THE INSTRUMENT CONSTANT IN DTA.
THEORY OF SENSING UNITS IN DTA INSTRUMENTS

I. State of the art

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The theory of block-type sensing units is reviewed. The two-point method of DTA is described and appropriate computation formulae are derived. The failure of the existing block-type sensing units to conform to the assumptions of the theory is demonstrated.

The instrument constant (calibration constant) is by definition the proportionality coefficient between the experimentally determined heat of reaction and the peak area under the differential curve corresponding to this reaction:

$$\Delta H_t = \Delta H_0 M = -KA_t$$

where $\Delta H_t$ is the total heat of reaction, J; $\Delta H_0$ is the specific heat of reaction, J/g; $M$ is the mass of the reactant, g; $K$ is the calibration constant; and $A_t$ is the total peak area under the DTA curve. The minus sign in Eq. (1) indicates that positive heats of reaction correspond to negative peak areas, i.e. in the case of an endothermic reaction the DTA curve bends downwards from the base line (towards negative temperatures). If $A_t$ is expressed in cm$^2$, the dimension of $K$ is J/cm$^2$; if it is expressed in deg.$^\circ$s, the dimension of $K$ is W/deg.

To find unknown heats of reaction by means of Eq. (1), it is necessary to determine the value of $K$, i.e. to calibrate the instrument. For this purpose, the following methods exist:

1. A set of standard substances with known heats of transformation are used, yielding the value of $K$ in the studied temperature interval by means of Eq. (1).

2. Instead of a reference material, a calibrated microheater is placed in the corresponding cell of the instrument and a known current is passed through it. $K$ is found by the formulae
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\[ K = \frac{Q}{A_t} = \frac{I^2Rt}{A_t} \quad (a) \]
\[ K = \frac{C^1U^2}{2A_t} \quad (b) \]

where \( Q \) is the joulean heat evolved in the cell, \( I \) is the current intensity, \( R \) is the resistance of the microheater, and \( t \) is the period during which current passes through the heater. Formula (2b) is applied in cases when calibration is carried out by means of an electrolytic condenser with the known capacity \( C^1 \), charged from a source with voltage \( U \). The condenser is discharged through the microheater, evolving heat equivalent to the electric energy of the condenser.

3. For instruments in which insulated sample holders are applied [1], the tail-end of the peak to the right of the end-point of the reaction (the inflexion point) is used, and \( K \) is found from the formulae

\[ C \frac{d\Delta T_n}{dt} \quad (a) \]
\[ K = \frac{\bar{C}}{A_n} \Delta T_n \quad (b) \]

where \( C \) is the total heat capacity of the sample holder and the sample, \( A_n \) is the area of the peak confined within the height of the peak \( \Delta T_n \), the base line and the tail-end of the DTA curve, and \( \frac{d\Delta T_n}{dt} \) is the slope of the tangent to the curve at the point with peak height \( \Delta T_n \).

4. Constant \( K \) is calculated from the known thermophysical and geometric parameters of the sample holder and the sample.

The value of constant \( K \) depends (in the general case) on many factors, such as the experimental temperature, the gas medium in the cell, the state of the sample, the geometry of the sample holder, etc. During the change from calibration conditions to experimental conditions, some of these factors may change, resulting in a change of \( K \) to an unknown extent; this major deficiency in calibration methods 1 and 2 is eliminated to a certain extent in method 3, for in this method constant \( K \) is determined directly at the moment of the experiment, in the process of recording the thermal curve. With method 4, the accuracy of calibration depends on the extent to which the mathematical model by which the explicit expression for constant \( K \) is derived corresponds to the true DTA instrument. The potential of method 4 has not been studied satisfactorily in the literature. An explicit expression for \( K \) has been developed only for block-type instruments [2–4] for the particular case of heat exchange by conduction, without accounting for convection and radiation. In principle, various types of DTA instruments are feasible, to each of which a particular kinetic equation and instrument constant correspond. In this paper an attempt is made to classify DTA instruments on the basis of the physical and geometric characteristics of the heat barrier and of the mathematical assumptions.