

Types of curves for the temperature dependence of the heat capacity of pure liquids

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(Received 29 May 1992)

Abstract

Compounds which have an atypical dependence of the liquid heat capacity on temperature have been selected from a large database containing experimental and critically evaluated heat capacities. Compounds have been assembled into four groups according to the shape of their curve of the heat capacity as a function of temperature. An explanation of some unusual dependencies has been proposed and presented together with accounts given in the literature.

INTRODUCTION

There is no exact relationship for the description of the heat capacity of a liquid as a function of temperature. In the literature, it is usually stated for a pure isotropic liquid, that a monotonic increasing convex function exists which is unbounded at the critical point. Recently, a critical compilation of the liquid heat capacities of more than 1500 organic and inorganic compounds which have melting temperatures lower than 300°C, has been assembled [1–3]. When assessing the compiled data and calculating parameters of a smoothing equation that correlates heat capacity with temperature, we have observed that for some compounds the dependence of the heat capacity on temperature differs from the most typical function.

We have classified the curves of the temperature dependence of the heat capacity and have attempted to explain some phenomena that may lead to various kinds of heat capacity curves. The curves of the heat capacity dependence on temperature, $C = f(T)$, have been divided into

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four groups: 1, monotonically increasing curves; 2, curves with a shallow minimum; 3, curves with an inflection point; and 4, curves with a sharp maximum.

Several different kinds of heat capacities have been defined in the literature for the condensed phase [4]. The isobaric heat capacity C_p and the saturation heat capacity C_{sat} have been used more frequently than others. They are defined as

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad (1)$$

$$C_{\text{sat}} = T \left(\frac{\partial S}{\partial T} \right)_{\text{sat}} \quad (2)$$

The isobaric and the saturation heat capacities differ quantitatively above the normal boiling temperature. The difference between them becomes substantial as the critical temperature is approached. As there is no qualitative difference in the temperature dependence of the isobaric and the saturation heat capacities, all observations and conclusions obtained in this work apply equally to both of these defined heat capacities.

TYPES OF CURVES

Monotonically increasing curves

A monotonically increasing function exhibits the typical dependence of the heat capacity of a liquid on temperature as it occurs most frequently. For a temperature range broader than about 30 K, this is mostly a convex function. An example of this curve shape is given in Fig. 1 which shows the temperature dependence of the heat capacity of liquid *n*-alkanes from propane to *n*-nonane. The heat capacities depicted in Fig. 1 have been calculated from recommended values obtained from a critical assessment and correlation of calorimetrically determined heat capacities reported earlier [5].

A sharp increase in the curve for *n*-butane and, particularly, for *n*-heptane at high temperatures indicates their proximity to the critical point. The heat capacity of a liquid becomes infinite at the critical point.

Curves with a shallow minimum

A shallow minimum on the heat capacity curve has been observed for several compounds. The minimum is usually located a few degrees above

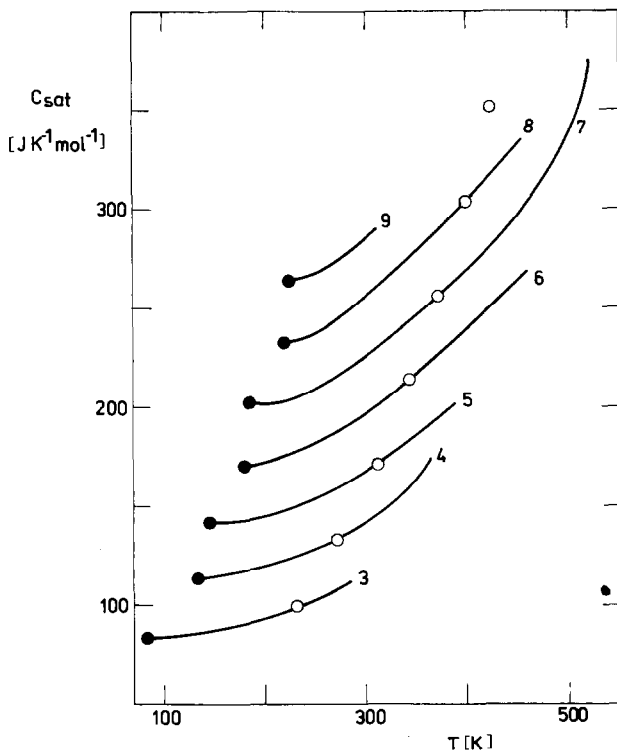


Fig. 1. Temperature dependence of the heat capacity of *n*-alkanes. The numbers adjacent to the curves denote the number of carbon atoms in the molecule: ●, melting temperature; ○, normal boiling temperature.

the melting temperature. An example of this shape of curve is shown in Fig. 1 for *n*-heptane. Although this shape has been observed for a rather large number of compounds, we expect that it would be even more frequent if all measurements were performed immediately after the melting temperature with a low imprecision of not more than 0.2%, and with compounds of extremely high purity.

In addition to those compounds that have a minimum just above the melting temperature, there are other compounds that exhibit a minimum on the heat capacity curve located far beyond the melting temperature. This shift in the minimum for liquids to higher temperatures has been observed for both organic and inorganic compounds. The organic compounds usually have up to six carbon atoms in a molecule and the minimum occurs for most first members of the homologous series. The families of alkanes and alkenes are an exception to this rule. A very shallow minimum located 5–10 K above the melting temperature was observed for *n*-alkanes as high as *n*-nonane. A clearly distinct minimum was found for most of the first ten members of the family of 1-alkenes.

To describe the location and the depth of the minimum in a semi-quantitative manner, two criteria slightly modified from those suggested by Wilhoit et al. [6] have been adopted

$$\Delta T = T_{\min} - T_{\text{mp}} \quad (3)$$

$$\Delta C = \frac{C_{\text{mp}} - C_{\min}}{C_{\min}} 100 \quad (4)$$

where subscripts min and mp denote quantities corresponding to the minimum and the melting temperature, respectively. For very accurate measurements, the triple-point temperature rather than the melting temperature is determined. However, the differences between quantities at the triple point and at the melting point are usually negligible compared to measurement errors and uncertainties involved in further considerations.

The heat capacity of a liquid at the melting temperature cannot be measured accurately because impurities cause the heat capacity curve to rise substantially as the melting temperature is approached. Measurements are usually started 3–8 K above the melting temperature and the value of the heat capacity at the melting temperature is determined by linear extrapolation. The temperature dependence of the heat capacity is typically measured with an increment of about 5–10 K. Thus, accurate values of T_{\min} and C_{\min} are not known. In this work, T_{\min} and C_{\min} have been determined by linear interpolation. Often, we have compared measurements by different authors who reported a measurement error that lies in the range from 0.1% up to several percent. The uncertainty in the determination of the minimum and the low precision of some data lead us to the conclusion that the two criteria defined by eqns. (3) and (4) are an approximate quantification of the location and the depth of the minimum.

A survey of organic compounds with an observed minimum on the heat capacity curve is given in Table 1. Organic compounds are divided into families according to their chemical structure and functional groups. In each family, compounds both with and without a minimum are listed. However, it is quite difficult to make a complete comparison among different families of compounds and to draw conclusions, because heat capacities for some compounds in a certain family have either been measured with low precision or have not been measured at all. Some families of compounds which contain sparse heat capacity data are not given, for example, the nitro compounds. A minimum was observed for nitromethane and nitroethane, whereas the heat capacity values of higher members of this homologous series of nitro compounds have not been determined at all.

TABLE 1

Representative examples of organic compounds with and without a minimum on the $C = f(T)$ curve

Minimum observed on the curve	Minimum not observed on the curve	No reliable data available
HYDROCARBONS		
<i>Alkanes</i> ^a		
Methane	Butane	
Ethane	Octane	
Propane	Decane	
Pentane		
Hexane		
Heptane		
Nonane		
<i>Alkenes</i> ^b		
<i>Cycloalkanes</i>		
Cyclopropane	Cyclobutane	Methylcyclobutane
Methylenecyclobutane	Cyclopentane and higher cycloalkanes	
<i>Unsaturated cyclic hydrocarbons</i>		
Cyclopentene	Cyclohexene and higher cycloalkenes	Cyclobutene
<i>Aromatics</i> ^c		
HALOGEN COMPOUNDS		
<i>Fluorine compounds</i>		
Trifluoromethane	1,1,1-Trifluoroethane	Fluoromethane
Tetrafluoromethane	Tetrafluoroethylene	Difluoromethane
	Hexafluoroethane and higher fluorinated hydrocarbons containing more than three carbon atoms	Other fluoroethanes
<i>Chlorine compounds</i>		
Chloromethane	1,1-Dichloroethane	Tetrachloromethane ^c
Dichloromethane	1,2-Dichloroethane	1,1,2-Trichloroethane
Trichloromethane ^d	1,1,1-Trichloroethane	1,2-Dichloroethene
Chloroethane	1,1,1,2-Tetrachloroethane	Trichloroethene
1,1-Dichloroethene	Chloroethene and higher chlorinated hydrocarbons containing more than three carbon atoms	
Tetrachloroethene		
<i>Bromine compounds</i>		
Bromomethane	Tribromomethane	
Dibromomethane	Tetrabromomethane	
1,2-Dibromoethane	Bromoethane	
2-Bromopropane	1,1-Dibromoethane	
1-Bromobutane	Tribromoethane	
1-Bromopentane	Tetrabromoethanes and higher brominated hydrocarbons	
<i>Iodine compounds</i>		
Iodomethane		Data for other compounds not available

TABLE 1 (continued)

Minimum observed on the curve	Minimum not observed on the curve	No reliable data available
COMPOUNDS CONTAINING NITROGEN		
<i>Amines, Nitriles^f, Heterocyclic compounds^c</i>		
COMPOUNDS CONTAINING OXYGEN		
<i>Esters^c</i>		
<i>Alcohols^g</i>		
<i>Aldehydes</i>		
Pentanal	Ethanal ^h Propanal ^h Butanal ^h Hexanal ^h Heptanal and higher aldehydes	
<i>Ketones</i>		
2-Propanone ⁱ	2-Butanone	
1,2-Propadiene-1,3-dione	3-Methyl-2-butanone 2-Pentanone 3-Pentanone and higher ketones	
<i>Acids^c</i>		
<i>Esters</i>		
Ethyl acetate	Butyl acetate	Methyl formate
Ethyl butanoate		Methyl acetate Ethyl formate and other esters with single carbon bonds
<i>Heterocyclic compounds</i>		
Oxirane	Furan	Oxetane
Methyloxirane	2-Methylfuran	1,3-Dioxane
Ethyloxirane	1,3-Dioxolane	1,4-Dioxane
Tetrahydrofuran	1,3,5-Trioxane	Dihydrofuranes
COMPOUNDS CONTAINING SULFUR		
<i>Sulfides</i>		
Dimethyl sulfide	Methyl propyl sulfide	
Dimethyl disulfide	Isopropyl methyl sulfide	
Ethyl methyl sulfide	Diethyl sulfide	
Diethyl disulfide	Methyl <i>sec</i> -butyl sulfide	
Ethyl propyl sulfide	Methyl <i>tert</i> -butyl sulfide	
<i>Thiols^j</i>		
<i>Heterocyclic compounds^c</i>		

^a Very shallow minimum located 5–10 K above the melting temperature. ^b See Table 2 for details. ^c No minimum has been found for any member of this family. ^d No data in the low temperature region are available. Minimum was determined at 278 K ($\Delta T = 70$ K) by Al'per et al. [9]. ^e No reliable data are available. Minimum was determined at different temperatures by Hicks et al. [8] ($\Delta T = 4$ K) and by Staveley et al. [7] ($\Delta T = 50$ K). ^f No minimum was found for acetonitrile whereas a very distinct minimum was observed for trifluoroacetonitrile. ^g A minimum was found for methanol only ($\Delta T = 12$ K) in an old measurement by Kelley [10] and by Staveley and Gupta [11]. No other authors reported a minimum either for methanol or for other alkanols. ^h The compound exhibits a sharp maximum on the $C = f(T)$ curve. ⁱ No reliable data at low temperatures are available. Minimum was observed only by Kelley [12]. ^j See Table 3 for details.

TABLE 2

Location (ΔT) and depth (ΔC) of the minimum on the $C = f(T)$ curve for alkenes and dienes. Values of ΔC are for some compounds very close to the measurement error. We have included such compounds in the table only when experimental data follow a certain pattern as described in the section *Curves with a shallow minimum*

Compound	ΔT (K)	ΔC (%)	Reference
Ethene	54.6	3.2	13
1-Propene	53.3	7.5	14
1-Butene	56.6	4.1	15
<i>cis</i> -2-Butene	45.7	2.7	16
<i>trans</i> -2-Butene	No minimum		17
2-Methylpropene	No minimum		18
1-Pentene	22.0	0.8	19
<i>cis</i> -2-Pentene	44.1	2.1	20
<i>trans</i> -2-Pentene	No minimum		20
2-Methyl-1-butene	15.9	0.1	20
2-Methyl-2-butene	20.6	0.1	20
3-Methyl-1-butene	No minimum		20
1-Hexene	7.4	0.2	21
<i>cis</i> -2-Hexene	30.0	0.7	19
<i>trans</i> -2-Hexene	Data not available		
2,3-Dimethyl-2-butene	No minimum		22
3,3-Dimethyl-1-butene	No minimum		23
1-Heptene	7.2	0.1	21
1-Octene	16.1	0.4	21
1-Nonene	9.3	0.1	19
1-Decene	14.1	0.6	21
1,2-Butadiene	33.0	0.5	24
1,3-Butadiene	No minimum		25
2-Methyl-1,3-butadiene	13.6	0.3	26
3-Methyl-1,2-butadiene	No minimum		26
1,2-Pentadiene	13.4	0.2	26
<i>cis</i> -1,3-Pentadiene	41.3	2.1	26
<i>trans</i> -1,3-Pentadiene	8.5	0.2	26
1,4-Pentadiene	29.2	1.1	26
2,3-Pentadiene	7.9	0.1	26

Tables 2 and 3 list two families of organic compounds containing a fairly large number of members—the alkenes and thiols. Values of ΔT and ΔC calculated from eqns. (3) and (4), together with literature references, are given in both tables; Table 2 lists the alkenes and dienes, Table 3 the thiols and cyclothiols. The curves $C = f(T)$ for the first four members of the homologous series of 1-thiols are shown in Fig. 2.

The values of ΔC for some compounds given in Tables 2 and 3 are very close to the measurement error. The temperature dependence of the heat capacity of these compounds, measured at the National Institute for

TABLE 3

Location (ΔT) and depth (ΔC) of the minimum on the $C = f(T)$ curve for thiols and cyclothiols. Values of ΔC for some compounds are very close to the measurement error. We have included such compounds in the table only when experimental data follow a certain pattern as described in the section *Curves with a shallow minimum*

Compound	ΔT (K)	ΔC (%)	Reference
Methanethiol	74.5	3.1	27
Ethanethiol	82.6	2.7	28
1-Propanethiol	41.3	0.9	29
2-Propanethiol	No minimum		30
1-Butanethiol	42.9	1.8	31
2-Butanethiol	45.3	1.1	32
2-Methyl-1-propanethiol	No minimum		33
2-Methyl-2-propanethiol	6.9	0.2	34
1-Pentanethiol	No minimum		35
2-Methyl-2-butanethiol	No minimum		36
3-Methyl-1-butanethiol	26.1	0.8	37
3-Methyl-2-butanethiol	19.1	0.4	37
1-Hexanethiol	13.6	0.3	38
1-Heptanethiol	No minimum		38
Cyclopentanethiol	31.6	1.2	39
Cyclohexanethiol	No minimum		40
Benzenethiol	No minimum		41

Petroleum and Energy Research (NIPER) at Bartlesville, OK, follows the same pattern. The measured data start at 3–4 K above the melting temperature. The next data point drops below the first measured value, whereas heat capacities of all remaining data points increase as the temperature increases. We considered that the exclusion of such compounds from Tables 2 and 3 is inappropriate because this would imply that heat capacities of the compounds increase with temperature in the whole range.

A minimum on the heat capacity curve has been observed for some chemical elements. For all halogens the heat capacity decreases with increasing temperature almost up to the normal boiling temperature. Only fluorine exhibits a minimum, approximately in the middle of the interval between the melting temperature and the normal boiling temperature. A value of ΔT equal to 14.50 K is calculated from eqn. (3). For other halogens, a minimum may exist but has not been reported as heat capacity data at temperatures around and above the normal boiling temperatures are not available.

For other chemical elements that are gaseous at ambient temperatures a minimum has only been observed for oxygen, with the value of ΔT approximately equal to 10 K, whereas no minimum has been found for

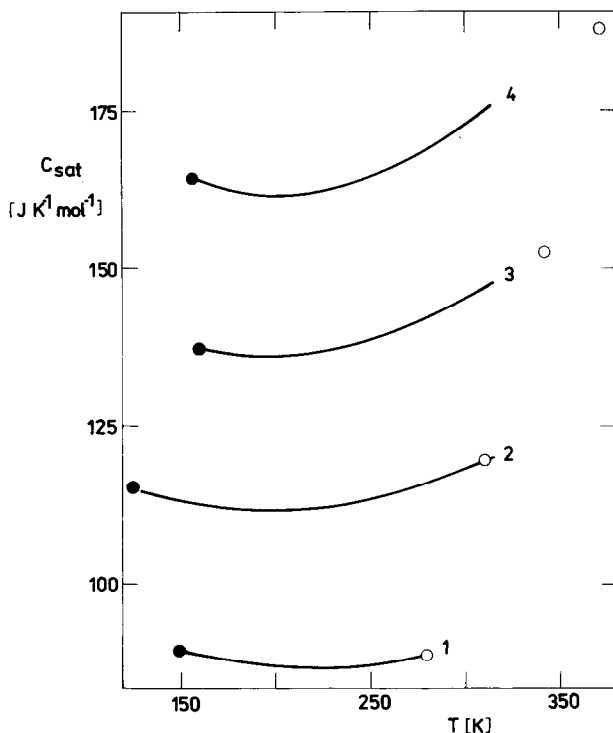


Fig. 2. Temperature dependence of the heat capacity of 1-thiols. The numbers adjacent to the curves denote the number of carbon atoms in the molecule: ●, melting temperature; ○, normal boiling temperature.

nitrogen and hydrogen. No conclusion can be drawn for the rare gases that are liquid in a narrow temperature interval, typically 3–4 K, because only old, less accurate measurement of heat capacities are available.

We have also examined the temperature dependence of the heat capacity of metallic elements that have melting temperatures lower than 300°C, because these metals are included in the compilation [1]. The experimental heat capacities of most metallic elements that have been measured in a broad temperature interval exceeding several hundred K, usually drop as temperature increases. A negative slope of the dependence of the heat capacity with temperature over the whole temperature interval of the measured data has been observed for bismuth, gallium, indium, lithium and tin. A minimum was found on curves $C = f(T)$ of mercury, potassium, sodium and selenium. A quantitative description of the location of the minimum is difficult because the average heat capacities were usually measured in a drop calorimeter using a temperature increment of about 100 K.

A minimum was detected by all authors who studied simple inorganic compounds consisting of carbon, hydrogen, oxygen, nitrogen, sulfur and

TABLE 4

Location (ΔT) and depth (ΔC) of the minimum on the $C = f(T)$ curve for some inorganic compounds exhibiting the most distinct minimum

Compound	ΔT (K)	ΔC (%)	Reference
Carbonic dichloride (COCl_2)	65	5.4	42
Nitrogen fluoride (NF_3)	44	4.2	43
Sulfuryl fluoride (SO_2F_2)	63	4.1	44
Carbonyl sulfide (COS)	50	3.6	45
Water	40	0.9	46

halogens. The only exception from this group of compounds are carbon monoxide, carbon dioxide, ammonia and hydrogen cyanide, which exhibit a monotonically increasing dependence of the heat capacity with temperature. Table 4 gives values of ΔT and ΔC for some simple inorganic compounds with the most distinct minimum, and for water.

Only a few authors have tried to explain the minimum on the curve of the dependence of the heat capacity on temperature. Todd and Parks [18] accounted for an experimentally determined minimum for 1-butene and *cis*-2-butene by an association in the liquid phase as a result of small electric moments arising from molecular structures. Wilhoit et al. [6] observed a minimum for some oxygen-containing organic compounds when calculating their thermodynamic properties. They ascribed the presence of a minimum to the so-called “pre-freezing” phenomena that are associated with the formation of molecular clusters in liquids. Al’per et al. [9] account for a minimum by the temperature dependence of the vibrational contribution to the isochoric heat capacity of liquids.

To explain the existence of a minimum, we used the equation that relates the difference between the molar isobaric heat capacity of a liquid C_p^l and that of an ideal gas $C_p^{g\ominus}$ to the P - V - T behavior of a liquid [47]

$$C_p^l = C_p^{g\ominus} - \left(\frac{d\Delta H_{\text{vap}}}{dT} \right)_{\text{sat}} + \left[V^l - T \left(\frac{\partial V^l}{\partial T} \right)_p \right] \left(\frac{dp}{dT} \right)_{\text{sat}} \quad (5)$$

where ΔH_{vap} is the molar enthalpy of vaporization, V^l is the molar volume of the liquid and subscript sat refers to properties on the vapor–liquid saturation curve. The following condition must be fulfilled in order to find a minimum on the $C = f(T)$ curve

$$\left(\frac{\partial C_p^l}{\partial T} \right)_p < 0 \quad (6)$$

If we assume that the heat capacity of a liquid does not depend on pressure, which is reasonable below the normal boiling temperature, it

holds that

$$\left(\frac{\partial C_p^1}{\partial T}\right)_p = \left(\frac{\partial C_p^{g\ominus}}{\partial T}\right)_p - \left(\frac{d^2\Delta H_{\text{vap}}}{dT^2}\right)_{\text{sat}} + \left[V^1 - T\left(\frac{\partial V^1}{\partial T}\right)_p\right] \times \left(\frac{d^2p}{dT^2}\right)_{\text{sat}} - T\left(\frac{\partial^2 V^1}{\partial T^2}\right)\left(\frac{dp}{dT}\right)_{\text{sat}} \quad (7)$$

The first term on the right-hand side of eqn. (7) contains a temperature derivative of vibrational contribution to the heat capacity of an ideal gas, because translational and rotational contributions do not depend on temperature. This derivative is always positive.

To describe the temperature dependence of the enthalpy of vaporization in the second term of eqn. (7), either the Thiesen equation

$$\Delta H_{\text{vap}} = A(1 - T_r)^\beta \quad (8)$$

or the extended Thiesen equation proposed by Majer et al. [47] is used

$$\Delta H_{\text{vap}} = A[(1 - T_r)^\beta e^{-\alpha T_r}] \quad (9)$$

where A , α , β are empirical constants and T_r is the reduced temperature ($T_r = T/T_c$, and T_c is the critical temperature). The second derivative of ΔH_{vap} with respect to temperature calculated from eqn. (8) is always negative over the entire liquid region up to the critical point, as both parameters A and β are positive and β is smaller than unity [47]. Parameter A in eqn. (9) is always positive and parameters α and β are approximately equal to 0.3 for the majority of simple organic compounds. Then, the second derivative of ΔH_{vap} with respect to temperature is also negative. In addition, the temperature dependence of ΔH_{vap} is almost linear for most organic compounds when the temperature is below T_r equal to 0.5. Therefore, the absolute value of the second derivative of the enthalpy of vaporization with respect to temperature below $T_r = 0.5$ is very small.

The third term in eqn. (7) $[V^1 - T(\partial V^1/\partial T)_p](d^2p/dT^2)_{\text{sat}}$ is a product of two parts. The first part enclosed in square brackets is equal to the product of the Joule–Thompson coefficient and of the molar isobaric heat capacity C_p . For almost all compounds, the Joule–Thompson coefficient is negative below $T_r = 0.8$. The second derivative of vapor pressure with respect to temperature is always positive as the vapor pressure is a monotonically increasing convex function of temperature. Thus, for liquids below $T_r = 0.8$, the third term in eqn. (7) is always negative. The last term in eqn. (7) $T(\partial^2 V^1/\partial T^2)(dp/dT)_{\text{sat}}$ is often positive because the molar volume of most liquids is an increasing convex function of temperature. Thus, according to eqn. (6), there is a minimum on the curve of the heat capacity as a function of temperature if the sum of the absolute values of the third and fourth terms in eqn. (7) is greater than the sum of the absolute values of the first and second terms. This condition can be

fulfilled for compounds having a small number of atoms per molecule because the contribution to the heat capacity of the ideal gas due to vibrational motions is small compared with the values of the sum of the third and fourth terms on the right-hand side of eqn. (7). This is demonstrated in Tables 1–3 where compounds exhibiting a minimum can be called simple organic compounds.

Some polar compounds associate in the liquid phase. Then, even for large organic molecules containing usually more than about five atoms, eqn. (6) may be fulfilled despite the large value for the vibrational contribution to the heat capacity of an ideal gas that overrides the second, third and fourth terms on the right-hand side of eqn. (7), resulting in a positive value of the derivative of the heat capacity. For the molar isobaric heat capacity of an associate of n molecules of a monomer, it holds that

$$(C_p^l)_{\text{as}} = n(C_p^l)_{\text{mon}} + \left(\frac{\partial \Delta H_{\text{as}}}{\partial T} \right)_p \quad (10)$$

where ΔH_{as} is the enthalpy of association and $(C_p^l)_{\text{mon}}$ denotes the liquid heat capacity of a monomer. The derivative of the enthalpy of association with respect to temperature is negative, because the stability of associated species decreases with increasing temperature. This leads to a drop in the heat capacity of a liquid according to eqn. (10), and may account for the occurrence of a minimum on the heat capacity curve. The assumption about the decrease in the stability of associated species is in accordance with the theory of formation of clusters as described by Ubbelohde [48], who discusses pre-freezing phenomena in liquids.

Curves with an inflection point

An inflection point on the curve of the temperature dependence of the liquid heat capacity has been observed for 1-alkanols. Reliable data with a clearly distinct inflection point are available for 1-propanol to 1-decanol. For 1-alkanols higher than 1-decanol, only low accuracy data presented in the form of a correlating equation are available [49]. The form of the data that provides smoothed rather than raw experimental values and the low reliability of the data does not justify an unambiguous decision about the presence of an inflection point on the heat capacity curve. Curves $C = f(T)$ for some 1-alkanols are shown in Fig. 3. The curves have been drawn using recommended data obtained by a critical assessment of experimental calorimetrically measured data (see Záborský et al. [49]). Similar curves with an inflection point located in the vicinity of the temperature $T_i = 0.66$ were reported by Hoffman et al. [50] for 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol.

No attempt to explain the behavior of a liquid leading to the dependence of the heat capacity on temperature having an inflection point

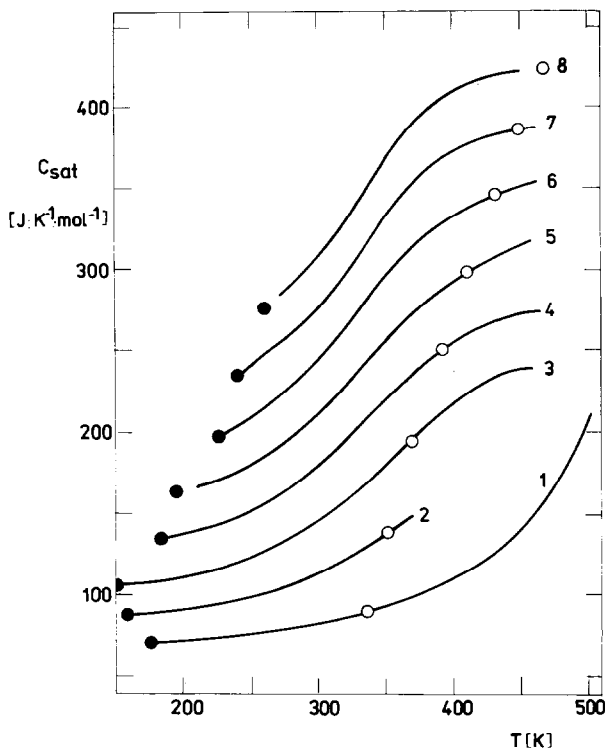


Fig. 3. Temperature dependence of the heat capacity of 1-alkanols. The numbers adjacent to the curves denote the number of carbon atoms in the molecule: ●, melting temperature; ○, normal boiling temperature.

has been published in the literature. Ginnings and Corruccini [51], who reported a “hump” on the heat capacity curve of 2-propanol, explained the unusual shape of the $C = f(T)$ curve by a possible low reliability of experimental data. We assume that a relationship exists between an inflection point on the heat capacity curve and a breakdown of hydrogen bonds in alcohols: hydrogen bonds begin to decay as temperature increases. The decay of bonds consumes energy, and this leads to a larger value of the heat capacity as more energy is required for heating up the compound. When the destruction of the hydrogen bonds is complete, the energy consumption required for heating up a compound decreases, this is exhibited as a smaller slope on the $C = f(T)$ curve.

No inflection point was observed on the $C = f(T)$ curve for methanol and ethanol. These two lowest members of the homologous series exhibit a slightly different behavior compared to higher members of the series as exemplified, for example, by the melting temperature.

It is obvious that the above proposed theory linking the inflection point on the $C = f(T)$ curve to the decay of hydrogen bonds in liquid alkanols could also be applied to other compounds that form hydrogen bonds in

the liquid phase. Therefore, we have thoroughly analyzed the heat capacity curves $C = f(T)$ for organic fatty acids. Reliable data are available in a broad temperature interval for acetic acid (upper temperature limit of experimental data at $T_r = 0.67$), propanoic acid (upper limit at $T_r = 0.73$), and butanoic acid (upper limit at $T_r = 0.59$) [52]. For acetic and propanoic acid the inflection point on the heat capacity curve is not as apparent as on curves for some 1-alkanols because the heat capacity data for the acids are less accurate particularly at higher temperatures. For higher molecular weight acids there is a complete lack of data at superambient temperatures. Thus, it is not possible to prove or reject a hypothesis of the similarity of the shape of the $C = f(T)$ curves of liquid organic acids and alkanols.

A very clear inflection point was determined experimentally on the heat capacity curve of the heterocyclic nitrogen compound, pyrrolidine, at around 280 K. Two independent measurements were reported in the same year by McCullough et al. [53] and by Hildenbrand et al. [54]. The measurement error claimed by the authors was 0.2% in the former case and 0.3% in the latter. The purity of the compound was the same in both cases, 99.85 mol%. Both sets of experimental data [53, 54] are shown in Fig. 4. McCullough et al. [53] attempted to explain the atypical shape of the $C = f(T)$ curve of pyrrolidine using the results of the study of vibration spectra by Evans and Wahr [55]. They concluded that association at ambient temperature due to hydrogen bonds is weak and vanishes at higher temperatures. They suggested that an inversion transition of the

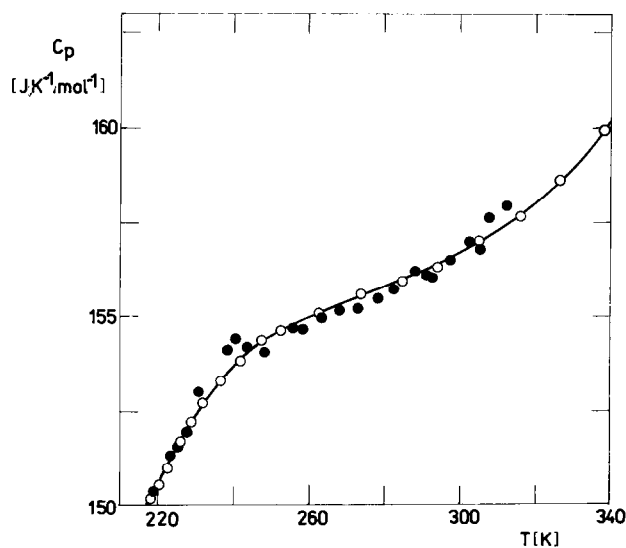


Fig. 4. Temperature dependence of the heat capacity of pyrrolidine: O, McCullough et al. [53]; ●, Hildenbrand et al. [54].

pyrrolidine ring may account for the appearance of an inflection point on the heat capacity curve. It follows from vibration spectra that the pyrrolidine molecule forms a “puckered ring”. Thus, Hildenbrand et al. [54] concluded that the unusual behavior was due to shifting equilibrium among conformations with different energies. However, the contribution of this “isomerism” to the heat capacity is not large enough to account for the observed anomaly. There is also no explanation presented as to why a similar anomaly does not occur for other compounds that form a “puckered ring” configuration.

Aldehydes form very strong hydrogen bonds, sometimes leading to polymerization. The anomalous behavior of some aldehydes is exhibited on the heat capacity curve in a specific manner that will be dealt with in the next section.

Curves with a sharp maximum

A sharp discontinuous maximum on the heat capacity curve in the liquid region was observed and described in the literature for helium and sulfur. Experimental heat capacities for sulfur determined by several authors [56–58] are plotted in Fig. 5 as a function of temperature. Differences between measurements by different authors are due to

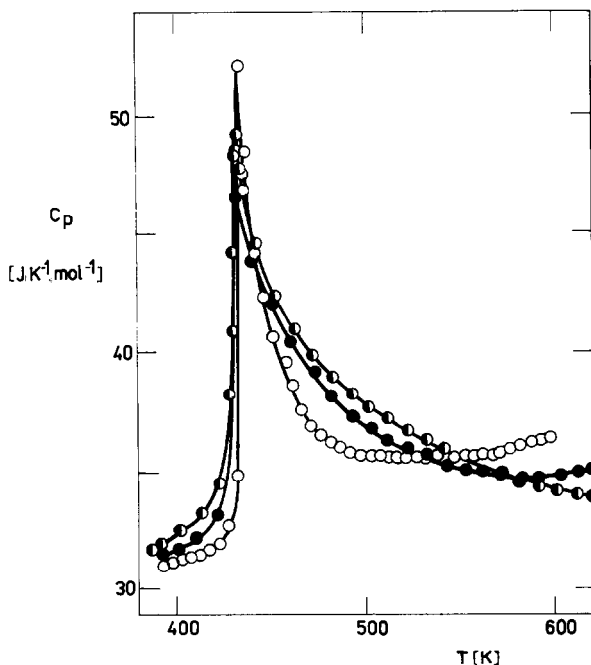


Fig. 5. Temperature dependence of the heat capacity of sulfur: ●, Braune and Moeller [56]; ◆, West [57]; ○, Komarek et al. [58].

impurities in the sulfur samples. A similar effect of impurities in sulfur on the scatter of melting temperatures and heats of fusion was described by Feher et al. [59]. The sharp maximum resembles the Greek letter λ which is the reason why for helium the maximum is denoted the λ -transition. However, the shape of the heat capacity curve $C = f(T)$ of helium and of sulfur is the only identical feature of the temperature dependence of the heat capacity for the two compounds. Whereas in the case of helium, this is a second-order phase transition [60] according to the Ehrenfest classification [61, 62], not accompanied by any discontinuous change of entropy and volume, an evolution of heat occurs for sulfur at around 435 K that leads to a step change in entropy. Despite the fact that the term λ -transition was used for the first time for the second-order phase transition in helium, it was subsequently used by other authors to describe a dependence of the heat capacity on temperature that has the shape of the Greek letter λ .

The anomalous behavior of liquid sulfur is well understood. It is due to the homolytic split of S–S bonds in S_8 rings leading to the formation of a linear chain. This is also the reason for a sharp increase in the liquid viscosity of sulfur at around 435 K [63].

Until recently, such behavior as has been encountered for helium and for sulfur has not been described for any liquid organic compound. In the last few years, new data on aldehydes have been published in the Soviet literature showing sharp maxima on the heat capacity curve $C = f(T)$ for ethanal [64], propanal [65], butanal [66], and hexanal [67]. The heat capacities of ethanal, propanal, and butanal as a function of temperature are shown in Fig. 6. All heat capacity measurements for ethanal, butanal, and hexanal were performed using an adiabatic calorimeter with a measurement accuracy 0.2% in the liquid region. Another calorimeter was used for propanal, and a measurement error of 0.3–1.0% was reported. Heat capacity data for pentanal were obtained with a measurement error better than 1% [68] and no maxima were found on the heat capacity curve for this compound. Except for measurements on aldehydes reported in refs. 64–68, the only other data on heat capacities of aldehydes obtained in a different laboratory are those reported by Parks et al. [69] for butanal. Parks et al. presented smoothed heat capacities with a temperature increment of 10 K and a measurement error of 1% that show no maximum on the heat capacity curve.

Lebedev and Vasil'ev [64] also performed an additional study using IR spectroscopy and concluded that maxima on the heat capacity curve are related to the breakdown of associated aldehyde molecules held together by hydrogen bonds. According to Vasil'ev and Lebedev [66], several maxima reported for a single aldehyde correspond to the possible formation of associated molecules of different kinds held together by bonds of different strength which thus split at different temperatures.

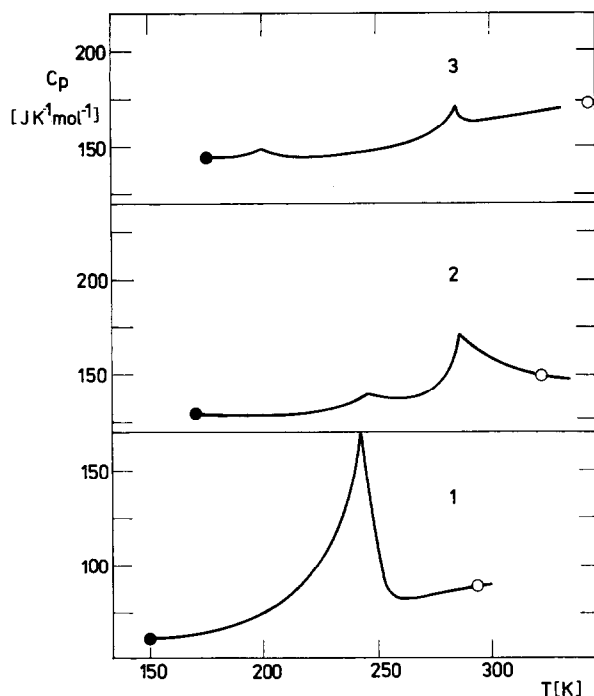


Fig. 6. Temperature dependence of the heat capacity of aldehydes: 1, ethanal; 2, propanal; 3, butanal.

Podoski et al. [70] published experimental heat capacities of 3,4-dimethylpyridine in a graphical form with a claimed measurement error of 1%. They reported a discontinuous sharp maximum at 293.5 K. The heat capacity at the maximum exceeds those at adjacent temperatures by about 4–5%. Podoski et al. supported the anomalous shape of the $C = f(T)$ curve by a similar unusual dependence of the shear viscosity on temperature at around 298 K measured in a previous study [71]. They explained the anomalous behavior by the decay of molecular clusters. It is worth mentioning that Steele et al. [72] who published smoothed heat capacities of all the isomers of dimethylpyridines did not find any maxima on the heat capacity curves.

Seyer [73] reported a sharp increase in the heat capacity by almost 50% for *cis*-decahydronaphthalene, with a subsequent decrease to the original value in the temperature interval from 323.2 to 323.6 K. He attributed the maximum to the λ -transition and substantiated it by a similar discontinuity observed in the measurement of surface tension as a function of temperature [74]. McCullough et al. [75] subsequently performed very accurate measurements with a reported accuracy of 0.2% using a sample containing 0.12 mol.% of impurities. A series of measurements in the temperature range from 310 to 330 K with temperature increments as

small as 1 K did not confirm the presence of the λ -transition. McCullough et al. concluded that an impurity in the sample used by Seyer, but not reported by him, was a possible cause for some of the unusual results he obtained.

CONCLUSIONS

A classification of heat capacity curves of pure liquid compounds into four categories is outlined. The shape of the curve that depicts the dependence of the heat capacity of a liquid as a function of temperature has been used as a criterion. The information was drawn from a large, comprehensive, critical compilation of experimental heat capacities of isotropic liquid compounds that contains almost 25 000 data points for more than 1550 compounds.

The most extensive group includes compounds showing a “typical” monotonically increasing dependence of the heat capacity on temperature. The second group, containing a fairly large number of compounds, includes compounds that exhibit a shallow minimum on the $C = f(T)$ curve located from a few to several tens of Kelvin above the melting temperature. It is reasonable to expect that this group would be more numerous if more accurate experimental data were available in the range from the melting temperature to the normal boiling temperature. The formation of clusters is most probably the cause leading to a minimum on the $C = f(T)$ curve. The absence of accurate experimental data on complete homologous series prevents a deeper understanding and explanation of the phenomenon. A thermodynamic analysis is presented that discusses conditions leading to the existence of a minimum. The third group of compounds showing an inflection point on the $C = f(T)$ curve contains only alcohols, with more than two carbon atoms in the molecule, and pyrrolidine. It has been proposed that there is a relationship between the inflection point and the breakdown of hydrogen bonds in the liquid phase. To verify this, more accurate data are required in the reduced temperature range above 0.6 for other compounds that form hydrogen bonds. The last group includes compounds that show a sharp peak on the $C = f(T)$ curve. This shape of the curve has been observed for helium and sulfur in several independent measurements. A similar anomalous shape has recently been reported for several aldehydes. However, all data on aldehydes that exhibit a sharp maximum have been reported by the same laboratory. Confirmatory heat capacity measurements from another high-quality low-temperature thermodynamic laboratory would provide important confirmation and support of the data from the Lobachevski State University at Gor’kii.

This work has been concerned with a phenomenological description of the dependence of the liquid heat capacity on temperature. To gain a

deeper insight into phenomena leading to various types of $C = f(T)$ curves, the existing experimental data must be complemented with more accurate measurements. The new measurements should both extend the temperature range of the data already available and provide new heat capacity data for compounds in some homologous series. A comprehensive interpretation would also need comparison with other properties, for example viscosity.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Eugene S. Domalski for helpful comments. We also appreciate the assistance of Dr. Jaroslav Šesták.

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