論　文

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A Simple Conduction-type Calorimeter

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A simple, inexpensive conduction calorimeter is described which can determine the melting and other transition temperature to within 0.1 K on IPTS-68, the impurity concentration, the enthalpy changes to within 1 per cent, and the heat capacities to within 5 per cent. Test runs revealed the existence of a metastable phase in *n*-octadecane which melts at 300.27 K and in *n*-eicosane which melts at 309.34 K. Solid-solid transitions were also recorded in *n*-nonadecane at 295.50 K and in *n*-docosane at 317.04 K.

1. Introduction

There are occasions in which melting and other phase-transition temperatures need to be determined with moderate accuracy. One such example is the construction of a phase diagram for which a large number of runs are to be taken on a series of specimens of different composition.

A conduction-type calorimeter[1] has a feature of easy operation and permits a relatively rapid determination of not only the transition temperature but also an approximate value of the enthalpy change associated with it.

The present paper describes the construction of a simple, inexpensive calorimeter which operates between 77 K and 430 K to determine the transition points and the amount of impurities. The calorimeter can also be used to obtain rough values of the heat capacities.

2. Description of the calorimeter

The requirements of the basic design were

a. to give the precision of 1/100 K for the temperature measurements
b. to be able to determine the liquid-soluble, solid-insoluble impurities
c. to be able to determine the heat of fusion to within 1 per cent

and

d. to be able to determine the heat capacities to within several per cent both in the heating and cooling directions.

The major portion of the calorimeter is shown in Fig. 1. The calorimeter vessel A is made of chromium-plated copper and has an inside capacity of 3 cm^3. Its cylindrical portion can be removed from the cap C for cleaning and sample-loading and weighs about 10 g. The cap has a re-entrant

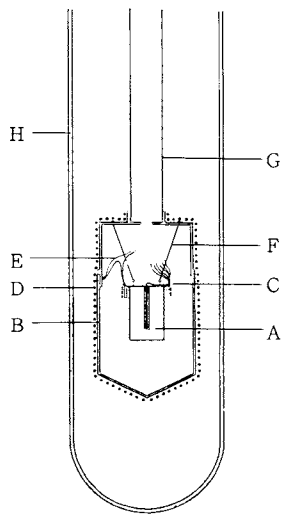

Fig. 1. The calorimeter.
A: sample container, B: heated mantle, C: cap of the container, D: heater winding, E: difference thermocouple, F: nylon cords, G: stainless-steel tubing, H: glass jacket.

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well (1 mm in inside diameter, 20 mm in length) at its center which houses the working thermometer, three pairs of copper-constantan thermocouples connected in series (B.S. #36, double silk-insulation, Driver-Harris Co.). A folded copper vane is inserted in the vessel to aid in the thermal diffusivity. The cap is hung from the mantle B with three nylon cords F.

The mantle (copper, 1 mm in wall-thickness) is also made of two parts; The lower part can be screwed onto the upper part, both having closely wound heaters D (manganin, total resistance of 100Ω). The lower part of the mantle can be completely detached from the upper portion for mounting the calorimeter vessel inside it. The mantle is silver-soldered to a stainless-steel tubing G (15 mm in diameter, 0.2 mm in wall-thickness, and 30 cm in length), which serves for evacuation and support. There is a radiation trap under the lower opening of the tubing G. The upper end of the tubing is fixed to the flange to which is also fixed (vacuum-tight) the outside Pyrex tube H (7 cm in outside diameter and 40 cm in length).

The temperature difference between the calorimeter and the mantle was measured and controlled using a copper-constantan thermocouple E. The temperature thermocouple was wound first around the cap of the calorimeter vessel and then around the upper portion of the mantle with a spiral length of the wires of about 30 cm between the two anchors. Good thermal contact of the insulated wires with the hardware was established with glyptal cement (GE Adhesive 7031). The wires were taken out of the vacuum through hermetic sealing plugs at the top flange.

The assembly is placed in a Dewar vessel which was used either empty or filled with a coolant, water, ice, Dry Ice, or liquid nitrogen, depending on the operating temperature.

3. The temperature scale

The thermocouple was calibrated against a standard platinum resistance thermometer (Leeds & Northrup #8164) which was originally calibrated on IPTS-68 at the U.S. National Bureau of Standards. There were 81 points of comparison between 80 and 423 K which were fitted to a five-term polynomial

$$E = \sum_{i=1}^{5} A_i T^{i-1}$$

by the least-squares method, where E is the electromotive force (emf) of the thermocouple. As the standard deviation of the least-squares fitting was 1.03 μV, the temperature determined should be accurate to within ± 0.01 K. However, the extraneous emf which inherently exists and can not be eliminated amounted to a couple of microvolts which also was a cause of temperature uncertainty. The emf of the thermocouple was determined with an integrated digital voltmeter (Takeda Riken, model TR-6656) and recorded on a digital printer (TR-6196) at pre-determined times (digital clock, TR-7414). The overall sensitivity was 123 μV K^{-1} at room temperature.

4. Operation of the calorimeter

Figure 2 is the block diagram of the apparatus. The calorimeter is usually operated with a constant (in terms of the emf) off-set of the difference thermocouple (conduction-mode). The output emf of the difference thermocouple was fed into a DC amplifier which can be biased to a preset suppression voltage. Its output was then fed into a PID controller and a DC power supply (Shinku Riko Co., models 5202, 5301, and 5405).

When operated in the conduction-mode, a small amount of dry air was used as the ambient atmosphere for heat-conduction. The system can also be operated in the adiabatic mode with the zero bias to the difference thermocouple and with the inside of the glass jacket evacuated.

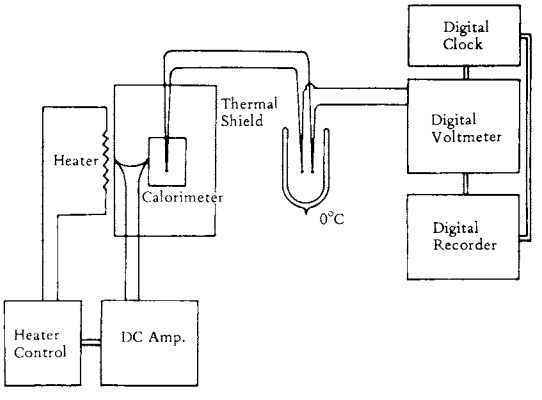

Fig. 2. Block diagram of the system.

The temperature of the calorimeter vessel is recorded on the printer at pre-determined time intervals which constitutes a cooling or heating curve in the conduction-mode. The bias voltage was chosen to be about 84 μV which corresponds to a difference in temperature of 2 K giving a cooling/heating rate of 0.20 K min^{-1} in the case of *n*-octadecane shown in Fig. 3. In certain cases, the off-set bias caused a significant temperature gradient in the calorimeter vessel to develop. However, the temperature difference between the two places on the calorimeter vessel where the thermocouples are attached can be measured by temporarily reducing the bias to zero during the freezing/melting halt. This was done with *n*-octadecane, indicating the difference to be 0.11 K. The correction of this magnitude was applied to the melting point data.

5. Examples of the results

Figure 3 is the cooling curve of *n*-octadecane obtained at the bias voltage of 84 μV as mentioned in the preceding section. Slight undercooling is seen which is followed by almost a horizontal halt corresponding to freezing. The small drift of the temperature due to the presence of impurities can be used to analyze for the impurity concentration. Thus, for a reasonably pure specimen, the observed 'equilibrium' temperature is given by

$$T_{obs} = T_m^* - \left(\frac{RT_m^{*2}}{\Delta H_f}\right) x f^{-1}$$

where T_m^*, ΔH_f, x, and f are the melting point of the ideally pure specimen, the molar heat of fusion, the impurity concentration in terms of mole fraction, and the fraction of the liquid. R is the gas constant. Figure 4 is such a 'purity plot' which gives x = 0.0129 and T_m^* = 301.33 K after being corrected for the temperature gradient of 0.11 K. A further purification of *n*-octadecane revealed the existence of a metastable solid phase immediately below the melting point, which appears only in the cooling run. This phase is transformed into the stable phase spontaneously.

n-Eicosane has also been found to exist in a metastable phase similar to that of *n*-octadecane.

In the cases of *n*-nonadecane and *n*-docosane, a solid-solid transition was recorded at 295.50 K

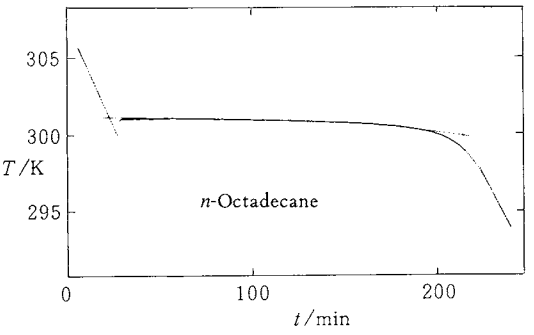

Fig. 3. Cooling curve of *n*-octadecane.

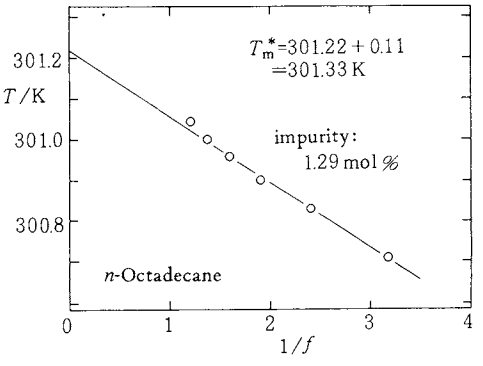

Fig. 4. Purity plot of *n*-octadecane.

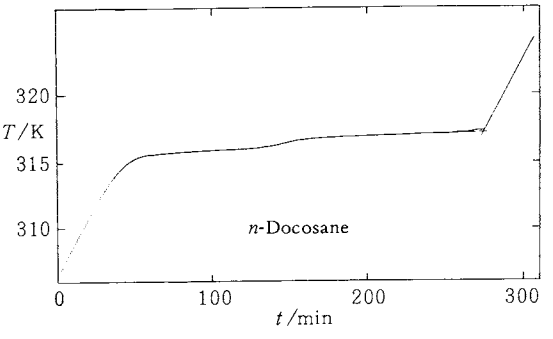

Fig. 5. Heating curve of *n*-docosane showing the existence of a solid-solid transition.

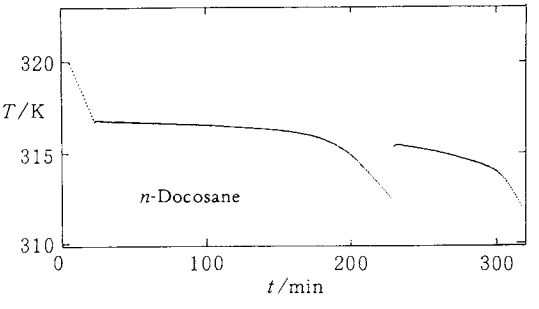

Fig. 6. Cooling curve of *n*-docosane.

Table 1. Temperatures of transitions found in the present study. Literature values[2] are given in square brackets.

	T_{tr}/K	T_m/K	T_m^*/K	
n-octadecane *n*=18		301.22 ± 0.10 (metastable) 300.17 ± 0.10	301.33 ± 0.15 (metastable) 300.27 ± 0.15	[301.3]
n-nonadecane *n*=19	295.50 ± 0.4 [295.2]	305.08 ± 0.10	305.15 ± 0.15	[305.2]
n-eicosane *n*=20		309.37 ± 0.10 (metastable) 309.22 ± 0.10	309.60 ± 0.2 (metastable) 309.34 ± 0.2	[309.8]
n-docosane *n*=22	317.04 ± 0.4 [316.2]	317.09 ± 0.10	317.19 ± 0.2	[317.2]

and 317.04 K, respectively.

The measured temperatures of the phase transitions are summarized in Table 1 and compared with the literature values[2]. The listed values correspond to purified specimens. Such transitions as those found in the present study are frequently difficult to observe by a differential thermal analysis particularly when they lie very close to the melting transitions.

It is interesting to note that the melting and the transition points of a series of *n*-alkanes fall on smooth curves as shown in Fig. 7 as a function of the number of carbon atoms in the molecule. The melting points of the metastable phases of *n*-octadecane and *n*-eicosane which are indicated by arrows in Fig. 7 also fall on the curve for the melting points of molecules having an odd number of carbon atoms. It can therefore be predicted that *n*-hexadecane and other even-numbered alkanes will also have metastable phases.

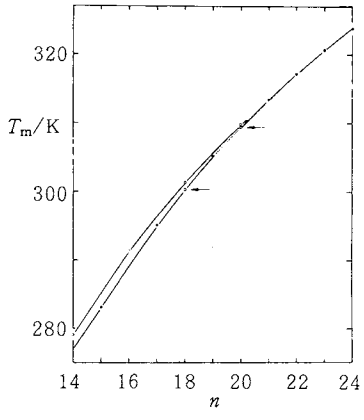

Fig. 7. Melting points of *n*-alkanes as a function of the number of carbon atoms. upper curve: triclinic crystal ⟷ liquid, lower curve: hexagonal crystal ⟷ liquid, arrows: melting points of metastable phases of *n*-octadecane and *n*-eicosane found in this study.

6. Discussion

The general performance of the calorimeter conforms the original objective of its design. One of the most crucial problems in relation to the use of the thermocouple in the determination of temperature is that a certain degree of uncertainties is inevitable because of the extraneous emf which arises for various reasons. This, however, can be coped with by using a standard material for which the transition temperature is known with high accuracy. The results as given in Table 1 are of satisfactory quality and are considered to serve routine purposes.

The temperature gradient on the surface and inside of the calorimeter vessel could not be eliminated even when the bias off-set was reduced to zero. This was because the heat leak from top of the glass jacket could not be ignored. Specimens in the pulverized form were melted in the calorimeter vessel prior to measurements, thereby improving the thermal homogeneity.

The calorimeter can be used to determine the heat capacity and the enthalpy change at a transition point if one employs a reference material for which these properties are known. Thus, the heating/cooling rate can be obtained to within ± 3 per cent in 2 min intervals and therefore the heat capacity values to within 5 per cent. The enthalpy change at a transition can be determined

with greater accuracy. In the case of *n*-octadecane (see Fig. 3), the horizontal halt lasted for as long as 190 min. The uncertainty in the enthalpy value, therefore, depends on the accuracy with which the bias off-set can be fixed. The error that arises from this cause was estimated to be less than 1 per cent.

An improved version of the calorimeter reported in this paper is commercially available, which has an additional thermal shield between the glass jacket and the heated mantle, thus eliminating the temperature gradient on the calorimeter vessel substantially. The use of chromel-P vs. constantan thermocouple was also helpful in minimizing the heat leak from the outside.

References

1) W. T. Ziegler, C. E. Messer, *J. Am. Chem. Soc.* **63**, 2694 (1941).
2) M. G. Broadhurst, *J. Res. Natl. Bur. Std.* **66A**, 241 (1962).

「第4回熱測定講習会」報告

本年の熱測定講習会は70名(内正会員13名，学生14名)の参加者を得て，7月5日，6日の両日にわたり「高温における熱測定」と題して，東京の全ラ連会館で開かれた。参加案内やプログラムの詳細は熱測定 **6**，No.2 ('79) の会告を参照されたい。初日は，高温熱測定の基礎(Ⅰ)，(Ⅱ)，既存装置の使いこなし方，高温熱分析などと題し，高温の定義，電気炉作成，温度測定，TG，DTA，DSC，EGAおよびEGDなどの基礎的講義が行われた。2日目は，高温材料の熱物性(Ⅰ)，(Ⅱ)，高温非定常熱測定，高温熱力学データーの検索と使い方などと題し，材料の機械的性質，熱的性質，レーザーフラッシュ法，Tempered Gibbs Energyなど，ややアドバンスな内容の講義が行われた。この種の講義をまとめて聴講できる講座は大学では開講困難であり，現役の大学院生，若いあるいは中堅研究者，技術者が熱心に受講し，活発な討論が行われた。参加者の専門分野も多岐にわたり，電気，機械，金属，セラミックス，化学，原子力，機器分析メーカーなど多くの分野で，表題のような高温技術が広く必要とされることをうかがわせた。テキストの各項目を見るかぎり，一部内容に重複があるように感じられたが，これは事の重要さに関連し，それぞれベテランの講師陣による個性ある解説により，色々な角度からの見方が披露され理解を深めることに役立ったことは幸であった。　　(世話人代表　谷口雅男)

「高温における熱測定」講習会テキスト　1部　3,000円
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