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The Effect of Impurities on the Melting Temperature and the Heat of Fusion of Latent Heat Storage Materials

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Thermophysical properties of four normal paraffins (tetradecane, hexadecane, octadecane, eicosane) and three fatty acids (lauric acid, palmitic acid, stearic acid) were determined experimentally using a modified differential-thermoanalysis technique. For calibration of the measuring device, literature data in the temperature range from 5 to 70°C of six of these substances of at least 99% purity were used. Melting temperature, heat of fusion, and specific heat of a number of these "pure" and "technically pure" organic compounds were measured and compared to determine the effect of impurities and to give values of the application range of the properties required for the construction of thermal storage equipment.

KEY WORDS: latent heat storage material; impurities; melting temperature; heat of fusion; specific heat.

1. INTRODUCTION

Awareness and cost of energy raise the importance of energy storage. Thermal storage is a necessity for solar powered space heating and air conditioning, and it is advantageous for the application of heat pumps with waste heat as a heat source.

Thermal energy can be stored by either latent heat or sensible heat. In the case of latent heat storage, the physical state (phase) of a storage material is changed. The most suitable phase change here is the solid-liquid transition. In connection with a heat pump or any other thermodynamic cycle, there is the operational advantage of a nearly constant storage temperature. Theoretically, the phase change takes place at a constant temperature; in practice, a

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slight superheating is encountered. The total heat Q (latent and sensible) being stored by a material is

$$Q = m\left[\int_{T_1}^{T_f} c_{ps}\,dT + \Delta H_f + \int_{T_f}^{T_2} c_{pl}\cdot dT\right] \qquad (1)$$

where m is the amount of material, T_1 and T_2 are its lower and upper temperatures, T_f is the melting temperature, c_{ps} and c_{pl} are the heat capacities of the solid and liquid phase, and ΔH_f is the transition enthalpy of the phase change.

The selection of a particular storage material will depend on the given application and the values of T_f, ΔH_f, c_{ps}, and c_{pl}. In the present case, the interesting temperature ranges are $T_f = 5$–15°C for air conditioning, and $T_f =$ 20–70°C for space heating. Melting with high heat of fusion in a suitable temperature range occurs in many materials, especially in organic compounds.

2. SELECTION OF STORAGE MATERIALS

Lane et al. [1] performed an extensive literature survey to identify suitable materials for phase change energy storage. From some 20,000 compounds or mixtures, 205 substances, including 67 organic compounds, were found useful.

From these, the fatty acids were selected as the most suitable materials for constant temperature heat storage. In the lower temperature range, some normal paraffins were recommended. For the present investigation, the selected substances are given in Table I. Data of phase change materials (PCM), as required in Eq. (1), are found in the literature [2–11]. These data, however, show considerable scatter. This might be caused by different experimental methods or impurities in the substances used for the measurements. Substances used for reproducible measurements of physical properties

Table I. Selected Phase Change Materials (PCM)

Compound	Melting temperature from literature (°C)
Tetradecane ($C_{14}H_{30}$)	5.7
Hexadecane ($C_{16}H_{34}$)	18.3
Octadecane ($C_{18}H_{38}$)	28.2
Eicosane ($C_{20}H_{42}$)	36.6
Lauric acid ($C_{11}H_{23}\cdot COOH$)	43.8
Palmitic acid ($C_{15}H_{31}\cdot COOH$)	62.7
Stearic acid ($C_{17}H_{35}\cdot COOH$)	69.7

should be highly pure, while for commercial thermal energy storage, technical purity is sufficient and much less expensive. Materials of "technical purity" cost about $^{1}/_{10}$ to $^{1}/_{100}$ of highly pure materials; unfortunately however, their properties are scarcely known. To give an impression of the effect of impurities on the properties of phase change materials, the melting temperature, the transition enthalpy of phase change, and the heat capacities of the liquid and solid phase were measured here for both pure and technically pure substances.

3. EXPERIMENTAL EQUIPMENT AND TECHNIQUE

The so-called "dynamic difference calorimetry" (DDC), a modification of the differential thermal analysis (DTA), was used. The modified technique was first proposed by Boersma [12] and later on developed by Schwiete and Ziegler [13]. DTA is a technique in which the endothermic or exothermic heat effects associated with physical or chemical changes of a sample are recorded as a function of temperature or time when the substance is heated at a uniform rate. A comparison between sample temperature T and temperature difference ΔT between sample and reference material (shown as the horizontal curve) is presented in Fig. 1. The sample and reference temperature differ only during the actual transition (melting) of the sample. The melting temperature T_f can be determined at the intersection between the base and the inflection line of the temperature difference curve, as shown in Fig. 1, following a proposal of the International Conference on Thermal Analysis (ICTA) to standardize DTA measurements. From the shaded area under the peak, the heat of phase change can be calculated. The specific heat

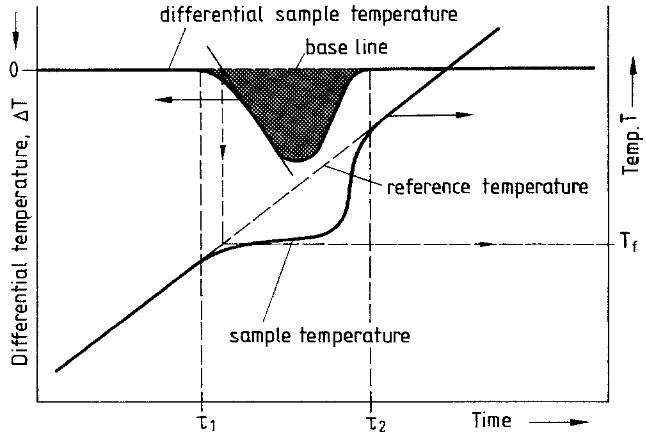

Fig. 1. Comparison between sample temperature and differential sample temperature.

can be determined following Adam and Müller [14], who derived the simplified equation

$$W_1(T) = W_0(T) + U(T)\frac{\Delta T}{v} \tag{2}$$

with the overall heat transfer coefficient U, which must be determined by calibration; heat capacity of the sample $W_1(T)$ and the reference substance $W_0(T)$; temperature difference ΔT between sample and reference substance; and heating rate v.

The main parts of a DTA apparatus (see Fig. 2) consist of a furnace (1); crucibles [sample (2) and reference substance (3)] with thermocouples; a controller for uniform rate heating (4), and recorders for temperature difference (5) and temperature (6). Usually, the thermocouples are located in the center of the sample and the reference substance; in this case, quantitative measurements of the heat of phase change were influenced by the packing density of the sample. To prevent this effect, another thermocouple arrangement is used in DDC (Fig. 3). The position of the thermocouples is no longer within the sample and the reference substance, but within the

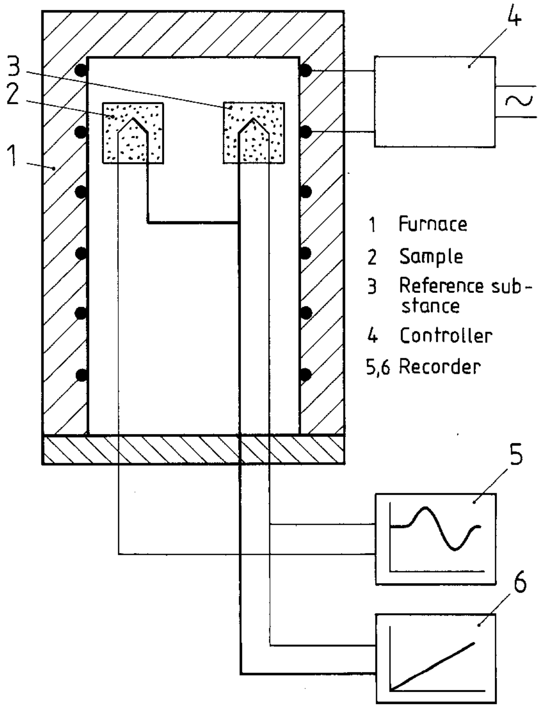

Fig. 2. DTA apparatus (schematic).

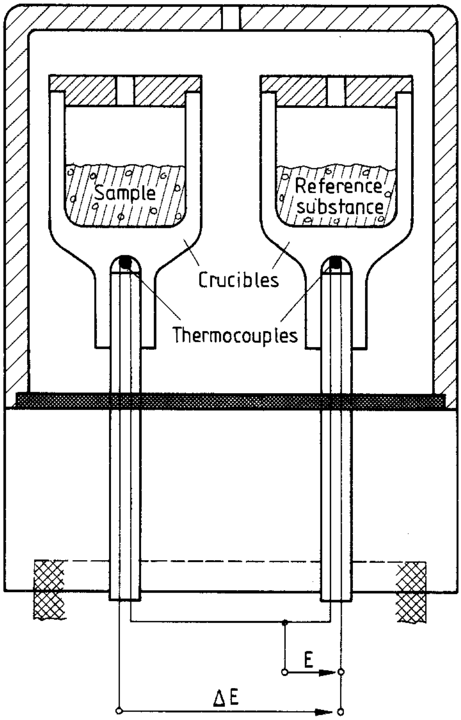

Fig. 3. Dynamic differential calorimetry thermocouple locations.

crucibles. Now the temperatures are measured indirectly. It is assumed that the temperature lag caused by the indirect temperature measurement is the same for the sample and the reference substance, respectively. Therefore a temperature correction is not necessary.

In the present investigation, a DDC apparatus by Netzsch-Gerätebau GmbH. was used (Fig. 4). The measuring device is suited for lower temperatures (up to 400°C). For measurements in the temperature range $5 < T < 50°\mathrm{C}$, an additional cooling system was installed.

This apparatus has two sample and two reference substance crucibles instead of only one for each as usual (see Fig. 5). The material of the crucibles is stainless steel, and that of the crucible holders is brass. Temperatures were measured with iron-constantan thermocouples of 0.5 mm wire diameter. The reference substance is Al_2O_3, which was used especially in its α-modification for the determination of the specific heat. The amount of sample and reference material was always in the range of 0.1–0.13 g per crucible. The average of the linear heating rate was 0.4 K/min, whereas for some specific heat measurements, 0.8 or 2 K/min were chosen.

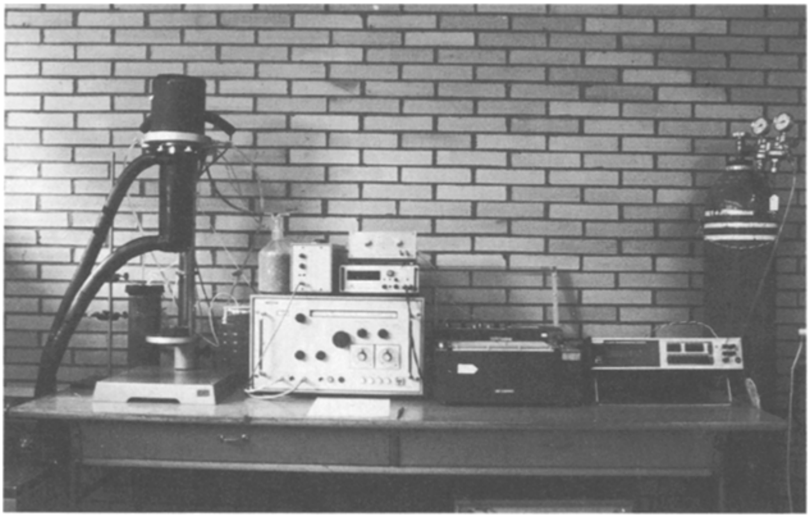

Fig. 4. DDC apparatus (furnace, controller, and recorders).

4. CALIBRATION OF THE DDC APPARATUS

The thermocouples were calibrated by comparison with a reference thermocouple, of which the function between measured temperature and electromotive force is well known. For calibration, the crucibles were replaced by a copper block bearing the DTA and the reference thermocouple. Following the theory of Speil et al. [15] and other authors, the shaded area enclosed by the differential curve (see Fig. 1) yields

$$\Delta H_f = \frac{\overline{K}}{m} \int_{\tau_1}^{\tau_2} \Delta T \cdot d\tau = \frac{K}{m} \int_{\tau_1}^{\tau_2} \Delta E \cdot d\tau \qquad (3)$$

where ΔH_f is the latent heat of phase change; m is the amount of the sample; $\overline{K}$ and K are proportionality coefficients, which depend on the apparatus and the temperature of the phase change; τ_1 and τ_2 represent initial and final time of the occurrence of the peak; and ΔT and ΔE are the differential temperature and the thermocouple voltage, respectively. The coefficient K can be considered a constant in the relatively narrow temperature range of a phase change; it has to be determined experimentally for each apparatus and comparable heating conditions and temperatures.

Pure organic compounds with a well known heat of melting were selected to determine the calibration coefficient

$$K = \Delta H_f \cdot m / \int_{\tau_1}^{\tau_2} \Delta E \cdot d\tau$$

from Eq. (3), with ΔH_f taken from Table III (see below) and the integral evaluated by planimetry of the peak area. Coefficients K for different melting temperatures are obtained as shown in Fig. 6. For each substance, the calibration runs were repeated two times with a new, but equal amount of sample mass. During a calibration run, three or four melting peaks were recorded. The arithmetic mean value of these six or eight peak areas was used to determine the calibration coefficient K.

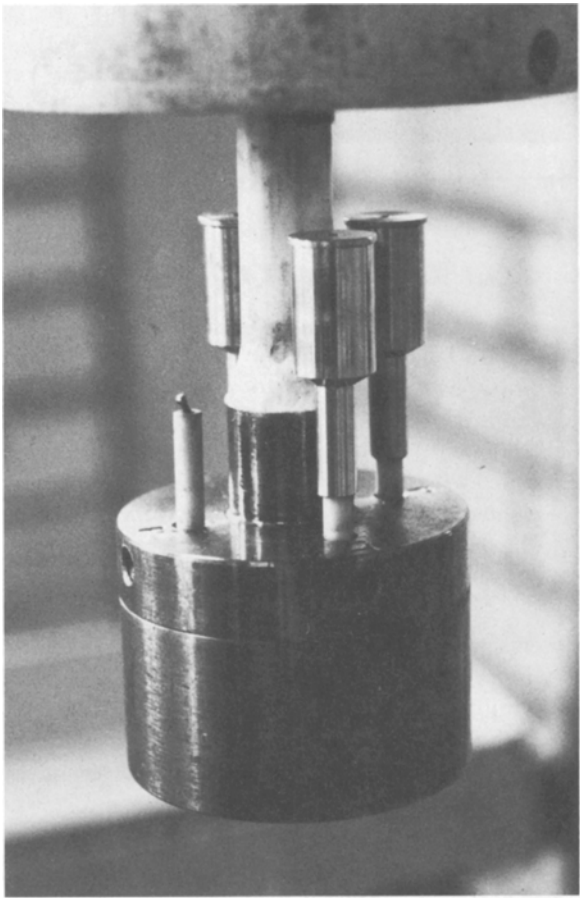

Fig. 5. Crucibles, thermocouples, and crucible holder.

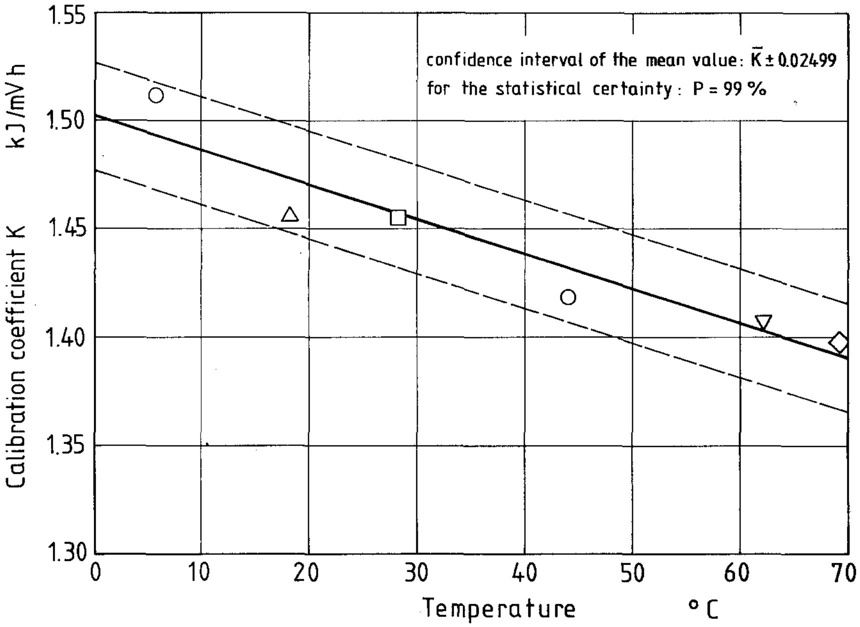

Fig. 6. Calibration coefficient K versus temperature.

For the shift of the baseline, resulting from different specific heats of the solid and liquid phase, a correction has to be taken into account following a proposal by Adam and Müller [14]. The average scatter of the mean values of ΔH_f as obtained from the literature was calculated to be ±2%. With the peak area being determined with a maximum error of ±0.5%, the unknown heat of phase change of a substance can be determined within ± 2.5%.

5. EXPERIMENTAL RESULTS

Four different n-paraffins (tetradecane, $C_{14}H_{30}$; hexadecane, $C_{16}H_{34}$; octadecane, $C_{18}H_{38}$; eicosane, $C_{20}H_{42}$) and three fatty acids (lauric acid, $C_{11}H_{23}COOH$; palmitic acid, $C_{15}H_{31}COOH$; stearic acid, $C_{17}H_{35}COOH$) were investigated. Except for eicosane, the paraffins were of high purity; fatty acids had a purity of about 99%. All these six materials were used for calibration.

In these measurements, the melting temperature was observed. For paraffins, the agreement with data from the literature was very good, with average deviations of 0.07 K. Measured values proved smaller than literature data in any case, but reliability of apparatus and procedure seemed satisfac-

Table II. Compilation of Materials Analysis

Name	No.	Supplier	Content G.C. (%)	Approximate chain distribution (%) C10	C12	C14	C16	C17	C18	C18′	C19	C20	C21	C22	C23	C24	C25	C26	Unsaponifiable parts (%)	Sulfate (%)	Undefined (%)
	1	I[a]	99.8																		0.2
n-Tetradecane	11	II	99.7																		0.3
	21	IV	99.3																		0.7
	2	I	99.7																		0.3
n-Hexadecane	12	III	98.4																		1.6
	22																				
	3	I	99.3																		0.7
n-Octadecane	13	III	>99																		<1
	23	IV	98.6																		1.4
	4																				
n-Eicosane	14	III	>99																		<1
	24	V	21.3				0.4	2.5	8.1		16.1	21.3	20.7	16.4	9.1	3.8	1.1	0.5			
	5	I	99																0.5 saponifiable	0.05	0.45
Lauric acid	15	IV	99	0.5	99	0.5													0.2		
	25	III	>98																		<2
	6	I	99																0.5 saponifiable	0.05	0.79
Palmitic acid	16	IV	98			1	98		1										1		
	26	III	98																		2
	7	I	99																0.16	0.05	0.79
Stearic acid	17	IV	98				0.5		98	1									1.5		
	27	III	92.5																		7.5

[a] I, E. Merck, Darmstadt; II, Riedel-de Haën AG, Hannover; III, Dr. Theodor Schuchardt & Co., München; IV, Henkel KGaA, Düsseldorf; V, "ter Hell Paraffin," Hamburg.

tory. For fatty acids, average deviations amount to 0.25 K; this is accounted for by their lower purity.

All seven materials were also investigated with purities between 98 and 99.7%, as used for synthesis, and finally, except hexadecane, also with a wider range of hydrocarbon additives. In Table II, the materials analysis are compiled as provided by the manufacturers. The melting temperatures range from 4 to 70°C, with temperatures and latent heat increasing with increasing number of carbon atoms within the molecule. As an example, the DDC diagram for technical octadecane (13) is presented in Fig. 7, together with the curves of the pure substance (3). In this case, the technical (synthesis) material is still quite pure, and the diagram gives a distinct peak. This, however, is clearly flattened and stretched compared to the peak of the pure substance.

A typical diagram for a technical paraffin (24), with eicosane being its main component, is shown in Fig. 8. For comparison, the result for eicosane

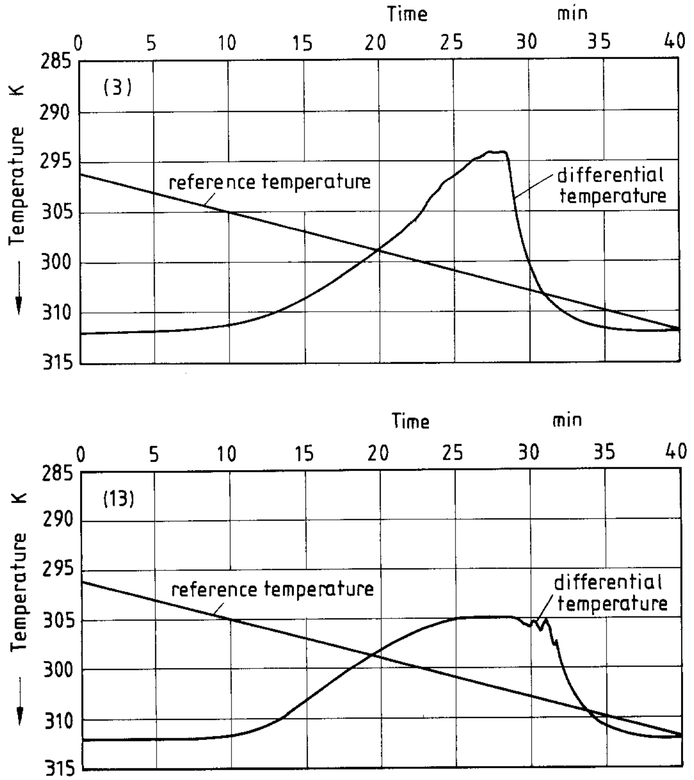

Fig. 7. DTA diagram for melting of octadecane (3) of purity 99.3%, and (13) of purity 99%.

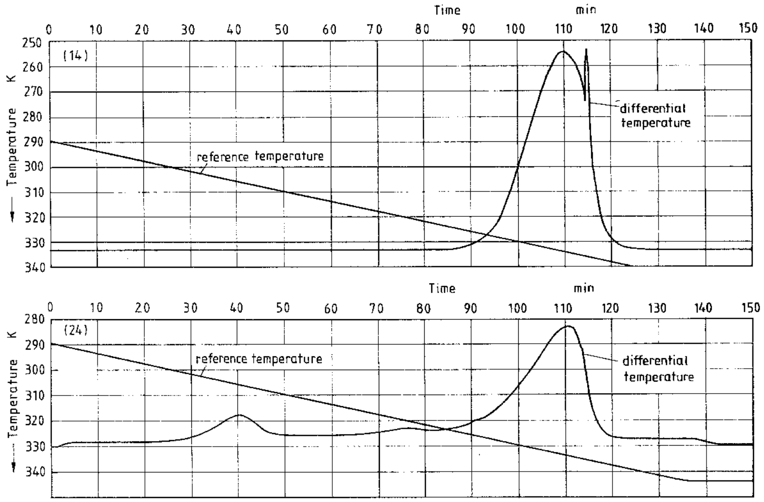

Fig. 8. DTA diagram for melting of eicosane (14) and paraffin mixture (24).

for synthesis (14) is also given. Three peaks appear, which merge into each other, so that it does not appear useful to indicate a certain melting point related to a certain heat of melting.

All melting temperatures and enthalpies as measured are compiled in Table III; also given are the deviations from the literature data. The deviations of heat of fusion from that of pure materials increase with increasing amount of impurities. As long as the compound contains more than 90% of a pure substance, these deviations remain smaller than 12%.

The comparison of a raw paraffin containing 21.3% eicosane as the largest portion of one substance with eicosane for synthesis yields the following result. As shown in Fig. 8, for raw paraffin there appears one pronounced peak in the diagram, accompanied by two smaller maxima. Considering the peak as the only representative for the heat of fusion, one obtains a value which amounts to 60% of that of eicosane for synthesis. It is noteworthy that this raw paraffin contains at least 46% components with a heat of fusion higher than eicosane and, at the most, 32.5% with a lower heat of fusion. Considering the entire area found by the deviation of the differential curve to the base line in the diagram, a value for the heat of fusion is obtained which amounts to 77% of that of eicosane for synthesis. This heat, however, cannot be associated with one melting point, but rather with a melting region, thus questioning the specification "heat of fusion" for this raw paraffin.

In Fig. 9, the heats of fusion are alloted to the various materials of different purity, and heat of fusion is plotted as a function of melting

Table III. Melting Temperature and Heat of Fusion ΔH_f of Organic Compounds

	Pure substance				Substance for synthesis					Technical substance				
		T_f, melting temperature												
Name	No. of cpd.	Literat. (°C)	Exper. (°C)	ΔH_f, heat of fusion, literat. (J/g)	No. of cpd.	T_f, melting temp., exper. (°C)	$\Delta T_f = T_f - T_{f_{\text{Lit}}}$ (K)	ΔH_f heat of fusion, exper. (J/g)	$d(\Delta H_f) = \frac{\Delta H_f - \Delta H_{f_{\text{Lit}}}}{\Delta H_{f_{\text{Lit}}}}$ (%)	No. of cpd.	T_f, melting temp., exper. (°C)	$\Delta T_f = T_f - T_{f_{\text{Lit}}}$ (K)	ΔH_f, heat of fusion, exper. (J/g)	$d(\Delta H_f) = \frac{\Delta H_f - \Delta H_{f_{\text{Lit}}}}{\Delta H_{f_{\text{Lit}}}}$ (%)
n-Tetradecane	1	5.72	5.67	229.41	11	5.57	−0.15	223.68	−2.5	21	4.35	−1.37	203.3	−11.38
n-Hexadecane	2	18.25	18.05	232.14	12	18.31	−0.06	228.56	−1.54	22				
n-Octadecane	3	28.15	28.10	242.11	13	28.34	0.19	237.40	−1.95	23	27.25	−0.9	231.58	−4.35
n-Eicosane	4	36.62		243.39	14	36.0	−0.62	242.52	−0.36	24[a]	34.5	−2.12	145.35 187.30	−40.28 −23.05
Lauric acid	5	43.78	43.93	182.56	15	43.45	−0.33	180.15	−1.32	25	43.30	−0.48	178.95	−1.98
Palmitic acid	6	62.72	62.10	212.26	16	61.2	−1.52	212.71	0.2	26	61.65	−1.07	206.05	−2.93
Stearic acid	7	69.7	69.3	220.98	17	68.05	−1.65	229.52	3.9	27	64.80	−4.9	202.6	−8.3

[a] Paraffin mixture.

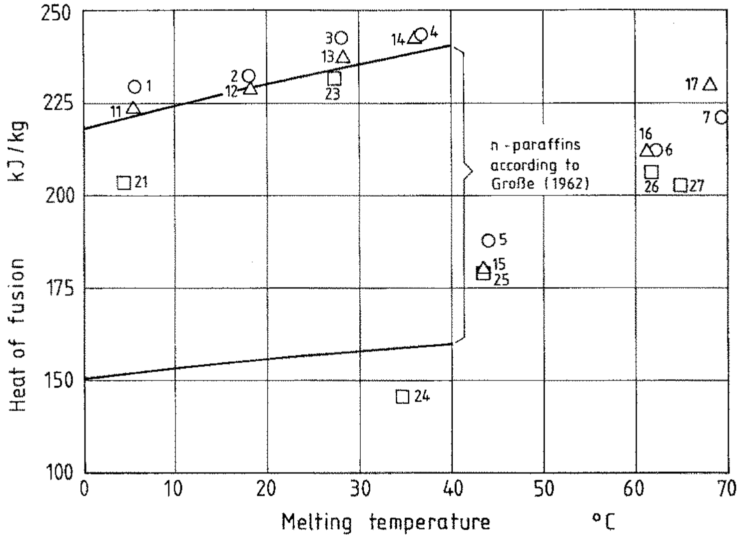

Fig. 9. Heat of fusion of organic compounds versus melting temperature.

temperature. A departure from the general trend appears for stearic acid, as the literature data do not give the highest heat of fusion within this group. The scatter of n-paraffin data obtained as an average from a large number of literature data falls beside the region given by Groβe [16] for these compounds.

The specific heats of the liquid and solid phase of the organic compounds given in Table I were measured as a function of temperature and calculated from Eq. (2). A typical DDC record for octadecane (23) is shown in Fig. 10.

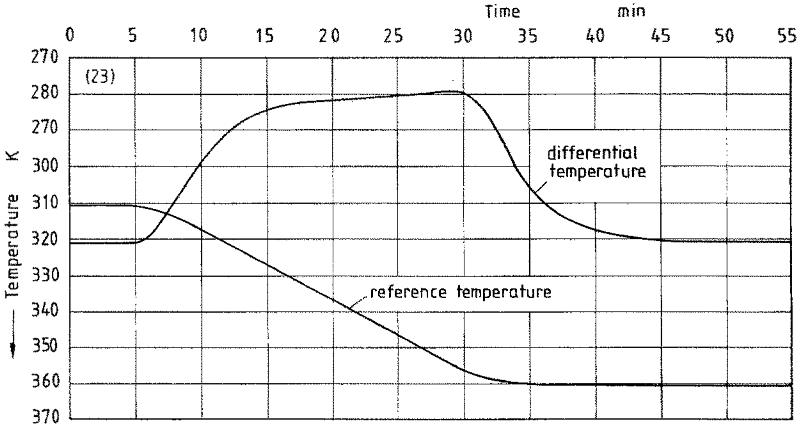

Fig. 10. DTA diagram for determination of specific heat of octadecane (23).

It was observed that there is no significant effect of the temperature on the specific heat in the given temperature range. Therefore, mean values of the experimental results are given in Table IV. It is difficult to compare the measured specific heat with values given in the literature [3–11, 16, 17]. There is only sparse information concerning the compounds for which the literature values are valid. Moreover, there are measurement uncertainties of about 5% in the liquid phase specific heat and about 10% in the solid phase specific heat values that are presented here.

6. DISCUSSION

This investigation was instigated by the fact that for the design of a latent heat storage device, usually only properties of pure materials are available while, for economic reasons, technically pure materials with unknown properties are used. Jurinak and Abdel-Khalik [18], using a simulating calculation, have investigated the effect of melting temperature and heat of fusion on the performance of a solar-heating system. Their results indicated that for a certain storage mass, the system performance is slightly affected by variations in the melting temperature and latent heat of the phase change material. In the case of an optimum system operation temperature, a change of 10 K in the melting temperature results in a decrease of performance of only about 2%. Beyond a latent heat of about 200 kJ/kg, the system performance would change by ±1% for a change in latent heat by ±40%. Finally, the effect of semicongruent melting on system performance remains extremely small (<1%) for values of the melting temperature band up to 16 K.

In the present case, the variations in melting temperature, heat of phase change, and the melting temperature band resulting from the impurities of n-paraffins and fatty acids are small. They would not affect the system performance appreciably. For systems design, the properties of pure substances can be used. On the other hand, the melting temperature band of the technical mixture of paraffins ranges up to 30 K, and this might affect the performance, depending on the operational conditions. It can be recommended to use the heat of melting of the main component of the mixture for design purposes, but it is warned to use its melting temperature.

Carling and Radosevich [19] studied the effect of specific heat variations of hydrocarbon liquid storage materials on cost and performance of solar applications. They pointed out that the variations in cost for a 10% variation in specific heat are less than 1–2% for three special storage designs. For other storage capacities, these fractions will not change greatly.

In the present investigation, it is shown, for instance, that the literature

Table IV. Specific Heat of Organic Compounds

			Experimental results					
	Values from literature		Pure substances		Substances for synthesis		Technical substances	
Name	c_p(J/g K)	Validity range, T(°C)	c_p(J/g K)	Validity range, T(°C)	c_p(J/g K)	Validity range, T(°C)	c_p(J/g K)	Validity range, T(°C)
n-Tetradecane								
Solid	1.68	−20–0						
Liquid	2.18	25	2.22	42–65	2.20	52–85	2.05	49–77
n-Hexadecane								
Solid	1.65	−20–0						
Liquid	2.19	25	2.05	48–75	2.08	46–86		
n-Octadecane								
Solid	1.75	−20–0						
Liquid	2.22	28	2.13	42–73	1.91	45–82	2.11	39–81
n-Eicosane								
Solid	1.97	0–30			1.72	16–23		
Liquid	2.08	127			2.08	65–87	2.42	55–95
Lauric acid								
Solid	1.80	−20–20	1.81	15–26	1.74	15–24	1.86	9–26
Liquid	2.16	50	2.08	62–96	2.03	60–92	2.12	58–98
Palmitic acid								
Solid	1.81	25	1.71	23–36	1.90	16–29		
Liquid			2.27	82–114	2.37	74–105		
Stearic acid								
Solid	1.83	15–25	1.63	18–33	1.93	16–36	2.07	15–34
Liquid	2.33	75–137	1.92	78–108	2.14	94–107	2.31	71–111

and experimental values of liquid phase specific heat of pure tetradecane agree well, whereas even better agreement was found for technically pure or impure liquid stearic acid. The very high specific heat of the "eicosane" paraffin mixture is remarkable. The differences of the experimental results for various purities are smaller than 10%, with the exception of the paraffin mixture and stearic acid. Therefore, the impact of substance impurities on thermal energy storage systems is small in most cases, following Carling and Radosevich [19]. But it is necessary to perform systematic investigations of the specific heat of paraffin mixtures.

7. CONCLUSIONS

The melting temperature, the heat of fusion, and the specific heat of seven organic compounds have been determined using a modified differential thermal analysis technique. The variation of sample purity results in a variation in the properties. For different sample purities, the melting temperatures differed by as much as 4.5 K, the heat of melting by as much as 11.4%, and the specific heat by as much as to 27%. The results for a mixture of paraffins are outside of these ranges.

The variation of melting temperature and heat of phase change resulting from impurities of the organic compounds does not affect the performance of a latent heat thermal energy storage system seriously. If paraffin mixtures for storage purposes are used, the mixture properties, in particular, the melting temperature, must be taken into special account.

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REFERENCES

1. G. A. Lane, D. N. Glew, E. Colin Clarke, H. E. Rossow, S. W. Quigley, S. S. Drake, and J. S. Best, in *Proceedings of the Workshop on Solar Energy Storage Substances for the Heating and Cooling of Buildings,* NSF-RA-N-75-041 ERDA, Washington, D.C., (1975), pp. 43–55.
2. D'Ans. Lax, *Taschenbuch für Chemiker und Physiker,* Vol. 2 (Springer-Verlag, Berlin, 1967), pp. 1084–1086.
3. *Handbook of Chemistry and Physics,* (CRC Press, Cleveland, 1975), pp. C718–C719.
4. F. K. Beilstein, *Handbuch der organischen Chemie,* Vol. I/1 (Springer-Verlag, Berlin, 1958), pp. 550–571.
5. H. Landolt-Börnstein R., *Zahlenwerte und Funktionen,* Vol. 2/4 (Springer-Verlag, Berlin, 1961), pp. 281–334.

6. J. A. Dean (ed.), *Lange's Handbook of Chemistry* (McGraw-Hill, New York, 1972), pp. 9–65.
7. *Handbook of Chemistry and Physics,* (CRC Press, Cleveland, 1978–1979), pp. C978–C979.
8. F. K. Beilstein, *Handbuch der organischen Chemie,* Vol. II/1 (Springer-Verlag, Berlin, 1960), pp. 868–883.
9. R. H. Perry, C. H. Chilton, and S. D. Fitzpatrick, *Chemical Engineer's Handbook,* (McGraw-Hill, New York, 1963), pp. 3/54–3/57.
10. F. Ullmann, *Enzyklopädie der technischen Chemie,* Vol. 11 (Verlag-Chemie, Weinheim, 1976), p. 526.
11. F. Ullmann, *Enzyklopädie der technischen Chemie,* Vol. 14 (Verlag-Chemie, Weinheim, 1976), p. 655.
12. S. L. Boersma, *J. Am. Ceram. Soc.* **38:**281 (1955).
13. H. E. Schwiete and G. Ziegler, *Ber Deutsch. Keram. Ges.* **35(6):**193 (1958).
14. G. Adam and F. H. Müller, *Kolloid-Z. u. Z. f. Polymere* **192:**29 (1963).
15. S. Speil, L. H. Berkelhamer, J. A. Pask, and B. Davis, U.S. Bur. Mines Tech. Paper no. 664, (1945), p. 81.
16. L. Groβe, *Arbeitsmappe für Mineralölingenieure* (VDI-Verlag, Düsseldorf, 1962), pp. H1–J1.
17. H. L. Finke, M. E. Gross, G. Waddington, and H. M. Huffman, *J. Am. Chem. Soc.* **76:**333 (1954).
18. J. J. Jurinak and S. I. Abdel-Khalik, *Solar Energy* **22:**377 (1978).
19. R. W. Carling and L. G. Radosevich, *Solar Energy* **22:**471 (1979).