Enthalpies of Vaporization of Organic Compounds

A CRITICAL REVIEW AND DATA COMPILATION

VLADIMÍR MAJER &

VÁCLAV SVOBODA

$\beta' \& \alpha'$	T_1	T_2	s	
		(K)	(J/mol)	
	298	387	10 A	
0.5179	298	387	10 A	
.78	0.4833	298	385	10 A
.34	0.4866	298		
2.82				
	298	377	10 A	
	298		0 B	
42.74	0.4963	328	368	
57.37	0.5855			
		328	368	0 B
	0.5584	328	368	
55.77				
.58				

A	$\beta \& \alpha$	T_1	T_2	s
		(K)	(J/mol)	
47.41	0.3602	293	469	20 B
	0.1231			A
7.19	0.2662	313	353	30 B
.09	0.2774	298	410	20 A
32	0.2823	295	437	20 A
	0.2768	298	440	30 A
	.2866	382	451	10 A

			A'	
$\beta' \& \alpha'$	T_1	T_2	s	
		(K)	(J/mol)	
0.3929	293	469	10 B	
0.8834			A	
1	0.4836	313	353	0 B
72	0.5029	298	410	20 A
.63	0.4577	295	437	10 A
	0.6312			
48.31	0.4509	298	440	10 A
	0.6262			
53.15	0.5186	382	451	10 A

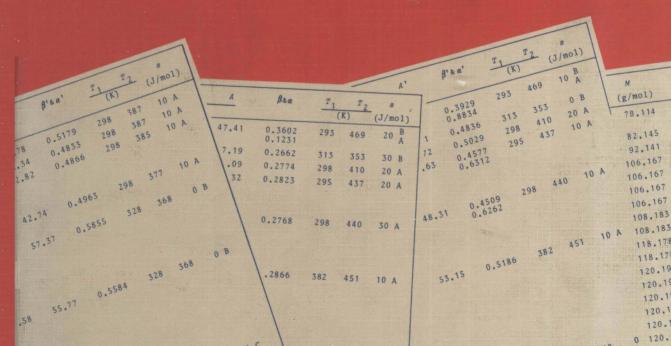| M |
|---|
| (g/mol) |
| 78.114 |
| 82.145 |
| 92.141 |
| 106.167 |
| 106.167 |
| 106.167 |
| 106.167 |
| 108.183 |
| 108.183 |
| 118.178 |
| 118.178 |
| 120.19 |
| 120.19 |
| 120. |
| 120. |
| 120. |
| 0 120. |

International Union of Pure and Applied Chemistry

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A CRITICAL REVIEW AND DATA COMPILATION

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CHEMICAL DATA SERIES No. 32

Commission on Thermodynamics
Subcommittee on Thermodynamic Tables

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International Union of Pure Applied Chemistry

Physical Chemistry Division
Commission on Thermodynamics
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Enthalpies of Vaporization of Organic Compounds

Contents

Foreword

Reliable physical property data are required for the efficient design in chemical engineering, as well as for the development of fundamental science.

The energy needed to produce phase changes, especially the transition from a condensed to the gas phase, is a quantity of considerable interest for many industries. It also represents a measure of intermolecular forces and, as such, it is used in molecular theories.

This book is the first comprehensive and truly critical compilation of enthalpies of vaporization of pure organic substances. The Authors confined themselves deliberately to calorimetrically determined enthalpies which meet a minimum level of accuracy. Indeed, enthalpies derived from the temperature dependence of chemical or phase equilibria, specifically, of vapour pressures, are rarely as accurate as those obtainable with modern calorimetric techniques. The rational trend is to combine equilibrium with calorimetric measurements in order to provide consistent data over a large temperature range. The data tabulated in this book should prove extremely useful in establishing vapor pressure correlations which assure interpolations or even extrapolations.

This book was completed under the auspices of the Sub-Committee on Thermodynamic Tables of the IUPAC Commission I.2 on Thermodynamics of the Division of Physical Chemistry.

The main activity of the Sub-Committee is to formulate the general policy of the Thermodynamic Tables Project Centre, a component of the Thermophysical Properties Data Centre located at the Imperial College of Science and Technology, London, UK. Until recently, only fluids, for which there exist reliable multi-property data over a wide range of the phase diagram, have been considered, and numerical data tables and equations have been given. Monographs on argon, ethylene, carbon dioxide, helium, methane, nitrogen and propylene have already appeared.

There are a considerable number important fluids for which the existing data, and any data which can be expected in the foreseeable future, are not adequate to form the basis of extensive tables using the above criteria. So, for fluids which are of industrial importance, but for which there are inadequate experimental data, the Thermodynamic Tables Project Centre has started to construct multi-property data tables by combining the best available data with data obtained by predictive methods. The monograph on chlorine is the first published containing such 'tentative' data tables for an individual fluid.

For fluids, for which the available experimental data are even more limited,

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the Sub-Committee on Thermodynamic Tables encourages the production of single-property data tables for a large number of systems. These tables are compiled and evaluated by one or several groups of experts and are internationally reviewed.

This book is the first in this series. The project has been realized, under the direction of Prof. J. Pick, in the Department of Physical Chemistry, Institute of Chemical Technology, Prague, Czechoslovakia. This is one among the few centers in the world where enthalpies of vaporization are measured with the highest accuracy. The Authors, Drs. V. Majer and V. Svoboda, in addition to the enormous work required to compile, correlate and evaluate the literature data, have personally determined and published in the best scientific journals a large number of enthalpies of vaporization. It is my pleasure to congratulate them.

I wish to express also my thanks to all the Members of the Commission I.2 on Thermodynamics, for their cooperation, and to acknowledge the continued encouragement and advise given by Dr. D. R. Lide, Jr., as President of the Division of Physical Chemistry, and Prof. G. M. Schneider, as Chairman of the Commission on Thermodynamics.

Special thanks are due to the Reviewers of the preliminary version of the manuscript: Dr. S. Angus (UK), Dr. J. D. Cox (UK), Dr. M. Ducros (France), Dr. A. I. Johns (UK), Prof. F. Kohler (FRG), Dr. S. Malanowski (Poland), Prof. A. Tamir (Israel), and Prof. I. Wadsö (Sweden).

Another useful piece of work has been thus accomplished as a result of the cooperation of scientists from many countries, in conformity with the tradition of the sponsoring organization, the International Union of Pure and Applied Chemistry.

HENRY V. KEHIAIAN
on behalf of the IUPAC Sub-Committee on
Thermodynamic Tables

Preface

This book is a result of a project of the IUPAC Sub-Committee on Thermo-
dynamic Tables performed at the Department of Physical Chemistry of the
Prague Institute of Chemical Technology. The purpose of the project was to
collect and critically evaluate all calorimetrically determined data on the
enthalpy of vaporization of organic compounds, to generate a set of recom-
mended values, and to evaluate standard enthalpies of vaporization and cohe-
sive energies. Every effort was made to furnish maximum amount of informa-
tion on the origin of experimental data, their reliability and consistency,
experimental techniques and the data treatment. Besides the recommended val-
ues with accuracy estimates, the tables list all the direct experimental
values with relevant comments. Also included is a survey of calorimetric
techniques which have been used to detrmine ΔH_v.

The work on the project started at the beginning of 1981 and in summer 1983,
a preliminary version of the manuscript was submitted to the IUPAC Sub-Com-
mittee on Thermodynamic Tables for international reviewing. A final version,
amended according to reviewer's suggestions and supplemented with latest
measurements, was completed in spring 1984, and a camera-ready copy was pro-
duced in winter 1984/85.

The authors have followed, in general, the terminology and symbols recom-
mended by the IUPAC in the following publications: Manual of Symbols and
Terminology for Physicochemical Quantities and Units (1979) and two Reports
of IUPAC Commission I.2 on Thermodynamics (1981, 1982). However, some minor
deviations from the latest IUPAC recommendations have been introduced in or-
der to achieve maximum simplicity in the notation. Specifically, the symbol
for vaporization is "v" instead of the recommended "vap", and the saturated
vapour (or gas) and liquid are indicated by "g" and "l", respectively, used
as superscripts. The guide in choosing the nomenclature has been the IUPAC
publication Nomenclature of Organic Chemistry (Rigaudy and Klesney, 1979).
Further information is given at the head of the Name Index. The molar masses
included in the tables are based on atomic masses as revised at 32nd IUPAC
General Assembly in Lyngby (1983).

The IUPAC Commission on Thermodynamics has recommended that tabulated thermo-
dynamic data should relate to a standard pressure of 10^5 Pa instead of the
traditional 1 atm (101 325 Pa). This alternation has no consequence upon the
values tabulated herein. With regard to the normal boiling temperatures, the
Commission specifically recognized that these are excluded from the recom-
mendation. Therefore, the original convention of referring the values to the
saturated vapour pressure of 101 325 Pa has been followed in the tables. The
issue of the standard-state pressure has been discussed in detail by Freeman
(1982).

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At this place, we wish to thank all those who contributed to this book. We are particularly indebted to Dr. H. V. KEHIAIAN, Chairman of the IUPAC Sub-Committee on Thermodynamic Tables, who stood at the cradle of the project and coordinated it up to its completion. Without his substantial organizational and scientific help, our intention could hardly have become an accomplished fact. We are grateful to all the reviewers, whose valuable suggestions and stimulating criticism helped improve the book. Our thanks are also due to Prof. J. PICK, Head of the Department of Physical Chemistry, Prague Institute of Chemical Technology, who made it possible to realize the project at his Department and gave it all the support. We are greatly indebted to Miss M. ŠKUBALOVÁ for her care in producing the English version of the text, and to Mrs. V. PETRÁNKOVÁ for the large amount of technical work she did for us throughout the course of the project. We should also like to acknowledge the assistance of our former students, Mr. J. PECHÁČEK and Mr. K. RŮŽIČKA, in treating and computer-handling the data, and the efforts of Mrs. L. KRAUSOVÁ and Dr. K. SGALLOVÁ in preparing the camera-ready copy. Our thanks also go to Mr. P. D. GUJRAL, Scientific Publication Secretary of the IUPAC, for his co-operation in publishing our work.

Prague, march 1985   The Authors

Summary of notation

Note: Minor symbols which occur at only one isolated place in the text are not
listed

Symbols

Roman letters:

A	correlation parameters referring to enthalpy of vaporization
A'	correlation parameters referring to cohesive energy
B	second virial coefficient
C	molar heat capacity
d	deviation
f	function
H	molar enthalpy
k	number of correlation constants
M	molar mass
n	number of experimental points
p	pressure
R	gas constant
S	molar entropy
s	standard deviation
T	temperature
U	molar internal energy
V	molar volume
w	statistical weight
Z	compressibility factor

Greek letters:

α, β	correlation parameters referring to enthalpy of vaporization
α', β'	correlation parameters referring to cohesive energy
Δ	difference function
δ	percentage deviation
ω	acentric factor

Subscripts

b	normal boiling temperature (p_{sat}=101325 Pa)
c	critical point
i	general index
o	one point only
p	constant pressure
r	reduced
sat	saturation curve
V	constant volume
v	vaporization

Superscripts

e	extrapolation
g	saturated vapour or gas
l	liquid
o	ideal gas at standard pressure (p^{o}=101325 or 10^{5} Pa)

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1. Introduction

The enthalpy of vaporization is a fundamental quantity characterizing the energetics of the vapour-liquid equilibrium. Traditionally, the enthalpy of vaporization was regarded as a quantity of primarily practical interest. Chemical engineering and technology required reliable, but not too complicated, methods for determining enthalpies of vaporization to be used as input parameters in designing unit operations, as well as in various engineering relationships. The demands on the accuracy were not very high, and attention was mainly focused on substances of technological importance.

The rapid development of thermochemistry, thermodynamics, and molecular theories of liquids over the last twenty years has, however, increased the need for accurate enthalpy of vaporization data measured over wide temperature and pressure ranges for a variety of substances. This has been reflected lately in an increased amount of published data of good accuracy. Apart from direct applications, the enthalpy of vaporization is used to determine other important quantities with which it is closely related. The most important of these are the standard enthalpy of vaporization, required mainly for interconversion of thermochemical quantites for the liquid state and the ideal gas, and the cohesive energy, used in engineering calculations, molecular theories of liquids, and other applications.

The enthalpy of vaporization is accessible by two routes: one is the direct experimental determination by calorimetric means, and the other comprises indirect pseudoexperimental procedures using secondary data. In the latter approach we use the Clapeyron equation to obtain enthalpies of vaporization from vapour pressure-temperature data.

As far as the availability and reliability of enthalpy of vaporization data is concerned, the situation is not satisfactory. The data are largely scattered throughout the literature, and information included in thermodynamic tables is mostly fragmentary. The values are sometimes confusing as they are given without any critical assessment. Frequently, the origin and the accuracy of the data are uncertain, and the reader is in doubt whether he is presented with direct calorimetric data, or values derived from indirect data, or even mere estimates. Moreover, data from different sources for the same compound are often strikingly discordant. ·

Due to extensive experimental activity in the last years, the few compilations which include enthalpy of vaporization data are becoming quickly out of date. More than a half of all calorimetric data have been published after 1970. The values have been presented mostly at 298.15 K only, and no effort has been made to summarize information on the temperature dependence of ΔH_v.

It is clear that we lack an up-to-date collection of critically evaluated

data, with a definite specification of the origin of the data and their accuracy.

As a contribution to establishing a reliable enthalpy of vaporization data base, we have undertaken an extensive project of critical compilation and correlation of data for ΔH_V of pure organic substances. Our objective was not to produce another collection embracing all sorts of available data from purely experimental to estimated ones; by contrast, we have focused only on those substances for which direct experimental data are available. This limitation has been dictated by an effort to present a consistent collection of well-defined data and so remove some of the confusion existing in this field. The scope of the project also reflects the range of activity of the compilers, who have been engaged for a fairly long time in measuring enthalpies of vaporization and in developing experimental methods and equipment.

The present compilation involves the following features:

(i)   it presents all available enthalpy of vaporization data determined by calorimetric means since 1932;

(ii)   the data have been critically assessed, and recommended values of ΔH_V are offered for 298.15 K and the normal boiling temperature; the temperature dependences of the enthalpies of vaporization are described in terms of correlation parameters;

(iii)   based on the recommended values for ΔH_V, calculated values are listed for the standard enthalpy of vaporization at 298.15 K, and for the cohesive energies at 298.15 K and the normal boiling temperature; also included are correlation parameters for the temperature dependence of cohesive energies. Special attention has been paid to correct conversion of ΔH_V to the above quantities.

The book is structured in the following manner:

The first section (Chapters 2 to 4) is of general introductory character, providing the reader with a brief account of the significance of the enthalpy of vaporization and the methods of its determination. The connection between the enthalpy of vaporization and other thermodynamic functions is briefly discussed, and major applications of ΔH_V and related quantities are outlined. Non-calorimetric methods of determination are shortly discussed, and some comment is made on the availability and quality of enthalpy of vaporization data. There follows a brief description of the principal experimental techniques, and a tabular survey of references to all papers describing the vaporization calorimeter designs.

The second section (Chapters 5 and 6) is an introduction to the tables: it describes the main features of the present critical compilation, i.e the rules adhered to in collecting, critically assessing, and selecting the data on ΔH_V. Attention is also paid to the temperature correlation, calculation of the derived quantities, to auxiliary data, and to methods of their estimation. The system of grouping the substances, and the conventions used in pre-

senting the data are explained. Finally, a detailed description of the tables is given, and the meaning of columns is identified.

In the third section of the volume are the actual tables, listing the quantities of interest. The data are presented separately for each group of compounds and the tables can be divided into two parts.

The first part will serve the reader who seeks information on original experimental values, their mutual consistency, and procedures adopted for their processing. The tables in this part summarize all experimental values found in the literature; for each group of substances they are introduced by information on the sources of the data, their temperature correlation, and further treatment.

The second part is addressed to the user who is rather interested in recommended values and their accuracy determined by the compilers on the basis of data presented in the preceding part. These tables give the enthalpies of vaporization and cohesive energies in the form of recommended correlation parameters for the temperature dependences, and of particular values for characteristic temperatures (298.15 K and the normal boiling temperature).