

Heat capacity and enthalpy of liquids: Organic sulphur compounds (thiols and sulphides)

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THE PREPARATION OF THIS DATA ITEM

The work on this particular Data Item was monitored and guided by the Physical Data and Reaction Kinetics Committee, which first met in 1966 and now has the following membership:

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The technical work involved in the assessment of the available information and the construction and subsequent development of the Data Item was undertaken (under contract to ESDU) by

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The person with overall responsibility for the work in this subject area is Mr R. Partington, Head of Internal Flow and Physical Properties Group.

HEAT CAPACITY AND ENTHALPY OF LIQUIDS: ORGANIC SULPHUR COMPOUNDS (THIOLS AND SULPHIDES)

1. INTRODUCTION

This Data Item presents values of saturated liquid heat capacity and enthalpy in tabular form for the thiols and sulphides listed in Table I.

The data on which these values are based are the most reliable available and for most compounds the range covered is from the melting temperature to a reduced temperature of 0.86. In common with other ESDU Data Items, quantities are expressed in SI units and conversion factors to other units are provided in Section 3.

Section 4 describes the procedure used to obtain the values of heat capacity presented and indicates the effect of pressure. Values of enthalpy have been derived from values of heat capacity as explained in Section 5. Section 6 gives an explanation of the Tables and indicates the uncertainties in the values presented in them.

Section 7 contains all the sources of data used in the preparation of this Data Item.

2. NOTATION AND UNITS

The SI unit of heat capacity is the joule per kilogram kelvin (J/kg K). A convenient multiple unit for the range of heat capacities in this Item is the kilojoule per kilogram kelvin (kJ/kg K) and is adopted here.

a_1, a_2, a_3, a_4	constants for each liquid in Equations (4.1) and (4.2)	kJ/kg K
b_1	constant for each liquid in Equations (4.3) and (5.1)	kJ/kg K
b_2, b_3, b_4	non-dimensional constants for each liquid in Equations (4.3) and (5.1)	–
c	heat capacity	kJ/kg K
h	enthalpy	kJ/kg
T	thermodynamic temperature	K

Subscripts

c	denotes value at critical point
m	denotes value at melting point
r	denotes reduced quantity, <i>e.g.</i> $T_r = T/T_c$
s	denotes value at saturation pressure.

3. CONVERSION FACTORS

$$\begin{aligned} 1 \text{ kJ/kg K} &= 0.239 \ 006 \text{ cal/g K} \\ &= 0.238 \ 846 \text{ Btu/lb } ^\circ\text{F} \end{aligned}$$

$$\begin{aligned} 1 \text{ kJ/kg} &= 0.239 \ 006 \text{ cal/g} \\ &= 0.429 \ 923 \text{ Btu/lb.} \end{aligned}$$

Issued September 1985
With Amendment A – May 2003

4. HEAT CAPACITY

4.1 Heat Capacity at Saturated Pressure

For many liquids it has been suggested that a good representation of heat capacity data over a wide range of temperature is given by the equation

$$c_s = a_1(1 - T_r)^{-2/3} + a_2(1 - T_r)^{-1/3} + a_3. \quad (4.1)$$

The range of applicability of Equation (4.1) is limited for compounds that exhibit a very sharp minimum in the heat capacity data at temperatures near the normal melting temperature. For these compounds, over the temperature range considered, a better representation of the data is obtained using the modified equation

$$c_s = a_1(1 - T_r)^{-2/3} + a_2(1 - T_r)^{-1/3} + a_3 + a_4(1 - T_r)^{1/3}, \quad (4.2)$$

which can be rearranged and used more conveniently in the form

$$c_s = b_1[1 + b_2(1 - T_r)^{-2/3} + b_3(1 - T_r)^{-1/3} + b_4(1 - T_r)^{1/3}]. \quad (4.3)$$

For the liquids considered in this Data Item, the derived values of b_1 , b_2 , b_3 and b_4 given in Table I (part 2) are a correlated set of values giving the best fit to the data for the liquid thiols and sulphides not only as individual compounds but also as members of their chemical series based on molecular structure.

Since the available experimental data do not cover the full liquid range, the data used to evaluate the constants in Equation (4.3) have been extended to $T_r = 0.86$ using data calculated from the saturated vapour enthalpies and estimated latent heats. For compounds where no experimental data exist the corresponding hydrocarbon has been used to estimate useful values.

Using the values of the constants in Table I (part 2) together with the values of T_c also given in Table I (part 2), values of c_s in kJ/kg K have been calculated for each compound from Equation (4.3) and are presented in Table II. Users' attention is drawn to the limits of applicability of Equation (4.3) given in Table I. Any extrapolation beyond these limits should be carried out with caution, particularly at temperatures near the critical temperature. An appropriate start temperature rather than the melting temperature is given in those cases where there are no data to define a point of inflection. Where experimental data do indicate this feature and it cannot be represented by Equation (4.3), smoothed values are given in Table II preceded by the letter 'x'.

4.2 Effect of Pressure

The experimental data reported in each Derivation are either at 1 atm pressure or at saturation pressure. Except at temperatures exceeding $0.9T_r$, the differences between the values of liquid heat capacity at 1 atm pressure and at saturation pressure are not significant.

5. ENTHALPY AT SATURATION PRESSURE

Values of liquid enthalpy for each compound may be calculated from the equation,

$$h_s = -b_1 T_c \left[(1 - T_r) + 3b_2(1 - T_r)^{1/3} + \frac{3}{2}b_3(1 - T_r)^{2/3} + \frac{3}{4}b_4(1 - T_r)^{4/3} \right] \frac{T_r}{T_r^*}, \quad (5.1)$$

obtained by integrating Equation (4.3). T_r^* denotes the reduced temperature at which the enthalpy is set to zero. The enthalpy base temperature for all compounds has been taken as $25^\circ\text{C} = 298.15\text{ K}$ at which the liquid was arbitrarily assigned an enthalpy of zero. The values of enthalpies in kJ/kg have been calculated

for each compound from Equation (5.1) and are presented in Table III.

6. EXPLANATION OF TABLES

6.1 Notes on Compounds Considered

The compounds are numbered from 1 to 34 in Table I and these numbers are used to identify the compounds in the subsequent Tables where space does not permit the use of the name. The compounds are identified by a systematic name but for most compounds alternative names are given by which the compounds may be identified in other literature.

The values of T_m and T_c for most compounds have been taken from Data Item 78034. Compounds for which no, or few, experimental data exist and for which values of the constants were estimated as described in Section 4.1 are indicated by an asterisk against their compound name in Table I.

Table II presents values of heat capacity and Table III presents values of enthalpy at 10 K intervals of temperature and the range covered is from the melting temperature or an appropriate starting temperature to $0.86 T_c$.

6.2 Accuracy of Data

The experimental data which are assessed to be the most reliable have a repeatability of about ± 1 per cent, although differences in the methods used by different workers, and also in the purity of samples, can increase the uncertainties to about ± 2 per cent. Reliable data are not available for all the compounds considered nor over the whole temperature range covered.

Although it is considered that the correlation procedures adopted keep the errors in the values presented to a minimum the user should allow for an uncertainty of ± 5 per cent in the values of heat capacity given to 3 decimal places and in the values of enthalpy given to 1 decimal place in the Tables. This uncertainty increases to ± 10 per cent for the values of heat capacity given to 2 decimal places and for the values of enthalpy given to the nearest integer in the Tables.

7. REFERENCES AND DERIVATION

References

The references given are recommended sources of information supplementary to that in this Data Item.

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Derivation

The Derivation lists selected sources that have assisted in the preparation of this Data Item.

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TABLE I (Part 1)
LIST of COMPOUNDS

The empirical formula, name, alternative name, if any, and structural formula of each compound considered in this Data Item are as follows. An asterisk against the compound name indicates that there are no experimental data for that compound.

No.	Empirical Formula	Name	Alternative Name(s)	Structural Formula
C₁ TO C₁₀ THIOLS				
1	CH ₄ S	Methanethiol	Methyl mercaptan	CH ₃ SH
2	C ₂ H ₆ S	Ethanethiol	Ethyl mercaptan	CH ₃ CH ₂ SH
3	C ₃ H ₈ S	Propane-1-thiol	Propyl mercaptan	CH ₃ [CH ₂] ₂ SH
4		Propane-2-thiol	Isopropyl mercaptan	(CH ₃) ₂ CHSH
5	C ₄ H ₁₀ S	Butane-1-thiol	Butyl mercaptan	CH ₃ [CH ₂] ₃ SH
6		Butane-2-thiol	<i>sec</i> -Butyl mercaptan	CH ₃ CH ₂ CH(SH)CH ₃
7		2-Methylpropane-1-thiol	Isobutyl mercaptan	(CH ₃) ₂ CHCH ₂ SH
8		2-Methylpropane-2-thiol	<i>tert</i> -Butyl mercaptan	(CH ₃) ₃ CSH
9	C ₅ H ₁₂ S	Pentane-1-thiol	Pentyl mercaptan	CH ₃ [CH ₂] ₄ SH
10		*Pentane-2-thiol		CH ₃ [CH ₂] ₂ CH(SH)CH ₃
11		*2-Methylbutane-1-thiol	<i>act</i> -Pentyl mercaptan	CH ₃ CH ₂ CH(CH ₃)CH ₂ SH
12		3-Methylbutane-1-thiol	Isopentyl mercaptan	(CH ₃) ₂ CH[CH ₂] ₂ SH
13		2-Methylbutane-2-thiol	<i>tert</i> -Pentyl mercaptan	CH ₃ CH ₂ C(SH)(CH ₃) ₂
14		3-Methylbutane-2-thiol		(CH ₃) ₂ CHCH(SH)CH ₃
15	C ₆ H ₁₄ S	Hexane-1-thiol	Hexyl mercaptan	CH ₃ [CH ₂] ₅ SH
16		*Hexane-2-thiol	<i>sec</i> -Hexyl mercaptan	CH ₃ [CH ₂] ₃ CH(SH)CH ₃
17		*2-Methylpentane-2-thiol		CH ₃ [CH ₂] ₂ C(SH)(CH ₃) ₂
18	C ₇ H ₁₆ S	Heptane-1-thiol	Heptyl mercaptan	CH ₃ [CH ₂] ₆ SH
19	C ₈ H ₁₈ S	*Octane-1-thiol	Octyl mercaptan	CH ₃ [CH ₂] ₇ SH
20		*Octane-2-thiol	<i>sec</i> -Octyl mercaptan	CH ₃ [CH ₂] ₅ CH(SH)CH ₃
21	C ₉ H ₂₀ S	*Nonane-1-thiol	Nonyl mercaptan	CH ₃ [CH ₂] ₈ SH
22	C ₁₀ H ₂₂ S	Decane-1-thiol	Decyl mercaptan	CH ₃ [CH ₂] ₉ SH
C₂ TO C₈ SULPHIDES				
23	C ₂ H ₆ S	2-Thiapropane	Dimethyl sulphide	CH ₃ SCH ₃
24	C ₃ H ₈ S	2-Thiabutane	Methyl ethyl sulphide	CH ₃ CH ₂ SCH ₃
25	C ₄ H ₁₀ S	2-Thiapentane	Methyl propyl sulphide	CH ₃ [CH ₂] ₂ SCH ₃
26		3-Thiapentane	Diethyl sulphide	CH ₃ CH ₂ SCH ₂ CH ₃
27		3-Methyl-2-thiabutane	Methyl isopropyl sulphide	(CH ₃) ₂ CHSCH ₃
28	C ₅ H ₁₂ S	2-Thiahexane	Methyl butyl sulphide	CH ₃ [CH ₂] ₃ SCH ₃
29		3-Thiahexane	Ethyl propyl sulphide	CH ₃ [CH ₂] ₂ SCH ₂ CH ₃
30		3,3-Dimethyl-2-thiabutane	Methyl <i>tert</i> -butyl sulphide	(CH ₃) ₃ CSCH ₃
31	C ₆ H ₁₄ S	*3-Thiaheptane	Ethyl butyl sulphide	CH ₃ [CH ₂] ₃ SCH ₂ CH ₃
32		4-Thiaheptane	Dipropyl sulphide	CH ₃ [CH ₂] ₂ S[CH ₂] ₂ CH ₃
33		2,4-Dimethyl-3-thiapentane	Diisopropyl sulphide	(CH ₃) ₂ CHSCH(CH ₃) ₂
34	C ₈ H ₁₈ S	5-Thianonane	Dibutyl sulphide	CH ₃ [CH ₂] ₃ S[CH ₂] ₃ CH ₃