

Heat capacity and enthalpy of liquids: Alkenes and alkadienes

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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: ALKENES AND ALKADIENES

1. INTRODUCTION

This Data Item presents values of liquid heat capacity and enthalpy in tabular form for the alkenes and dienes listed in Table I. It supersedes Item 78015 by extending the temperatures to $0.96 T_c$.

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 0.96. 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 the 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.

Appendix A presents a brief discussion of the theoretical relationships between alternative definitions of heat capacity and Appendix B some typical differences between reported values at the highest valid temperature.

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 Equation (4.1)	kJ/kg K
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
p	denotes constant pressure
r	denotes reduced quantity, e.g. $T_r = T/T_c$
s	denotes value at saturation pressure

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3. CONVERSION FACTORS

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

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

4. HEAT CAPACITY

4.1 Heat Capacity at Saturation Pressure

It has recently been suggested (Reference 15) that heat capacity data over a range of temperature can be represented by the equation

$$c_p = a_1 [1 + a_2(1 - T_r)^{-1} + a_3(1 - T_r) + a_4(1 - T_r)^2]. \quad (4.1)$$

For the liquids considered in this Data Item, the derived values of a_1 , a_2 , a_3 and a_4 given in Table I are a correlated set of values giving the best fit to the data for the liquid alkenes not only as individual compounds but also as members of their chemical series based on molecular structure. The relationship between measured values of heat capacity and c_p is discussed in Appendix A.

Since the available experimental data do not cover the full liquid range, the data used to evaluate the constants in Equation (4.1) have been extended to the melting temperature and to the critical point using as a guide the available data plotted on a reduced temperature scale. Where necessary, values at temperatures above $0.6 T_r$ have been predicted using methods recommended by Reid, Prausnitz and Sherwood, (Reference 10).

The method of Lyman and Danner, (Reference 9) was used for as many compounds as there were values of the radius of gyration. The method of Yuan and Stiel, (Reference 4) was used for the remainder. Both methods were shown to be reliable when tested against the NBS "standard" values for *n*-heptane in Data Item 86007.

The first two members of the alkenes series, ethylene and propylene have been fully studied in recent years (Derivations 40, 41) and the values given there were accepted as the basis of the correlation of these compounds.

The experimental data for the heat capacity of some compounds exhibit a minimum point at temperatures near the normal melting temperature; this behaviour is well established for ethylene and propylene, and it also occurs in butenes and pentenes. The four-constant equation could not reproduce this effect while accurately representing data at higher temperatures. An appropriate start temperature is given in these cases and values at lower temperatures are preceded by the letter x.

The range of available experimental data for each compound is indicated in the following tables by values given to three decimal places. Predicted values are given to two decimal places.

Using the values of the constants in Table I together with the values of T_c also given in Table I, values of c_p , in kJ/kg K have been calculated for each compound from Equation (4.1) and are presented in Table II. Users' attention is drawn to the limits of validity of Equation (4.1) given in Table I. Any extrapolation to higher temperatures beyond those limits should be carried out with caution as such an extrapolation may give high values of c_p for some compounds.

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 $0.9 T_c$, 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

Although it is not thermodynamically correct (see Appendix A2), values of liquid enthalpy for each compound may be calculated from the equation,

$$H_s = -a_1 T_c \left[(1 - T_r) + a_2 \log_e(1 - T_r) + \frac{1}{2} a_3 (1 - T_r)^2 + \frac{1}{3} a_4 (1 - T_r)^3 \right] \frac{T_r}{T_r^*} \quad (5.1)$$

obtained by integrating Equation (4.1). T_r^* denotes the reduced temperature at which the enthalpy is set to zero. The values obtained are within the accuracy claimed up to a reduced temperature of 0.96. The enthalpy base temperature for ethylene has been taken as the melting temperature and for all other compounds has been taken as 298.15 K at which each liquid was arbitrarily assigned an enthalpy of zero. For compounds where the melting temperature is above 298.15 K, Equation (5.1) has been extrapolated from the melting temperature to 298.15 K in deriving the enthalpy data. 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 43 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 7.

The values of T_m and T_c for most compounds have been taken from Data Items 85008, 85016 and 86001. For the others, the values have been taken from other literature or estimated. Compounds for which no, or few, experimental data exist and for which values of the constants for Equation (4.1) 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 the range covered is from the melting temperature or an appropriate starting temperature to a reduced temperature of 0.96.

6.2 Accuracy of Tabulated Data

The experimental data which are assessed to be the most reliable have a repeatability of about ± 1 per cent, although differences in the method 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. The prediction procedures are within ± 3 per cent of experimental data (where available) but could be considerably less accurate at temperatures in excess of $T_r = 0.9$.

In Appendix A, thermodynamic definitions of three values of heat capacity are given but only one of these is normally measured. However, the differences between the numerical values of heat capacity from all three definitions is insignificant below a reduced temperature of 0.8. Hence experimental data measured below this temperature are valid and were used for the correlation. The values of enthalpy obtained by integrating Equation (4.1) were checked against values reported by workers using an equation of state (Reference 13 and Derivations 25, 27, 35, 36, 37, 40, 41). An indication of the differences between the results reported here and those found in the literature at the highest valid temperature are given in Appendix B.

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 ± 3 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 ± 5 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

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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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