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**HANDBOOK
OF
HEATS
OF
MIXING:
SUPPLEMENTARY
VOLUME**

HANDBOOK OF HEATS OF MIXING: SUPPLEMENTARY VOLUME

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HECALC: Computer Methods for Calculating Excess Enthalpy

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To
V.B.C., V.V.R., and H.F.I.

Dr. James J. Christensen died suddenly on 5 September 1987. He was instrumental in the design and preparation of this supplementary volume. Jim was a highly respected teacher, researcher, and scholar. His loss will be felt deeply by his family, friends, and the scientific community.

PREFACE

We have undertaken the compilation of heats of mixing to aid those working in chemistry, engineering, and related fields, where these data are necessary and useful. The initial *Handbook of Heats of Mixing* was published in 1982 by John Wiley & Sons, Inc. and summarized the published literature values through 1980 for the mixing of liquids.

This supplementary volume is a compilation of enthalpy changes for mixing (ΔH) of pure liquids and gases at constant temperature and pressure. The change in enthalpy upon mixing pure fluids is commonly referred to either as the *enthalpy of mixing*, the *excess enthalpy* or the *heat of mixing*. We shall use the term *heat of mixing* in the compilation and both *heat of mixing* and *excess enthalpy* (h^E) somewhat interchangeably in the use and prediction sections; both terms are common in the fields of engineering and chemistry. The *Supplement* consists of two major sections: Section I, containing information concerning the prediction and use of heat-of-mixing data, and Section II, which is a compilation of heat-of-mixing data together with indexes and references. In Section I we have reviewed the uses of heat-of-mixing data and current methods for their prediction. We have attempted to document methods which can be used with at least moderate success, point out possible failures and shortcomings, critique or evaluate the methods, and provide detailed sample calculations. We have not attempted to make this a plenary review of all possible uses or predictive methods, but have chosen to focus on those methods which we find currently useable. We have independently tested the methods, written codes in BASIC for use on IBM-compatible personal computers (programs are available on the enclosed diskette), and made recommendations based on these tests. Emphasis on sample calculations, ready-to-run computer codes, and useable methods is designed to aid the user of heat-of-mixing data and to stimulate efforts in these areas. In Section II heat-of-mixing data are summarized from 1981 through 1986 under the headings of the various substances. The criterion for including measurements in the table was that a ΔH value must have been reported in the published literature. Values appearing in theses, technical reports, books, or other nonrefereed sources were not included. In addition to the ΔH values, the following information is included in the table: temperature, pressure, error, literature references, method and condition of measurement of ΔH , purity of materials used, and classification of system.

Five indexes—Empirical Formula, Reference, Synonym, System Classification, and Ternary and Quaternary Systems—are included in the *Supplement*. The Empirical Formula Index contains the empirical formula of each substance together with the location of the substance in the table. The Reference Index includes a year-by-year alphabetical listing of all references cited in the table. The Synonym

Index is an alphabetical listing of the common synonyms of and the location of the substances appearing in the table. The System Classification Index arranges all the binary systems in classes depending on the form, magnitude, and sign of ΔH . The Ternary and Quaternary Systems Index gives a list of all ternary and quaternary systems with information indicating their location in the table. Each index in the supplement except the Reference Index has been referenced to the appropriate material in both the *Handbook* and the *Supplement*.

The compilers have read the original of each paper, if possible, and data from other sources are reported only if the original paper could not be obtained through any of the means available, including interlibrary loans. All values are those reported by the original investigators. Values obtained from graphs and equations reported in the articles are indicated in each case. The authors do not claim to be infallible with respect to the selection of the correct value in these cases and are solely responsible for any errors that may have been made in either compiling or evaluating the data. Comments concerning errors and omitted data would be most appreciated.

We wish to acknowledge the many hours of effort by Dr. Krystyna Pawlak and Julie Whittaker in data collection, and in organizing and proofing the manuscript. We also express our gratitude to Joanna Pawlak for editorial assistance and to Beth Ferguson and Julie Whittaker for technical typing of the manuscript.

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April 1988

ERRATA

Errata for *Handbook of Heats of Mixing*. The following changes should be made in the previously published Handbook.

Page	System	Change from	Change to
59 71	A243	AMINE, DIETHYL N-NITROSO ETHANE, TRITHIAMETHYL	AMINE, DIETHYL, N-NITROSO ORTHOACETIC ACID, TRITHIO, TRIMETHYL ESTER
73	A254	(J/mol)	(kJ/mol)
146	B176	x_1 0.358	x_1 0.258
147	B178	x_2 1.30	x_2 0.30
252	B519	DIFLUORO (2)	DIFLUORO (1)
272	B584	x 0.711	x 0.7110
306	B685	T/P: 278.15K/ambient x 0.5 H 0	delete all
345		TETRAHYDROK	TETRAHYDRO
512	C344	2-PYRROLIDONE, 1-METHYL	PYRROLIDINE, 1-METHYL
566	D19	vapor phase	vapor space
619	E32	x 0.5535 H 651.3	delete all
627	E57	H 09,431	H -0.431
632	E71	ETHANEDIO1	ETHANEDIOL
633	E72 & E74	2.5%	20 at $x=0.5$
719	E288 & E290	2.5%	20 at $x=0.5$
720	E293	2.5%	20 at $x=0.5$
739	E362	2.5%	20 at $x=0.5$
742	E370	2.5%	20 at $x=0.5$
763	F64	x 0.4 0.4	x 0.4 0.5
766	F75	x 0.4 0.4	x 0.4 0.5
769	F88	negative H's	positive H's
792	H40	2.5%	20 at $x=0.5$
793	H47	ETHANE, TRITHIAMETHYL	ORTHOACETIC ACID, TRITHIO, TRIMETHYL ESTER
795	H51	2.5%	20 at $x=0.5$
796	H55 & H56	2.5%	20 at $x=0.5$

(Continued)

Page	System	Change from	Change to
826	H156	(1), HEPTENE (CIS) C_7H_{14}	2-HEPTENE (CIS) (1), C_7H_{14}
848	H218	vapor space	no vapor space
1014	H283	T/P: 273.15K/ambient x 0.734 0.735 H 105 109	T/P: 273.15K/ambient x 0.734 0.735 H -105 -109
1087	P2	(J/mol)	(cal/mol)
1244	P435	C_8H_8	C_8H_6
1306	P639	C_8H_9ON PYRROLIDINE, 1-METHYL/ SULFOXIDE, DIMETHYL see SULFOXIDE, DIMETHYL	$C_5H_{11}N$ delete
1347	T40	-41.800	-41,800
1355	T66	= 104.89	-104.89
1393	U1	$C_5H_{12}O_2N_2$	$C_5H_{12}ON_2$
1399	W17	The second set of data at 300.05K and ambient pressure is not for system W17; positive H's	New system: WATER (1), H_2O — ACETIC ACID, DICHLORO (2), $C_2H_2O_2Cl_2$ negative H's
1418	W78	positive H's	negative H's
1481	CH_3Cl	P167	P176
1485	$C_5H_{12}O_2N_2$	$C_5H_{12}O_2N_2$ U1	delete move to same page under $C_5H_{12}ON_2$
1486	$C_6H_{12}O_2$	C259	move to same page under $C_6H_{12}O$
1488	$C_7H_{14}O$	C204	move to p. 1486 under $C_6H_{14}O$
1493		POLYETHYLENE GLYCOL, DIMETHYL ESTER POLYPROPYLENE GLYCOL, DIMETHYL ESTER	POLYETHYLENE GLYCOL, DIMETHYL ETHER POLYPROPYLENE GLYCOL, DIMETHYL ETHER
1502	78Mc	Munsch	Munsch
1538	64Ae	(1064)	(1964)
1555			Synonym Index has been corrected and expanded in this Supplement

**HANDBOOK OF
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SECTION I

Use and Prediction of Heats of Mixing

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Diskette of Computer Programs (inside back cover)

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INTRODUCTION

A. Introduction

This review of uses of heat-of-mixing data and current methods for their prediction is intended to stimulate efforts in these areas as well as serve as a reference tool. In both the use and prediction parts of this section, we have attempted to (1) document methods which can be used with at least moderate success, (2) point out possible failures and shortcomings, (3) critique or evaluate the methods, and (4) provide detailed sample calculations. We have not attempted to make this an exhaustive review of all possible uses of heats of mixing, nor have we included all available predictive methods. We have chosen, rather, to focus on currently useable methods which are applicable to a reasonably wide range of components. We have independently tested the methods, written codes for use on IBM-compatible personal computers (programs are available on the enclosed diskette), and made recommendations based on these tests. While additional methods in various stages of development are to be found in the literature, only those methods for which sufficient development has taken place to allow easy and/or wide-spread implementation were included. We apologize to proponents of other yet developing methods for our inability to include their methods due to space constraints and this pragmatic approach.

As evidenced by the variety and complexity of the data compiled in this handbook, heats of mixing contain a substantial and significant amount of information about the nonidealities of liquid mixtures. Methods for measurement, correlation, calculation, and prediction of these nonidealities occupy much of the attention of the world's thermodynamicists because of the impact mixture nonidealities have upon nearly every facet of chemical processing. It seems to us that heat-of-mixing data are of fundamental importance in development of effective liquid mixture models and theories. Ultimately, as new theories and models more closely approximate reality, it may be possible to calculate most mixture properties from heat-of-mixing data. For example, most recent theories of liquid mixtures identify molecular size effects and molecular interactions as the primary sources of nonideal mixing behavior.

Consider, for example, the van der Waals partition function upon which many of the most successful liquid mixture models have been based. It contains both a free volume and a molecular interaction term which affect the mixture properties (Sandler, 1985). Mixture density measurements may provide molecular size information, but the interaction information is most easily obtained from heat-of-mixing studies. Of course the two properties are not independent. Strength and selectivity of intermolecular interactions will certainly influence effective molecular volumes and vice versa. While no definitive relationship between macroscopic measurements and actual molecular properties is yet available, the importance and relevance of heats of mixing to molecular model development and evaluation are apparent.

In part B we review uses of heats of mixing. Many other useful properties may be estimated from heats of mixing using standard thermodynamic identities and current liquid models. For example, the excess heat capacity and excess enthalpy (which is numerically equivalent to the heat of mixing) are related exactly by

INTRODUCTION

$$C_p^E = (\partial h^E / \partial T)_{p,x} \quad (A.1)$$

However, to determine C_p^E from h^E , one must know the latter as a function of temperature. It is important to make a distinction between thermodynamic identities and models. There are a number of identities which relate other thermodynamic properties to heats of mixing (e.g., Gibbs-Helmholtz, Gibbs-Duhem, and unnamed partial-derivative identities). These identities could be used to determine exactly other thermodynamic properties from heats of mixing if data at all temperatures, compositions, and pressures were available. Determination of C_p^E from h^E using eq. (A.1) would be an example of this method. Because such an infinite data compilation is not feasible, correlations, theories and models are used to smooth the actual data and to provide continuous functionalities with respect to the independent variables of temperature, pressure and composition. Thermodynamic identities such as eq. (A.1) can then be applied to these continuous functionalities. The results, however, are now limited not only by the accuracy of the experimental data, but also by the adequacy of the model. It should be kept in mind, then, that inadequacies in these methods are generally due to shortcomings in the model and not in the underlying identity upon which the method is based. In this example, the accuracy of C_p^E determined from h^E is limited by how well the temperature dependence is correlated, not by eq. (A.1) itself.

In part C we review major h^E prediction techniques. Emphasis is on use of the method though a brief background is provided for those interested in theory. We generally detail how to use the method, provide a sample calculation, illustrate some test comparisons, and make recommendations as to the method's usefulness and accuracy. Where applicable, constants and interactions are tabulated to make this presentation as autonomous as possible, enabling the reader to use the method directly from this handbook. Here too, a distinction between terms needs to be made. By prediction we mean those methods which can be used without any experimental h^E data from the system for which the calculations are to be made. This is opposed to correlation where an adjustable parameter in the model is regressed from at least some experimental data.

Predictive techniques are important in view of the many industrial uses of heats of mixing and the infinite number of mixtures of possible technical interest. This seems to be an appropriate time for a review of these techniques due to the recent proliferation of a number of distinct methods and theories.