

## Heat Capacity of Liquids. Critical Review

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### Abstract

New experimental data on heat capacities of pure liquid organic and some inorganic compounds were compiled, critically evaluated and recommended values provided. The bulk of the work covers data published in the primary literature between 1993 and 1999 and some data of 2000. Recommended data presented in terms of parameters of correlating equations for temperature dependence of heat capacities of liquids were developed by critical assessment of literature calorimetrically determined heat capacities. This work is carried out as the IUPAC Commission on Thermodynamic, Physical and Biophysical Chemistry Division project 2000-031-1-100 and is an update of a two volume monograph entitled "Heat Capacity of Liquids: Critical Review and Recommended Values", by M. Zábranský, V. Růžička, V. Majer, and E.S. Domalski, that was published in 1996 as the Monograph No.6 of the Journal of Physical and Chemical Reference Data and was the product of the IUPAC project 121/11/87.

**Key words:** heat capacity; pure liquids; data assessment and correlation; new data needs.

### Introduction

Heat capacities belong among the basic thermophysical and thermodynamic properties which characterize a liquid. They are directly linked with temperature derivatives of basic thermodynamic functions and are therefore indispensable for the calculation of differences in these functions between different temperatures. This information is widely used in chemical engineering for establishing energy balances, in thermodynamics for obtaining entropy and enthalpy values, and in thermochemistry for calculating changes in reaction enthalpies with temperature. A knowledge of heat capacities is also required for evaluating the effect of temperature on phase and reaction equilibria. Variations in heat capacities serve as a sensitive indicator of phase transitions and are an important tool for understanding changes in the structure of liquid solutions. Heat capacity may also be used for obtaining the temperature derivative of vapour

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pressure and thus enable a reliable extrapolation of vapour pressure, in particular down to and below the fusion temperature (see e.g. [1-3]).

## **Recent data compilations on liquid heat capacities**

Zábranský et al. [4] compiled and critically assessed heat capacities in the liquid phase measured calorimetrically of 1624 pure organic and inorganic compounds having the melting temperature below 573 K. The monograph [4] presents for each compound a survey of all sources of available literature data, gives a survey of some statistical data from critical selection and correlation of selected data as a function of temperature, presents parameters of a polynomial or cubic spline equations and for some compounds also parameters of an empirical equation allowing a meaningful extrapolation towards the critical temperature. The monograph also contains an annotation of 38 compilations giving survey of data published between 1897 and 1991 mostly for selected families of compounds.

Over the period from 1993 through 2000, only one large compilation by Palczewska-Tulińska et al. [5,6] was published which contains data on the heat capacity of organic compounds in the condensed phase. The compilers present for 480 compounds usually one or two sets of experimental data (altogether 610 data sets selected from about 350 literature references), which they consider the most reliable.

Since 1994 when compilation of data for the monograph by Zábranský et al. [4] was finished several new measurements were published in the open literature containing both data for compounds not included in the monograph as well as some either more accurate or more extensive data covering a wider temperature range for compounds already contained in the monograph. In table 1 a survey is given of reliable data measured over the period 1993 to 2000 in a temperature range wider than about 50 K. Compounds in table 1 are grouped into families. Division into families of chemically similar compounds in table 1 follows the pattern adopted by Zábranský et al. [4].

The following groups of compounds were subjected to investigation over the period 1993 to 2000 leading to measurement of heat capacities of pure liquids:

- (1) compounds occurring in solid and liquid fossil fuels,
- (2) polymers and monomers,
- (3) higher alkanes and 1-alkanols,
- (4) contaminants, covering both simple and complex compounds.

A laboratory, which carried out the measurements, is also given in table 1. The listed laboratories represent workplaces, which were involved in a systematic study of heat capacities of compounds in the condensed phase over the last decade.

## **Updated critical compilation on liquid heat capacities**

The abundance of new experimental liquid heat capacity data published since 1994 necessitated an update of the monograph by Zábranský et al. [4].

The objectives of the present work were as follows:

- (1) To provide an exhaustive survey of the literature for all isobaric and saturation heat capacities for pure organic and inorganic compounds in the liquid state which were published in the primary literature mainly between 1993 and 1999 and some data of 2000.
- (2) To compile newly published heat capacities supplemented by data omitted in the previous stage of the project that ended in 1993 and appeared in the Monograph No.6. To extend a database of raw experimental data established in the previous stage of the project. Only data for well-defined compounds in the isotropic liquid state, obtained by calorimetric measurements were considered. The criterion for inclusion of a compound in the compilation required the compound to have a melting point below 573 K.
- (3) To critically evaluate heat capacity data and prepare sets of selected data.
- (4) To correlate selected data and provide recommended values for the heat capacities of liquid compounds as a function of temperature. The recommended data are presented in terms of parameters of suitable correlating equations accompanied with an assessment of the data uncertainty.

The first supplement [7] to the monograph [4] contains a critical assessment of data taken from 359 literature references for 370 new compounds not included in the monograph and for 289 compounds already included in the monograph. For the latter group the new data either improve the overall reliability of the recommended data developed by the compilers and/or extend the temperature range of data. Table 2 gives a number of compounds for which liquid heat capacity data are covered in the works [4,7]. Also given in table 2 is the number of compounds having heat capacity value at one temperature only, mostly at 298 K.

Some statistical data about databases of raw data developed in the course of projects leading to compilations [4,7] are given in the table 3.

The target groups of prospective users of the data compilations [4,7] are:

- (1) chemical engineers employing process simulators which incorporate databases of several physical-chemical pure component data,
- (2) environmental engineers who need some physical-chemical pure component data in environmental relevant temperature range for predicting fate of pollutants in the environment,
- (3) thermodynamicists for developing theories of molecular structure of liquids or for developing heat capacity estimation methods.

### **Needs for new data on liquid heat capacities**

Calorimetrically measured heat capacities in the liquid phase are available for more than two thousands of compounds (two compilations by Zábanský et al. [4,7] contain data for almost 2000 organic and inorganic compounds having the melting point below 573 K). Obviously, there is still a substantial number of important compounds for which no experimental liquid heat capacity data have so far been measured, or the

available data are either unreliable or cover only a narrow temperature range (for example for about 20 % of compounds included in compilations [4,7] the data is available at a single temperature, most often at 298 K). Very often compounds with inadequate or completely missing data belong for example among those produced in large quantities or are classified as contaminants.

Table 4 gives a survey of contaminants with either missing or unreliable data on liquid heat capacities. The sources, from which the compounds in table 4 were selected, were mainly EPA contaminants lists [8,9], the EU directive [10], CRC Handbook of Chemistry and Physics [11].

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Table 1. Survey of some recent measurements of liquid heat capacity

Group of compounds		No. compounds	Compound	Laboratory <sup>1</sup>
Saturated hydrocarbons	aliphatic	4	n-alkanes C <sub>17</sub> , C <sub>18</sub> , C <sub>19</sub> , C <sub>20</sub>	Utrecht University, Netherlands
Saturated cyclic hydrocarbons		1	octadecane	NIPER, Bartlesville, Oklahoma, USA
		1	ethenylcyclohexane	Nizhny Novgorod State University, Russia
		3	α-pinene; β-pinene; limonene	University of Lisboa, Portugal
Unsaturated hydrocarbons	aliphatic	2	1-butene, 1-pentene	Osaka University, Japan
		1	4-methyl-1-pentene	Nizhny Novgorod State University, Russia
Aromatic and cyclic hydrocarbons	unsaturated	15	benzene and its 6 derivatives, norbornene, naphthalene and its 2 derivatives, tetrahydro-phenanthrene, -pyrene, hexahydro-pyrene; dimethylbiphenyl	NIPER, Bartlesville, Oklahoma, USA
		1	benzo[ <i>a</i> ]pyrene	ICT, Prague, Czech Republic
Fluorine derivatives		2	difluoromethane, pentafluoropentane	NIST, Boulder, Colorado, USA
		1	hexadecafluoroheptane	NIPER, Bartlesville, Oklahoma, USA
Chlorine derivatives		7	chlorinated benzenes	ICT, Prague, Czech Republic
		2	hexachloro- and 1,2-dichloro-propane	NIPER, Bartlesville, Oklahoma, USA
		3	chlorinated cyclopentane, cyclohexane	Belarusk State University, Minsk, Belorusk
Bromine derivatives		1	bromocyclohexane	Belarusk State University, Minsk, Belorusk
Mixed derivatives	chlorine-fluorine	2	1,1,2-trichloro-1,2-difluoroethane 1,2,2-trichloro-1,1-difluoroethane	Moscow State University, Russia

Amines	6	mono-, di-, tri-octylamine, diethylenetriamine; o-toluidine octamethylenetetramine	NIPER, Bartlesville, Oklahoma, USA
Heterocyclic compounds	nitrogen 11	pyridine; mono-, di-methylpyridines, piperazine, [1,2,4]triazolo[1,5- <i>a</i> ]pyrimidine, trans-(R,S)-decahydroquinoline	NIPER, Bartlesville, Oklahoma, USA
		7	derivatives of imidazole and derivatives of pyrazole
Azo-compound	1	trans-azobenzene	NIPER, Bartlesville, Oklahoma, USA
Ethers	2	1,2-dimethoxyethane butyl vinyl ether	NIPER, Bartlesville, Oklahoma, USA
Alcohols	6	1,2- and 1,3-butanediol, cyclohexanol, 4-tert-butylcatechol, 1-tetradecanol; 1,6-hexanediol	NIPER, Bartlesville, Oklahoma, USA
	7	1-alkanols: C6, C7, C8, C10, C12, C16, C18	ICT, Prague, Czech Republic
	3	1-alkanols: C18, C19, C20	Utrecht University, Netherlands
Carbonyl compounds	3	mesityl oxide, acetophenone 2-cyclohexen-1-one	NIPER, Bartlesville, Oklahoma, USA
Acids	1	2-ethylhexanoic acid	NIPER, Bartlesville, Oklahoma, USA
	3	stearic, palmitic, oleic acid	Oviedo University, Spain

Esters		5	dimethyl carbonate; butyl acrylate, pentyl acetate, dimethyl isophthalate, dimethyl 2,6-dicarboxylicnaphthalate	NIPER, Bartlesville, Oklahoma, USA
		3	dimethyl phthalate, diethyl phthalate, dibutyl phthalate	ICT, Prague, Czech Republic
Heterocyclic compounds	oxygen	1	2,5-dihydrobenzo-3,4-furan	NIPER, Bartlesville, USA
Miscellaneous compounds	oxygen	2	1-ethoxy-2-acetoxyethane, 2-(2-propoxyethoxy)ethanol	NIPER, Bartlesville, Oklahoma, USA
Sulfides		4	diphenyl sulfide; dicyclohexyl sulfide, dioctyl sulfide; ethyl octyl sulfide	NIPER, Bartlesville, Oklahoma, USA
Heterocyclic compounds	sulfur	2	dibenzothiophene thianthrene	NIPER, Bartlesville, Oklahoma, USA
Fluoro-oxygen compounds		1	pentafluorophenol	NIPER, Bartlesville, Oklahoma, USA
Nitrogen-oxygen compounds		3	isoxazole, isocyanatobenzene 2-(methylamino)ethanol	NIPER, Bartlesville, Oklahoma, USA
		2	dimethylperhydro-1,3-oxazin-2-one 2,2-bis(4-cyanatophenyl)propane	Nizhny Novgorod State University, Russia
Oxygen-sulfur compounds		2	tetrahydrothiophene phenoxathiin	NIPER, Bartlesville, Oklahoma, USA
Halogen-sulfur compounds		2	2-bromo and 2-chlorothiophene	Tokyo Institute of Technology, Japan
Organosilicon compounds		1	tetraethylsilane	NIPER, Bartlesville, Oklahoma, USA
Organometallic compounds		3	diethyltelluride, tripropylaluminium hydrobis(2-methylpropyl)aluminium	Nizhny Novgorod State University, Russia

<sup>1</sup> abbreviations for some laboratory names:

ICT - Institute of Chemical Technology

NIPER – National Institute for Petroleum and Energy Research

NIST – National Institute of Standards and Technology

Table 2 Number of compounds with measured liquid heat capacities included in compilations [4,7]

Group of compounds	No.com- pounds	At one temperature only
Elements	30	0
Inorganic compounds	109	14
Saturated aliphatic hydrocarbons	83	2
Saturated cyclic hydrocarbons	137	16
Unsaturated aliphatic hydrocarbons	40	2
Unsaturated cyclic hydrocarbons	125	17
Fluorine derivatives	56	16
Chlorine derivatives	64	13
Bromine derivatives	43	10
Iodine derivatives	16	2
Mixed halogen derivatives	50	10
Amines	65	32
Nitriles	30	12
Heterocyclic nitrogen compounds	56	6
Miscellaneous nitrogen compounds	14	1
Ethers	51	19
Alcohols and phenols	125	33
Carbonyl compounds	71	16
Acids and anhydrides	39	3
Esters	160	26
Heterocyclic oxygen compounds	31	7
Miscellaneous oxygen compounds	75	24
Sulfides	31	1
Thiols	18	0
Heterocyclic sulfur compounds	14	0
Halogen + oxygen compounds	55	9
Nitrogen + oxygen compounds.	174	84
Oxygen + Sulfur compounds.	8	0
Miscellaneous compounds	41	11
Organosilicon compounds	65	4
Organic compounds. with phosphor and boron	23	1
Organometallic compounds	54	9
Salts of organic acids	31	23
<b>Total number of compounds</b>	<b>1984</b>	<b>387</b>

Table 3 Statistical data for compilations [4,7]

Number of compounds	1984
Number of literature references	1867
Number of data sets <sup>a</sup>	4554
Number of data points	34583
Number of calorimeters	399

<sup>a</sup> set of experimental values from one calorimeter reported by an author for one substance in one original source

Table 4 Missing or unreliable data on liquid heat capacity for large production organic contaminants (L)<sup>a</sup>, hazardous air pollutants (A)<sup>b</sup> and drinking water contaminants (W)<sup>c</sup>

Substance	Category	CAS-RN	Note
Acetyl chloride	L	75-36-5	very old (1881)
Acrolein	L	107-02-8	none
Allyl alcohol	L	107-18-6	very old (1881)
Allyl chloride	L	107-05-1	very old (1881)
Bis(2-chloroethyl) ether	L	111-44-4	only at 293 and 313 K
Bis(chloromethyl) ether	L	542-88-1	none
2-Chloroaniline	L	95-51-2	none
4-Chloroaniline	L	106-47-8	none
Chloromethyl methyl ether	A	107-30-2	none
1-Chloro-2-nitrobenzene	L	88-73-3	none
1-Chloro-4-nitrobenzene	L	100-00-5	none
3-Chlorophenol	L	108-43-0	none
4-Chlorophenol	L	106-48-9	none
Chloroprene	A	126-99-8	only at 293 K
2,4-Diaminotoluene	L	95-80-7	none
1,2-Dibromo-3-chloropropane	A	96-12-8	none
1,2-Dichloroethene	W	540-59-0	old and inaccurate
1,3-Dichloropropane	W	142-28-9	only at 298 K
2,2-Dichloropropane	W	594-20-7	data only to 259 K
1,3-Dichloropropene	A,W	542-75-6	none
Diethyl sulfate	A	64-67-5	none
2,4-Dimethylphenol	L	105-67-9	none
Epichlorohydrin	A,L,W	106-89-8	none
Ethyl acrylate	A	140-88-5	none
Hexachlorobutadiene	A	87-68-3	none
Hexachlorocyclopentadiene	A	77-47-4	none
2-Methoxyaniline	A	90-04-0	none
2-Methylaziridine	A	75-55-8	none
Methyl isocyanate	A	624-83-9	none
N-Methyl-N-nitrosomethanamine	A	62-75-9	none
N-Nitrosomorpholine	A	59-89-2	none
2-Nitropropane	A	76-46-9	none
2-Nitrotoluene	L	88-72-2	none
Parathion	A	56-38-2	none
Pentachlorophenol	A	87-86-5	none
2-Phenyloxirane	A	96-09-3	none
Tetrachloromethane <sup>d</sup>	L,W	56-23-5	inaccurate
Trichloroethene	L,W	79-01-6	old and inaccurate
Trichloromethane <sup>e</sup>	L	67-66-3	inaccurate
$\alpha,\alpha,\alpha$ -Trichlorotoluene	L	98-07-7	none
Vinyl bromide	A	593-60-2	inaccurate only at 288 K

<sup>a</sup> taken from ref. [11]

<sup>b</sup> taken from ref. [8]

<sup>c</sup> taken from ref. [9]

<sup>d</sup> about 35 measured data points with very different measured values in temperature range 253 to 339 K.

<sup>e</sup> about 20 measured data points with very different measured values in temperature range 246 to 333 K (most data points at 298 K).