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Fitting the heat capacity of liquid *n*-alkanes: new measurements of *n*-heptadecane and *n*-octadecane

J.C. van Miltenburg*

Chemical Thermodynamics Group, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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Abstract

Literature data for the molar heat capacities of liquid *n*-alkanes from pentane to hexacosane were fitted to a function of temperature and number of carbon atoms in the chain. The part of the heat capacity curves directly after the melting point was not taken into consideration. The function $C_p = \{43.9 + 13.990\ (n-1) + 0.05430{\cdot}(n-1)T\}$ J K^{-1} mol^{-1} describes the experimental data to within the experimental error. The average percentage deviation is 0.18%. New measurements for the liquid heat capacity of heptadecane and octadecane are reported. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Fitting experimental data does not only serve to make the representation of the data easier, but can also be helpful to show underlying relations or point to deviating data. The *n*-alkanes form an well-investigated series of closely related compounds. It is our object to show that a simple function can be derived, which represents the data to within the experimental error.

Several series of investigations, using high precision adiabatic calorimetry, have been carried out to measure the thermal properties of linear alkanes in 1930–1950. Parks [1] and his co-workers at Standford University published in 1930 data of 14 saturated non-benzoic hydrocarbons, among which there are several *n*-alkanes. This group published more measurements in 1937 [2] and 1949 [3]. The Bureau of Mines published a large number of heat capacity data on the series of hydrocarbons (C_nH_{2n+2}) from $n = 8$ to $n = 16$ over the temperature range between 12 and 300 K [4,5]. These extensive studies led to the finding of relations in this family of compounds, for instance a formula for the absolute entropy at 298.15 K as a function of the number of carbon atoms was derived [4]. Atkinson et al. [6] considered the relations in the heat capacity of the *n*-alkanes between $n = 19$ and $n = 48$. He concluded that the heat capacities on a gram basis were essentially linear with temperature. A review of the available heat capacity data of the alkanes is to be found in the article of Zabránský et al. [7] who published a monograph on the heat capacity of liquids.

In this work only those publications have been taken into account, which state an accuracy of 0.5% or better.

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* Tel.: +31-302532386; fax: +31-302533946.
E-mail address: miltenb@chem.uu.nl (J.C. van Miltenburg).

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More recently [8] the interest in the *n*-alkanes and in their mixtures has been renewed, as they are excellent candidates for energy storage purposes. Research groups of Bordeaux, Barcelona and Utrecht (organised in the REALM) and of the University of Nancy work on these systems. In energy storage, not only the amount of latent heat or heat of fusion is important, also the absence or the relative small value of subcooling, which characterises these compounds, is an important factor. Furthermore, the non-toxicity and non-aggressive chemical behaviour are favourable properties.

A common feature of all *n*-alkanes is the anomalous behaviour of the heat capacity in the liquid state just above the melting point. Classification of different shapes of the heat capacity curves of liquids was published by Zabránský et al. [9]. The heat capacity of the *n*-alkanes with low *n*-number decreases immediately after the melting point with increasing temperature. At higher temperature, the heat capacity becomes a linear function of temperature. The same effect is observed when the number of carbon atoms increases. However, it becomes less outspoken and does not lead to a decrease of the heat capacity just above the melting point, only an increase of the slope of the heat capacity function with temperature is observed.

2. Reconsidering the liquid heat capacity data

Several authors mentioned the peculiar behaviour of the heat capacity of the *n*-alkanes just above the melting point. In a region of 30–40 K, the heat capacity does not show a linear relationship with temperature. In Fig. 1, this behaviour is illustrated for $C_{10}H_{22}$, between the melting point (243.5 K) and about 290 K the slope of the curve gradually increases. The experimental curve suggests that between 290 and 320 K a linear fit can be used. The most common explanation is that an ordering left over from the crystal state gradually disappears with raising temperature. Atkinson [6] stated that it is necessary to solidify the compound first in order to observe this effect. We made heat capacity measurements on samples of C_6H_{14}, $C_{19}H_{40}$ and $C_{20}H_{42}$ cooled from room temperature to just above the melting point. These data coincided with data obtained after first freezing and melting. This observation contradicts the remark made by Atkinson. The effect may be compared to the ordering in the liquid crystalline state, however, in the *n*-alkanes no phase transition to a disordered liquid state can be found. The same effect occurs in liquid water, where the minimum in the heat capacity curve is found at 4°C. For water theoretical explanations have recently been published [10,11]. We consider the effect as being an excess heat capacity superposed on the linear increase with temperature. The integral of the part between the two lines in Fig. 1 does than correspond to the enthalpy needed to randomise the liquid. That the heat capacity curve becomes linear at temperatures higher above the melting point was clearer in the data of $C_{19}H_{40}$ and $C_{20}H_{42}$ [12]. In these longer molecules, the curvature in the heat capacity ends about 30 K above the melting point. A linear part was measured over a temperature range of 60–70 K. We wanted to compare the linear fits as a function of temperature and number of carbon atoms. There is an element of arbitrariness in the choice of the temperature range used for a linear fit of the heat capacity data. When the experimental data span a large temperature range, the temperature range was selected by eye fitting the linear part of the curve. When however, as is the case with $C_{13}H_{28}$, the measuring range is small, this method could not be applied. In the case of $C_{13}H_{28}$ the last two data points were used for a linear fit. With $C_{14}H_{30}$ to $C_{16}H_{34}$, even this procedure could not be applied. These compounds were not taken into account. In Table 1 the coefficients of the linear fits of the *n*-alkanes are given. The Table

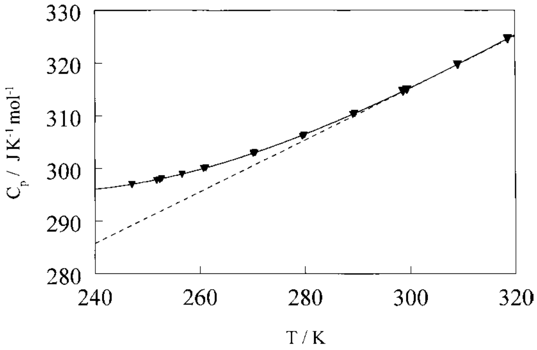

Fig. 1. The molar heat capacity of *n*-Decane. The data were taken from [4]. Between 290 and 320 K a linear function was fitted to the data. The integral of the part above this function is considered as an excess enthalpy.

Table 1
Results of the linear fits for the *n*-alkanes with carbon number between 2 and 26

Number of C atoms − 1, $n-1$	T-fusion (K)	a_0 ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	a_1 ($\mathrm{J\,K^{-2}\,mol^{-1}}$)	T_1-T_2 fit-range (K)	ΔH ($\mathrm{J\,mol^{-1}}$)	Reference
1	89.88	61.3	0.0599	142–180		[13]
2	85.46	66.6	0.1350	170–220		[14]
3	134.8	92.9	0.1382	135–270		[15]
4	143.4	92.8	0.2435	235–275	480	[5]
5	177.8	119.2	0.2489	220–280		[16]
6	182.5	141.4	0.2710	235–270	200	[17]
7	216.4	142.5	0.3740	269–297	160	[4]
8	219.7	157.7	0.4250	272–313	261	[4]
9	243.5	171.1	0.4813	289–318	136	[4]
10	247.6	212.6	0.4436	279–298	83	[4]
11	263.6	218.9	0.5264	299–317	38	[4]
12	267.8	238.8	0.5628	299–306	78	[4]
16	295.1	288.9	0.8002	350–380	85	[5]
16	–	266.4	0.8735	340–400	128	This work
17	301.3	313.9	0.8220	338–378	84	[5]
17	301.21	284.7	0.9150	335–400	124	This work
18	305.2	309.3	0.9395	344–400	119	[12]
19	309.8	325.4	0.9889	344–400	113	[12]
25	329.25	462.0	1.1620	348–358		[19]

also contains the temperature range used to make the fit and the integral of the excess heat capacity from the melting point to the temperature where the experimental data coincide with the linear fit. The latter value is a measure for the interaction enthalpy in the liquid phase just above the melting point. The coefficients of the linear fits do depend on the number of carbon atoms. The coefficients of $C_p = a_0 + a_1 T$ can each be fitted as a linear function of *n*. If the fit is made as a function of $(n-1)$, the function for a_1 versus $(n-1)$ passes within the error through the origin. This implies that the coefficients can be given as:

$$a_0 = A + B(n-1) \tag{1}$$

$$a_1 = C(n-1) \tag{2}$$

Combining these fits in the function for C_p leads to:

$$C_p\{(n-1), T\} = A + B(n-1) + C(n-1)T \tag{3}$$

Eq. (1) allows one to calculate directly

$$\left(\frac{\partial C_p}{\partial (n-1)}\right)_T = B + CT \tag{4}$$

$$\left(\frac{\partial C_p}{\partial T}\right)_n = C(n-1) \tag{5}$$

$$\frac{\partial^2 C_p}{\partial T \partial (n-1)} = C \tag{6}$$

It should be mentioned that in a mathematical sense differentiating to $(n-1)$ is not allowed, as $(n-1)$ is a discontinuous variable. Eq. (4) does however, give the increment of the heat capacity as a function of *n*.

Direct use of the coefficients of the aforementioned linear fits of a_0 against $(n-1)$ and a_1 against $(n-1)$ has the disadvantage that the coefficients are dependent of each other. Therefore, a data set was constructed using the experimental heat capacity values in the linear regions. This data set consists of — temperature; heat capacity; number of carbon atoms- triplets. Using the A, B and C values found in the linear fits of a_0 and a_1 as starting values, Eq. (1) was solved with the Solver option of the computer program Excel. The results of fitting different data sets, (to be described below) are given in Table 3. The standard deviation and the average absolute percentage deviation, defined as:

$$\sum_{i=1}^{nr} abs\left\{\frac{(c_{p,\exp,i} - c_{p,\mathrm{calc},i})}{c_{p,\exp,i}}\right\}\frac{100}{nr}$$

are also given.The best fit was found using the data of the *n*-alkanes between C_5H_{12} and $C_{26}H_{54}$. The *n*-alkanes with a number of carbon atoms below five deviated too much to be included in the fit. The standard deviation for the 136 data-points was 1.3 J K^{-1} mol^{-1}. The coefficients of this fit are given in the first row of Table 3. The standard deviation is very close to the expected experimental errors in the original data.

The largest deviations were found for $C_{17}H_{36}$ and $C_{18}H_{38}$. The heat capacities of these compounds showed maximum deviations from the fit of -0.7 %. Therefore, we measured the heat capacity of the liquid phase of these compounds. The adiabatic calorimeter used has been described before [17,18]. Samples were obtained from Aldrich Chemie ($C_{17}H_{36}$), with a purity of 99% and Fluka ($C_{18}H_{38}$), with a purity of >99.8%. Samples of 5.18 and 4.20 g, respectively, were used. Measurements were made in the intermittent mode with alternating stabilization and input periods of 600 and 800 s. The accuracy of the calorimeter, checked by measuring standard samples, was found to be better than 0.2% in this temperature region. The experimental data are given in Table 2. In the new data set, using our experimental values for $C_{17}H_{36}$ and $C_{18}H_{38}$, the standard deviation was reduced to 0.72 J K^{-1} mol^{-1}. The new values for $C_{17}H_{36}$ and $C_{18}H_{38}$ deviated no more than 0.15% from the fit. The calculated coefficients for this fit are given in the second row of Table 3.

The data of Atkinson et al. [6] for $C_{22}H_{46}$–$C_{48}H_{98}$ are given as linear fits for each compound, without error margins. To treat these data in the same way, heat capacity values were calculated at every 5 K between 350 and 410 K. Using all the data of Atkinson in the fit resulted in a standard deviation of 6 J K^{-1} mol^{-1}. The coefficients calculated are given in the third row of Table 3. The two compounds with the longest carbon chain contributed most to the standard deviation. For $C_{42}H_{86}$ the deviation is -1.7%, for $C_{48}H_{98}$ $+$ 1.2%. Omitting these two compounds resulted in a fit for a carbon number between 5 and 36, with a standard deviation of 2.4 J K^{-1} mol^{-1}. The coefficients are given in the fourth row of Table 3.

Obviously, the best fitting result is obtained using the experimental data up to $C_{26}H_{54}$, with the use of our new values for *n*-heptadecane and *n*-octadecane.

Table 2
Experimental molar heat capacities of the liquid phase of $C_{17}H_{36}$ and $C_{18}H_{38}$

$C_{17}H_{36}$		$C_{17}H_{36}$		$C_{18}H_{38}$		$C_{18}H_{38}$	
T (K)	C_p (J K^{-1} mol^{-1})	*T* (K)	C_p (J K^{-1} mol^{-1})	*T* (K)	C_p (J K^{-1} mol^{-1})	*T* (K)	C_p (J K^{-1} mol^{-1})
299.00	534.8	351.21	572.9	306.69	571.8	356.17	610.0
301.42	536.6	353.52	574.9	309.34	573.4	358.72	612.2
303.83	537.6	355.83	577.1	311.99	575.1	361.27	614.6
306.24	538.9	358.13	579.0	314.63	576.7	363.81	616.9
308.65	540.3	360.43	580.7	317.26	578.6	366.34	619.2
311.04	541.8	362.73	582.9	319.88	580.6	368.87	621.6
312.11	543.4	365.02	584.8	322.51	582.5	371.40	623.7
313.89	544.5	367.30	586.9	325.12	584.2	373.92	626.4
315.97	545.6	369.58	589.0	327.73	586.3	376.43	628.0
318.35	547.1	371.86	591.2	330.34	588.4	378.65	631.4
320.73	548.9	374.13	592.9	332.94	590.3	381.16	633.7
323.10	550.6	376.40	594.9	335.54	592.4	383.66	635.9
325.47	552.4	378.66	597.2	338.13	594.4	386.16	638.2
327.83	554.2	380.92	598.8	340.73	596.6	388.65	640.6
330.19	556.0	383.18	601.0	343.31	598.7	391.14	643.2
332.54	557.9	385.43	603.1	345.90	600.9	393.63	645.1
334.88	559.5	387.67	603.4	348.47	602.8	396.11	647.6
337.22	561.5	389.91	607.0	351.05	605.4	398.59	649.6
339.57	563.4	392.15	609.1	353.61	607.7	401.07	651.7
341.90	565.4	394.39	611.1				
344.23	567.1	396.62	613.1				
346.56	569.1	398.86	615.1				
348.89	571.2	401.08	617.2				

Table 3
The fit coefficients A, B and C of Eq. (3) with the number of data points, the standard deviation and the average absolute percentage deviation

A ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	B ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	C ($\mathrm{J\,K^{-2}\,mol^{-1}}$)	Standard deviation ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	Average absolute % deviation	No. of points
43.4	14.336	0.05328	1.3	0.28	136
43.9	13.990	0.05430	0.7	0.18	194
41.5	15.106	0.05154	6.0	0.37	302
41.6	15.125	0.05143	2.4	0.3	278
40.6	20.92	0.0342	8.0	1.8	136

Broadhurst [20] published an extensive analysis of the paraffin data in order to predict polyethylene properties. He also fitted the increments in the heat capacities of the liquid n-alkanes. The function given is $C_p(\text{–CH}_2\text{-group}) = \{0.0342T + 20.92\}\ \mathrm{J\,K^{-1}\,mol^{-1}}$. When we use the coefficients of this function for the coefficients C and B, respectively (see Eq. (4)) and optimise for A, A becomes $40.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$. Broadhurst mentioned that his fit of the liquid data contained an estimated error of 10%. As can be seen in the last row of Table 3, we find, using his fit, an error in the order of 1.8%. The large difference with the reported error is due to the restricted character of our data set. The heat capacity values in the region just above the melting points are not included.

The excess enthalpies given in Table 2 were calculated by fitting the heat capacity curve to a polynomial function of the third order. The enthalpy increment from the melting point until the starting point of the linear function was then calculated by integration of the polynomial function. The same procedure was repeated for the linear fit. The difference of these two calculations is the excess enthalpy. The values diminish with increasing number of carbon atoms in the chain. The excess enthalpy becomes more or less constant for the longer n-alkanes, reaching a value between 110 and 125 $\mathrm{J\,mol^{-1}}$.

When we express the heat capacity on a gram basis, Eq. (3) is transformed to:

$$c_p = \frac{A + B(n-1) + C(n-1)T}{n \times 14.027 + 2} \tag{7}$$

in which 14.027 stands for the molar mass of the –CH_2-group. From this function it follows by differentation that $(\partial c_p/\partial(n-1))_T$ is negative till 450 K (using the coefficients of the second row of Table 3.). At that temperature c_p is independent of the number of carbon atoms, above this temperature the derivative becomes slightly positive. Extrapolating Eq. (5) outside the range of the number of carbon atoms used in the fit, gives the possibility to compare the calculated c_p with the experimental values of liquid polyethylene. We calculate at 410 K for a linear chain of 100 carbon atoms $c_p = 2.586\ \mathrm{J\,K^{-1}\,g^{-1}}$, this value does deviate + 1.8% from the value given for linear polyethylene's by Varma-Nair and Wunderlich [21] of $2.54\ \mathrm{J\,K^{-1}\,g^{-1}}$. The influence of the choice of the number of carbon atoms in the polyethylene on c_p is very small at this temperature. Differentiating Eq. (5) gives for $(\partial c_p/\partial(n-1))_T$ a value of $-4.8\ \times 10^{-7}\ \mathrm{J\,K^{-1}\,g^{-1}}$ at 410 K. This means that the choice of the number of carbon atoms in the polyethylene can not be the cause of the difference.

3. Discussion

The second row of variables in Table 3 covers the series of n-alkanes from C_5H_{12} to $C_{26}H_{54}$, using the new data for $C_{17}H_{36}$ and $C_{18}H_{38}$. The function $C_p = \{43.9 + 13.990\cdot(n-1) + 0.0543\cdot(n-1)T\}\ \mathrm{J\,K^{-1}\,mol^{-1}}$ is able to describe the heat capacity of these liquid n-alkanes to within the experimental precision. The average percentage deviation is 0.18 %. The error margins for heat capacity measurements with adiabatic calorimetry are, depending on the apparatus, mostly given as 0.1–0.2%. Considering the different sources of the data used, the goodness of the fit is remarkable. The fact, that the first fit pointed out that two compounds ($C_{17}H_{36}$ and $C_{18}H_{38}$) deviated from the fit and, that after a new measurement these compounds do fall completely within the model, does indicate a certain predictive power. The 1.8% difference with the experimental heat capacity of polyethylene at 410 K is larger than could be expected on the basis of the error in the fit. It is however, probable that, when the chain length of the *n*-alkanes increases, new effects, like chain folding, come into play.

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