inception to the present day. Without their pioneering efforts in the collection and processing

of thermochemical data this book would not have been possible. We therefore wish to record our indebtedness by dedicating this book to them.

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S. P. K.

Contents

Introduction

The primary purpose of tables of thermochemical data is to enable chemists to explain why a given process occurs or alternatively, to allow them to predict which chemical processes are thermodynamically feasible using the equation:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = -RT \ln K_a$$

where $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are the standard Gibbs energy, enthalpy and entropy changes for the process concerned. K_a is the equilibrium constant in terms of activities and is a quantitative measure of the allowed maximum extent of a chemical reaction if equilibrium is attained. Values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ can be calculated from tabulated values for the standard enthalpies of formation and entropies of the species involved in the process.

Thermochemical calculations can be carried out at two extreme levels of accuracy. For example, the chemical engineer in the petrochemical industry often requires the accurate prediction of the equilibrium composition of a mixture in a reactor, possibly at temperatures appreciably higher than ambient. The calculations involved can be carried out only if accurate data are available for both standard enthalpies of formation and for entropies as a function of temperature. At the other extreme, organic chemists (and more recently biologists and biochemists) usually study processes at or near room temperature, where the $T\Delta S$ term is quite small and may often be estimated with sufficient accuracy by rule of thumb procedures. Under these conditions the most important thermochemical parameter is the standard enthalpy change for the reaction and, if this is negative, the process is assumed to be feasible provided the kinetic factors are favourable.

The tables in the first chapter of this book contain selected values for the standard enthalpies of formation of approximately 3000 organic compounds of the elements C, H, O, N, S, F, Cl, Br, and/or I and the experimental measurements from which these data were derived. These tables are printed directly from computer files at the University of Sussex. In establishing the data system, provision has been made for contributions from other assessors of thermochemical data and for the inclusion of a wide range of properties such as entropies and heat capacities.

The number of organic compounds of interest to chemists is of the order of millions but the number of compounds for which standard enthalpies of formation are accurately known is very limited and likely to remain so. It is often possible however, to make accurate predictions of unknown values of thermochemical properties by equating these properties to a sum of contributions from atoms, bonds and groups and their interactions within the molecule. A new approach to this method has been devised at the University of Sussex and is described in detail in Chapters 2 to 4. Tables of parameters required by the described procedure for the prediction of values for standard enthalpies of formation of acyclic compounds in the ideal gaseous state are also given. Calculations involved in the prediction of standard enthalpies of formation are routine but rather tedious and hence prone to error. The procedure has therefore been computerized and magnetic tapes containing parameters and software in several different computer languages are available from the authors. The method is currently being extended to give values of standard enthalpies of formation for cyclic compounds and values for other

properties such as standard enthalpies of vaporization, heat capacities, entropies etc. Supplementary tables of new sets of parameters will be produced at suitable intervals.

It is also possible to predict unknown thermochemical properties of compounds by examining trends in data for structurally related compounds. It is difficult, however, to locate such sets of compounds in printed tables; filing systems are almost invariably based on molecular formulae only and the most elaborate indexing systems will not identify sets of compounds having even simple combinations of structural features. The data base at The University of Sussex overcomes this problem by assigning to each species structural codes which can be searched by computer to identify compounds having specified combinations of functional groups and/or ring systems. An equivalent indexing system would be virtually impossible in a printed book; it is therefore suggested that the search system be used in association with the data tables presented in this book. The computer system identifies the required types of compound in the computer files; the data can then be found in the printed data tables. Examples of this procedure are given in the Appendix; further details of data files and software are available from the authors.

CHAPTER ONE

Standard Enthalpies of Formation Derived from Experimental Data

1.1 Data tables

The large data tables 1.1, 1.2 and 1.3, which make up much of this book, may be found on pages 87, 233 and 617 respectively.

Table 1.1 contains values for standard enthalpies of formation of about 3000 organic compounds of the elements carbon, hydrogen, nitrogen, sulphur, fluorine, chlorine, bromine and iodine. These values are derived from the experimental thermochemical data given in Table 1.2 using the assessment procedure and method of calculation described in Section 1.2. Table 1.3 contains values of standard enthalpies of formation of inorganic compounds needed for the calculation of values for organic compounds. The contents of Tables 1.1 to 1.3 are stored in computer files which can be updated and reprocessed at any time; the printed tables are generated by a computer program.

Table 1.1 (see page 87)

All the thermochemical data given in Table 1.1 refer to 298.15 K and to substances in their standard states except for a few aqueous solutions of specified concentration. For gases (g) the standard state is that of the ideal gas at a pressure of 101 325 Pa (1 standard atmosphere) and for crystalline solids (c) and liquids (lq) the standard state is that of the pure substance under a pressure of 101 325 Pa. For species in aqueous solution (aq) the standard state is the hypothetical ideal solution of unit activity which, for enthalpies of formation, is equivalent to infinite dilution. Finite dilution states are indicated by the number of moles of water per mole of solute, e.g. $C_2H_4O_2$ (aq : 1200), where the number gives the number of moles of water per mole of solute. However, data for aqueous species are not included unless they are needed for the prediction of standard enthalpies of formation of pure substances. Data on gaseous ions and radicals are excluded from the tables.

The elements in a formula are in the order

C H O N S Halogens

and the presentation of compounds follows this order, as illustrated by the list of contents for this table.

Isomers are distinguished from each other by a number in brackets after the formula. This number is given even if there is only one isomer present.

Names are generally consistent with *Chemical Abstracts* nomenclature, but have also been checked by the publishers, Chapman and Hall, to ensure consistency with their publication *Dictionary of Organic Compounds* [82BUC]. Some data in the literature are for compounds which appear to have been incorrectly or ambiguously named in the original reference. In these cases, there is no option but to quote the 'incorrect' name (followed by the comment 'ambiguous name') in the hope that the reader can derive some benefit from the associated data.

The penultimate column of the table contains values for the standard enthalpies of formation of condensed states (crystalline(c), liquid(lq) or aqueous(aq)), and the last column corresponding values for the gaseous states. Uncertainties are given below the corresponding values for the standard enthalpies of formation. The methods by which these values are derived from standard enthalpies of reaction are described in Section 1.2.

Table 1.2 (see page 000)

Table 1.2 contains the experimental data from which the values in Table 1.1 have been derived and are presented in the same order. Most of the experimental measurements are of standard enthalpies of combustion by bomb and by flame calorimetry and are generally of the high precision required to calculate standard enthalpies of formation to within kJ mol^{-1} accuracy. Approximately 1000 enthalpies of reactions other than combustion and a few data derived from second and third law analyses of chemical equilibria are also included. Enthalpies of vaporization are derived mainly from vapour pressures, although some data are from direct measurements or have been estimated by assessors using methods described by Cox and Pilcher [70COX/PIL]. Each process is listed under the formula of each organic compound present in that process, for example, the hydrogenation of ethene is listed under both ethene and ethane.

Processes labelled 'Combustion . . .' refer to the complete combustion of the compound in the specified state to give CO_2(g), H_2O(lq), N_2(g), H_2SO_4(aq : 115), HCl(aq : 600), Br_2(lq) and/or I_2(c). (In some cases H_2O(lq) has to be present as a reactant rather than a product.) Combustion of fluorine compounds leads to variable amounts of CF_4(g) and HF solutions. Since the enthalpy of formation of CF_4(g) is not well defined the combustion process is given explicitly so that the effect of selecting a new value for CF_4 can be introduced immediately.

Processes labelled 'Vaporization . . .' correspond to the production of the hypothetical ideal gaseous state at one atmosphere pressure from the specified condensed state. The reverse process, to the specified state, is indicated by 'Condensation . . .'. Where separate thermochemical measurements have been carried out on both condensed and gaseous phases, the enthalpy of vaporization is included as both a 'Vaporization' and a 'Condensation' process in the catalogue of reactions for all states of the compound.

The column headed 'Reference code' contains codes for the references for each data item. These codes give the date of the publication and three letter contractions of the surnames of up to two authors. The references are listed in date order, and, for a given date, in alphabetical order of the author codes. References to papers by the same authors in the same year, are distinguished by a number at the end of the reference code, e.g. 73HAM/MIT, 73HAM/MIT2.

The four-digit codes underneath the reference code represent the group of assessors who retrieved data from the literature, and the time at which their assessment was carried out. The key to these codes is given below:

CP70 J. D. Cox and G. Pilcher	literature from 1926–1969
PR77 J. B. Pedley and J. Rylance	literature from 1967–1975
PB82 J. B. Pedley and P. M. Burkinshaw	literature from 1974–1982
PB83 J. B. Pedley and M. K. Baynham	literature from 1980–1983

Most of the data on the original measurements prior to 1968 have been taken directly from Cox and Pilcher's monograph [70COX/PIL]. Data from the period 1968 to 1975 are mainly from *Sussex–N.P.L. Computer Analysed Thermochemical Data* [77PED/RYL]. In general, assessors have not reassessed earlier data unless they are thermochemically related to more recent data.

The accepted unit for an enthalpy change is the Joule. However, the great majority of original experimental data are given in calories (1 cal = 4.1840 J). Standard enthalpies of reaction are therefore given in both kcal mol^{-1} and kJ mol^{-1} and the corresponding uncertainties are given below each value.

The column headed $\Delta_f H^{\ominus}$ contains values and uncertainties for standard enthalpies of formation of the compound under which the process data are listed. Each value is derived from the measurement described in the preceding columns using the methods given in Section 1.2. The physical state of the substance is specified in the column headed 'State'. Where the last three columns are blank, the measurement is assumed to define a value for the standard enthalpy of formation of a compound other than that under which it is listed. For example, most of the reactions in which $CH_4(g)$ occurs are used to derive possible values for the standard enthalpies of formation of the other compounds present in those reactions, using a previously selected value for $CH_4(g)$. Only the three combustion measurements are used to derive possible values for the standard enthalpy of formation of methane.

Values labelled with an asterisk are those which the assessors regard as being derived from definitive measurements for that compound. Values not so labelled are not necessarily suspect and different assessors could give different assignments; the labelling of definitive processes is the most important part of the assessment procedure.

1.2 Processing of experimental data

The procedure for calculating standard enthalpies of formation from data in Table 1.2 is as follows.

Initial values, $H(i)$ are selected for the standard enthalpies of formation of all species i in the data base. (In this context, 'species' refers to different states of the same compound). The sets of values for standard enthalpies of formation given in the last two columns of Table 1.2 are then derived using equation 1.1. Values for inorganic species given in Table 1.3 are defined as constants in subsequent calculations.

$$H(i, j) = \Delta H(j) - \sum \bar{H}(k) \tag{1.1}$$

Where $H(i, j)$ are the set of values for species i;
$\Delta H(j)$ are the enthalpy changes of the processes, j, regarded as definitive for the species, i;
$\bar{H}(k)$ are the current selected values for the standard enthalpies of formation of the species other than i.

For example, the enthalpy of hydrogenation of ethene (reference code 35KIS/ROM) is used to calculate a value for the standard enthalpy of formation of ethene using the provisional value for ethane; it is also used for the calculation of a value for ethane using the provisional value for ethene.

For the process 'Vaporization' the standard enthalpy of formation of the gaseous state is calculated from the present selected value for the specified condensed state. For the process labelled 'Condensation' the value for the specified condensed state is calculated from that selected for the gas.

Uncertainties on $H(i, j)$ are calculated from equation 1.2:

$$UH(i, j) = \sqrt{\left(U\Delta H(j)^2 + \sum \overline{UH}(k)^2\right)} \tag{1.2}$$

Where $UH(i, j)$ are the set of uncertainties on the standard enthalpies of formation of species i, derived from processes j;
$U\Delta H(j)$ is the uncertainty on the standard enthalpy change for the process j;
$\overline{UH}(k)$ are the uncertainties on the current selected values for the standard enthalpies of formation of species other than i.

New values for $\bar{H}(i)$ are calculated using equation 1.3:

$$\bar{H}(i) = \sum H(i, j) \times W(i, j) / \sum W(i, j) \tag{1.3}$$

Where $\bar{H}(i)$ is the new value for the standard enthalpy of formation of species i;
$H(i, j)$ are the set of values for the standard enthapy of formation of species i derived from the process j;
$W(i, j)$ are weighting factors on $H(i, j)$ defined by equation 1.4.

$$W(i, j) = 1/\{UH(i, j)\}^2 \tag{1.4}$$

Where $UH(i, j)$ is the set of uncertainties on $H(i, j)$.

New average values for the uncertainty $\overline{UH}(i)$ on the standard enthalpy of formation of species i are calculated in two different ways, using equations 1.5 and 1.6.

$$\overline{UH}(i) = \sqrt{\left[\sum UH(i, j)^2 \times W(i, j) / \sum W(i, j)\right]} \tag{1.5}$$

$$\overline{UH}(i) = \sqrt{\left[\sum (\bar{H}(i) - H(i, j))^2 \times W(i, j) / \sum W(i, j)\right]} \tag{1.6}$$

Equation 1.5 gives an uncertainty equal to the weighted root mean square of the uncertainties on the values of $H(i, j)$ derived from processes j, and is a suitable measure of average uncertainty if the values of $H(i, j)$ are very consistent with each other. The second method, equation 1.6, is the more applicable when the values for $H(i, j)$ are very different from each other and the uncertainties $UH(i, j)$ are quite small. The greater of the two values is taken as the 'best' value for $\overline{UH}(i)$.

The set of calculations represented by equations 1.1 to 1.6 is repeated until two successive treatments give the same set of values for $\bar{H}(i)$ and $\overline{UH}(i)$ to within 0.1 kJ mol^{-1}.

CHAPTER TWO

Prediction of Standard Enthalpies of Formation

2.1 Component enthalpies

A number of methods for relating the standard enthalpy of formation of a compound in its ideal-gaseous state to its molecular structure are considered in detail by Cox and Pilcher [70COX/PIL]. The most generally applicable parametric schemes are the 'Benson', 'Laidler' and 'Allen' procedures; Cox and Pilcher show that these three methods are mathematically equivalent. However some important steric interactions between non-bonded atoms and conjugative effects between formally localized bonds are not explicitly allowed for in the values for the parameters. They are thus often difficult to estimate to $kJ\,mol^{-1}$ accuracy.

As in the three models mentioned above, the model devised at the University of Sussex assumes that the standard enthalpy of formation of the ideal-gaseous state is equal to the sum of contributions from substructural components within the molecule. However, in the new scheme substructures are chosen which allow for many steric and conjugative effects. The procedure for calculating standard enthalpies of formation is easy to program and uses a simple structural code as input. At present, only standard enthalpies of formation of gaseous acyclic compounds can be predicted, but the method is currently being extended to cyclic compounds and to other thermochemical properties.

The substructures used in the new method are denoted 'components' and their contributions to the standard enthalpy of formation denoted 'component enthalpies'. A component is defined as a group plus the groups to which it is formally bonded; the groups, and their assigned codes, used in the model are given in Table 2.1. The codes assigned to the groups are needed to simplify the description of a component and indicate where possible the valency of the group when it is attached to other groups listed in the table. (Note that hydrogen is not considered as a group). For example $-CH_3$ can bond to *one* other group and is assigned the code 1, $>NH$ can bond to *two* other groups and is assigned the code N2. Letters in the code are related either to the accepted chemical notation or the name of the group. For example, N1, O1 and S2 represent $-NH_2$, $-OH$ and $>S$ groups respectively and K2 and Sp represent *K*etone and *Sulp*hone groups respectively. To simplify the notation the letter C is not included in the code for groups containing carbon and hydrogen only.

Using the newly defined group codes it is possible to define a simple notation to represent the structure of a component. This consists of the code for the central group (denoted the 'principal group') followed in parentheses by the group(s) to which it is formally bonded (denoted 'attached groups'). Table 2.2 gives a list of examples indicating in each case the molecular structure, the structure using group codes and the constituent components with attached groups (in parentheses) ordered from right to left in the sequence defined in Table 2.1. A multiple bond between the principal group and an attached group is indicated by a letter u on the code for the attached group.

The new model assumes that the standard enthalpy of formation, $\Delta_f H^{\ominus}$, is given by the equation: