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DTA DETERMINATION OF SPECIFIC HEATS OF LIQUIDS

W. Balcerowiak

BLACHOWNIA" INSTITUTE OF HEAVY ORGANIC SYNTHESIS, 47–225 KEDZIERZYN–KOŹLE, POLAND

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A method is described for conversion of the experimentally measured total heat capacity of a sample of low-boiling liquid, heated in a closed, pressure-proof pan, to its specific heat.

The method initiated by O'Neill [1] for determination of the specific heats of solids by DSC is also used in DTA. Papers treating this subject have discussed the possibility of this method in the case of liquids too [2,3]. Attention has been drawn to the condition of constancy of the sample mass during the experiment [3]. However, liquid samples heated under isobaric conditions vaporize from open crucibles and the determination of their specific heat is then impossible by this means. In this situation the use of isochoric conditions is of promise. Freeberg and Alleman [4] first reported the use of closed, pressure-proof pans in DSC. The performance of DSC and DTA on liquid samples with pans of such type has been reported in many papers, mainly relating to the curing of phenolic resins [5].

In the present paper the use of isochoric conditions for the liquid sample (vapour – liquid system) to determine the specific heats of liquids by means of DTA is described.

Physical principles

The heat flux $\frac{dq}{dt}$ flowing to a sample (when it is heated) is related to its heat capacity C_s:

$$\frac{dq}{dt} = C_s \cdot \frac{dT}{dt} \tag{1}$$

where dT/dt is the heating rate.
In quantitative DTA we have:

$$\frac{dq}{dt} = \frac{\Delta U}{E} \tag{2}$$

where the voltage signal of the differential thermocouple $\Delta U = \beta \cdot \Delta T$; β is the sensitivity of the thermocouple, ΔT is the differential temperature, and E is the caloric sensitivity of the apparatus. If the empty pan is used as a reference, the expression resulting from Eqs (1) and (2):

$$\Delta U = E \cdot C_s \cdot \frac{dT}{dt} \tag{3}$$

underlies the principle for determination of the total heat capacity of the sample by means of DTA.

When the sample is a thermally stable solid or a non-volatile liquid, and it is heated under isobaric conditions:

$$C_s = m_s \cdot c_p \tag{4}$$

where m_s is the mass of the sample, and c_p is its specific heat under the constant pressure. Equations (3) and (4) then afford possibilities for the comparative determination of c_p by means of DTA.

When a volatile, low-boiling liquid is heated under isobaric conditions it vaporizes. The experimentally determined, total heat capacity of such a sample is

$$C_s = m_{liq} \cdot c_p + L \cdot \frac{dm}{dt} \tag{5}$$

where m_{liq} is the momentary quantity of the liquid phase, and L is the heat of vaporization. Thus, it is not possible to determine the specific heat of a liquid from measurements of the heat capacity of a sample of it under isobaric conditions by means of DTA as well as DSC. The same conclusion is easily reached for sublimating solids and systems with volatile elements.

When a sample of low-boiling liquid fills only part of the closed pan, at constant temperature it is in equilibrium with its saturated vapour. If the temperature is not constant, but is slowly changed, there are quasi-equilibrium conditions inside the pan. The momentary heat capacity of the sample system in the pan is then

$$C_s = (m_{liq}c_{liq} + m_{vap}c_{vap} + L \cdot V_{vap} \cdot \frac{d\rho}{dT}) \tag{6}$$

where m_{liq} and m_{vap} are momentary quantities for the liquid and the vapour, $m_{liq} + m_{vap} = m_s$, c_{liq} and c_{vap} are their specific heats, while V_{vap} is the volume, and ρ is the density of the saturated vapour.

It is easy to establish that

$$\lim_{V_{vap} \to 0} C_s = \lim_{V_{vap} \to 0} (m_{liq}c_{liq} + m_{vap}c_{vap} + L V_{vap} \frac{d\rho}{dT})$$

$$= m_s c_{liq} \tag{7}$$

As the condition $V_{vap} \to 0$ is tantamount to $m_s \to m_{max} = V_c \cdot \rho_{liq}$, where V_c is the total pan capacity (volume), and ρ_{liq} is the density of the liquid, we have:

$$\lim_{m_s \to m_{max}} \frac{\Delta U}{m_s \cdot E \cdot \frac{dT}{dt}} = c_{liq} \tag{8}$$

This expression supplies the principle for determination of the specific heats of liquids from measurements of their heat capacities by means of DTA using closed pans.

Practical considerations

The determination of the specific heat of the liquid resolves itself into measurements involving the method for determination of the specific heats of solids by means of DTA as well as DSC [1–3] for:

(i) the closed, empty pan;
(ii) a few masses of a standard liquid (the specific heat of which is known);
(iii) a few masses of the examined liquid.

From a comparison of the DTA curves for scans (i) and (ii) the values of

$$A = \frac{\Delta U}{c_p \cdot m_s \cdot \frac{dT}{dt}} \tag{9}$$

are computed at selected temperatures and the caloric sensitivities E are found by extrapolation of the A values to $m_s = m_{max}$ at each individual temperature. These values of E are then used to compute, at the same temperatures, values of

$$B = \frac{\Delta U}{E \cdot m_s \cdot \frac{dT}{dt}} \tag{10}$$

for the examined liquid, taking the ΔU values from a comparison of the DTA curves for scans (i) and (iii). Extrapolation of the computed B values to $m_s = m_{max}$ yields values of c_{liq} at selected temperatures.

When the function $\rho_{liq} = \rho_{liq}(T)$ is known for the standard liquid as well as for the examined one, the extrapolation at any temperature can be made to the m_{max} value resulting from the density of the liquid at this temperature. However, for examined liquids this function is rarely known. It must then often be assumed that the m_{max} values are the same within the temperature range of measurement.

Example

To illustrate the above considerations, the course of the determination of the specific heat of *liquid benzene in the temperature range* 60—100° is described. Benzene of p.a. grade from POCh Gliwice was used. DTA (heat-flux DSC in the Mackenzie classification [6])was carried out with a Mettler TA 2000 A apparatus. High-pressure-proof, stainless steel pans were used, the covers of which could be screwed down. Their total capacity was 0.5 cm^3. The experiments were performed at a heating rate of 1.2 deg/min, between the isotherms at 35 and 1000°. Distilled water was used as standard liquid and an empty pan as reference.

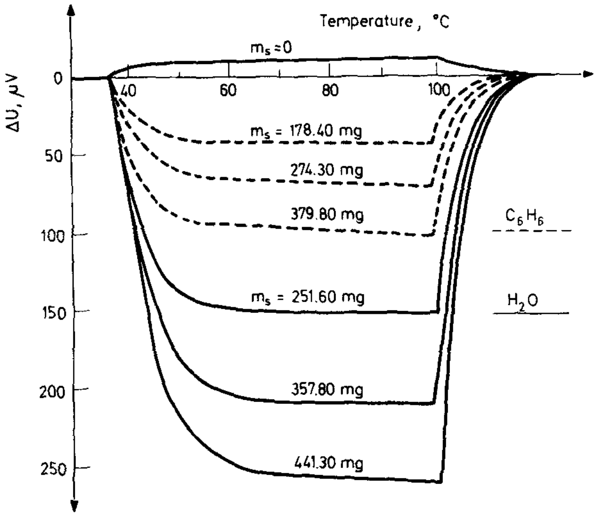

Fig. 1 DTA curves for different weighed portions of benzene and water

DTA curves recorded during the experiments are shown in Fig. 1. It was found that, in the temperature range 60—100°, the *A* values computed for water according to Eq. (9) are in linear relationship with m_s. This interdependence was then described by linear equation at each temperature and extrapolated to the same value of m_{max}, resulting from the density of water at 80° (972 mg/cm^3). It was established that in the examined temperature range the caloric sensitivity of the apparatus was practically constant. *B* values were next computed for benzene. Their dependence on m_s was also described by linear equations and extrapolated to m_{max} resulting from the density of benzene at 80° (815 mg/cm^3). In Fig. 2 both the *A* (for water) and *B* (for benzene) values at 80° are shown. Figure 3 gives the values found for the specific heat of benzene in the temperature range 60—100° in comparison with literature data [7].

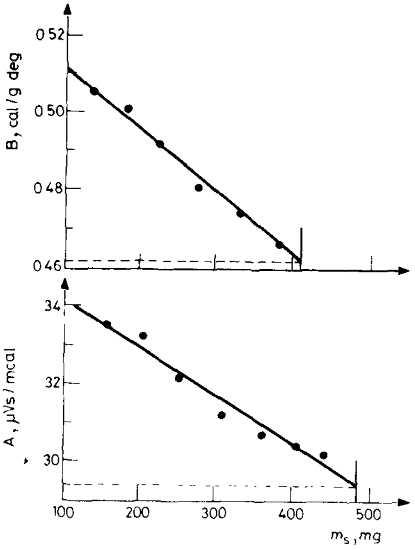

Fig. 2. Interdependence of *A* and *B* values on m_s at 80°

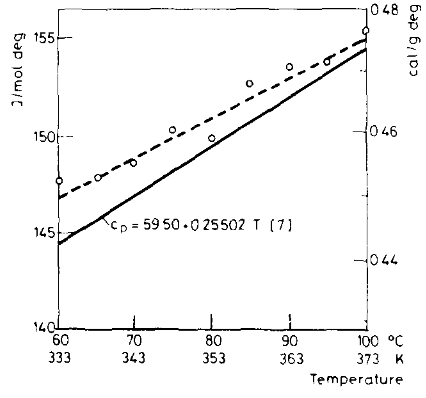

Fig. 3 Dependence of specific heat of liquid benzene on temperature

Discussion

The essence of the measurement of specific heat appears to be appropriate regard to the processes accompanying the heating of the sample and influencing the measured total heat capacity. The method suggested for the conversion of the experimentally measured total heat capacity of a sample of low-boiling liquid, heated in a closed pan, to its specific heat, can solve this problem, in relation to both DTA and DSC.

As pans and samples of relatively high heat capacities are used, Laye's considerations about the sources of error [3] are of great importance. All measurements must then be made with great care to ensure an acceptable accuracy of the results.

The suggested method of determination gives values of the specific heats of low-boiling liquids accurate to about 5 per cent, which seems to be sufficient for utilization in engineering design and engineering calculations, especially when the heat balance of a chemical reactor is concerned.

The determined specific heat is in nature the specific heat at constant pressure.

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Zusammenfassung — Es wird eine Methode zur Bestimmung der spezifischen Wärme aus der experimentell bestimmten totalen Wärmekapazität von niedrigsiedenden, in der geschlossenen drucksicheren Pfanne erhitzten Flüssigkeiten beschrieben.

Резюме — Описан метод перехода от экспериментально определяемой общей теплоемкости для образцов низкокипящей жидкости, нагретой в закрытом сосуде под давлением, к ее удельной теплоемкости.