DTA DETERMINATION OF SPECIFIC HEATS OF LIQUIDS

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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 \( C_s \):

\[
\frac{dq}{dt} = C_s \cdot \frac{dT}{dt}
\]  

(1)

where \( \frac{dT}{dt} \) is the heating rate.

In quantitative DTA we have:

\[
\frac{dq}{dt} = \frac{\Delta U}{E}
\]  

(2)

where the voltage signal of the differential thermocouple \( \Delta U = \beta \cdot \Delta T \); \( \beta \) is the sensitivity of the thermocouple, \( \Delta T \) 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):

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

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:

$$C_s = m_s \cdot c_p$$

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

$$C_s = m_{liq} \cdot c_{liq} + L \cdot \frac{dm}{dt}$$

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

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

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 $\rho$ is the density of the saturated vapour.

It is easy to establish that

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

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