

Heat capacity and enthalpy of liquids: Aliphatic ketones

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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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Dr G. Hobson — Imperial Chemical Industries Ltd, Petrochemicals & Plastics Division, Wilton, UK

Dr D.T. Jamieson — National Engineering Laboratory, East Kilbride, UK

Mr S.R. Knight — Stone & Webster Engineering Ltd, Milton Keynes, UK

Mr G.M. Rowell — Humphreys & Glasgow Ltd, UK

Dr M. Schoenberg[†] — Hoechst AG, Frankfurt, Germany

Dr L.A.K. Staveley — Oxford University, Oxford, UK

Dr H.J. White, Jr[†] — National Bureau of Standards, Washington D.C., USA.

[†] Corresponding Member.

The technical work involved in the assessment of the available information and the construction and subsequent development of the Data Item was undertaken by

Mrs S.D. Sriskandarajah — Engineer.

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: ALIPHATIC KETONES

1. INTRODUCTION

This Data Item presents values of saturated liquid heat capacity and enthalpy in tabular form for the aliphatic ketones 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 0.8. 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 Data 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, $e.g. T_r = T/T_c$
s	denotes value at saturation pressure.

3. CONVERSION FACTORS

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

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

4. HEAT CAPACITY

4.1 Heat Capacity at Saturation Pressure

For many liquids it has been suggested (Reference 5) that a good representation of heat capacity data over a wide range of temperature is given by the equation

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

For the compounds considered in this Data Item, 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 are a correlated set of values giving the best fit to the data for the liquid ketones 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, where possible, been extended to the melting temperature and to the maximum temperature for which values are tabulated (see Table I). The Lyman and Danner (Reference 6) correlation was used to extrapolate the known data to higher temperatures for butan-2-one, pentan-2-one and pentan-3-one. This enabled a generalised reduced temperature curve to be drawn which was then used to extend the data for the other key compounds.

The complete range of data for each compound was fitted by Equation (4.3) and correlation of the values of the constants in Equation (4.3) with molecular structure was used to estimate the heat capacities of those liquids for which either very few or no data were available.

Using the values of the constants in Table I together with the values of T_c also given in Table I, 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. Further extrapolation may lead to unreliable results.

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 very near the critical point, 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,

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

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 the compounds has been taken as 25 °C = 298.15 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 20 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 names in bold type are those based on BSI recommendations, see References 3 and 4.

The values of T_m and T_c for most compounds have been taken from Data Items 75025 and 80014. Compounds for which no, or few, experimental data exist and for which values of constants were estimated as described in Section 4.1 are indicated by an asterisk against their compound number in Table I.

Table II presents values of heat capacity and Table III presents values of enthalpy at 10 K intervals of temperature and for most compounds the range covered is from the melting temperature to a temperature corresponding with $T_r \approx 0.8$.

6.2 Accuracy of Data

The experimental data which are assessed to be the most reliable have a repeatability within ± 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.