Numerical treatment of cooling and heating curves at thermal analysis

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Voltage of PtRh10—Pt thermocouple was measured by a digital voltmeter and recorded on a punched tape. Numerical treatment of the record of cooling or heating curve makes it possible to measure the temperature of primary crystallization with reproducibility 0.1 K. Application of the method is demonstrated on the example of determination of temperature of fusion of pure salts.

Напряжение термопары PtRh10–Pt снималось цифровым вольтметром с переносом на перфаленту. Численная обработка записи кривой охлаждения позволила определить температуру первичной кристаллизации с воспроизводимостью 0,1 K. Использование метода демонстрируется на примере определения температуры плавления чистых солей.

The equilibrium between phases can be determined using a series of different methods. Often used, especially at higher temperatures, is the method of thermal analysis (TA) which is based on the registration of cooling or heating curves. The obtained data are important for technological and also theoretical applications because a theoretical treatment of a phase diagram can furnish information on the structure of solid and liquid phases. However, the theoretical analysis can be done successfully only if we possess reliable and sufficiently accurate experimental data. In this work a method for numerical treatment of cooling and heating curves is described which allows substantial improvement of sensitivity and reliability of the TA method.

Experimental

The cooling and heating curves were registered using an apparatus consisting of a vertical shaft furnace (length 600 mm, inner diameter 60 mm) heated by three resistance wire heating elements. Homogeneous temperature field was 70 mm high. The furnace was equipped with a programmable unit which allows to control the rate of decrease or increase of temperature in the region 0.5—5 K min^{-1}. The furnace and all electronic equipments

were grounded and galvanically separated from network by means of transformers, which helped to minimize noise in measured thermoelectric voltage. Temperature was measured by means of PtRh10—Pt thermocouple (Safina, Czechoslovakia). The cool junction of the thermocouple was immersed in mercury placed in stirred crushed ice mixed with distilled water and kept in a Dewar flask. Calibration and stability checking of the entire system was carried out three times during the acquisition of one set of data. The measurement was carried out in a flow of dry nitrogen (20 cm^3 min^{-1}). Geometry of the experimental arrangement was kept constant (position of platinum crucible, position of thermocouple, level of the melt — its volume being 60—70 cm^3).

The thermoelectric voltage was measured in 5-s intervals by a digital voltmeter MT-100 (Metra, Blansko), the sensitivity of which is 1 μV, and transferred and stored on a punched tape. The data were further treated using the programmable calculator HP 9821A to which was connected the plotter HP 9862A. Details concerning the transformation of parallel BCD code (output of voltmeter) to series ASCII code (input of calculator) are described in [1].

Treatment of the digital record of an analogue signal

By a classical TA method, the cooling curves are registered by means of a recorder. However, if a digital voltmeter is used for measurement of thermoelectric voltage the output values can be recorded in constant time intervals on paper tape or by means of another appropriate method. It is the first step for numerical treatment of the experimental data. The experimental values of the thermoelectric voltage are partially depreciated by random errors caused mainly by fluctuation of temperature. Smoothing of digital representation of analogue signals can be done using the method of regression analysis described by *Savitzky* and *Golay* [2]. This method is well-suited to off-line or on-line computers and, of course, it is not limited only to the treatment of TA data.

The principle of the method is as follows. The sequence of the thermoelectric voltage data, corresponding to the dependent variable y, is stored on a paper tape. Independent variable x equals time measured from the beginning of measurement. Because the time intervals between "sampling" of voltage are constant time is proportional to the number of samplings and we do not need to know the absolute value of time. Smoothed value f_0 in the centre point of a given set of data can be calculated as the weight average, or convolution, by multiplying the y values by the corresponding C_i constants [2, 3]

$$f_0 = \sum_{-l}^{+l} \frac{C_i y_i}{F} \qquad (1)$$

where F is an integer constant (normalizing coefficient), i is the integer and runs from $-l$ to $+l$ for $2l + 1$ consecutive values. In this work we used for smoothing of experimental data five points and a quadratic polynomial.

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To obtain the next convolute at the next point the paper tape is slid by one value y and the process is then repeated. The constants C_i can be obtained in many ways, *e.g.* by fitting $(2l+1)$ x, y values to a polynomial using the least-squares method. In our case $(l=2)$ the smoothed value f_0 in the centre of five points can be obtained using the relation

$$f_0 = (-3y_{-2} + 12y_{-1} + 17y_0 + 12y_1 - 3y_2)/35 \qquad (2)$$

The signal-to-noise ratio increases approximately with the square root of the number of points $(2l+1)$, used in the convolution set. However, we cannot use too much points because of danger that we could "smooth" also the temperature effect we are looking for. The results can be improved by enhancing the frequency of sampling and/or by repeating the smoothing procedure.

An example of smoothing of a cooling curve is shown in Fig. 1 (curve *1a* corresponds to original data, curve *1b* is twice smoothed).
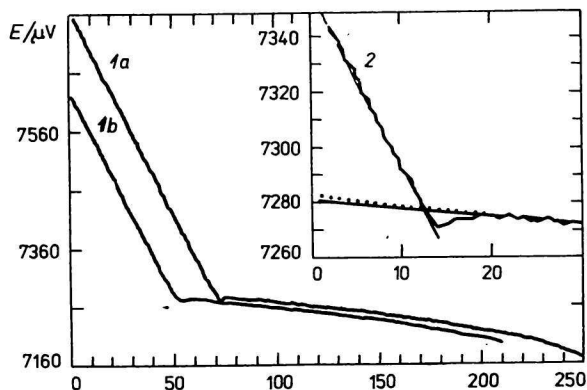

Fig. 1. Numerical treatment of cooling curve of sodium chloride.
1a. Original record of the cooling curve; *1b*. the cooling curve twice smoothed; *2*. magnified part of the cooling curve.
————— Fitting with the polynomial of the first degree;
· · · · · · fitting with the polynomial of the second degree.

In a similar way as smoothing also the first and the second derivative of the signal can be obtained, which can be used for the determination of an extremum on the studied curve [2, 3].

The treatment of cooling or heating curves becomes much simpler if we can use a plotter connected with calculator or computer. Then it is possible with relatively simple programs to magnify a selected part of the experimental curve and to treat it using the methods of regression analysis. In the case of cooling and heating curves we found that it is sufficient to replace parts of these curves by the first or second

degree polynomial. The corresponding temperature of phase transition is obtained as the intersection of these polynomials. The complete procedure of the determination of temperature of phase transition by this method is following:

1. Thermoelectric voltage is recorded on a paper tape with constant timing.

2. Data are transferred from the paper tape to calculator.

3. Optimum scale of graph is calculated and the data are plotted (curve *1a* in Fig. 1).

4. If desired, it is possible to choose an arbitrary part of the curve and plot it again using another scale. *E.g.*, the curve *2* in Fig. 1 corresponds to a magnified part of cooling curve with the studied temperature effect.

5. We choose on the curve the regions before and after "break". Then using the method of least squares we replace the parts of the curve by the polynomial of the first or second degree. Dependent variable is the thermoelectric voltage of thermocouple, independent variable is the sequence of measurement. In Fig. 1 the straight lines were fitted to the data between the numbers 1—13 and 20—35.

6. The coordinates of the intersection of these two lines are calculated. The ordinate corresponds to the searched thermoelectric voltage.

The method was tested by the determination of melting points of pure salts and their mixtures which are often used as secondary standards for calibration of thermocouples (KNO_3, eutectic mixture $NaCl$—Na_2SO_4, KCl, $NaCl$, Na_2SO_4, NaF). Regarding sensitivity of the method it is necessary to know exactly the purity of chemicals used. *E.g.*, an addition of 0.3 mole % of foreign substance which yields in the melt $NaCl$ one new particle results in a decrease of temperature of fusion by *ca.* 1 K. If the substance yields more new foreign particles the situation is even more unfavourable.

The reproducibility of the method was tested by measurement of the temperature of solidification of sodium chloride (Merck, anal. grade). The following set of 11 values of thermoelectric voltage (μV) was obtained: 7287.4, 7287.5, 7289.8, 7287.7, 7286.2, 7286.8, 7286.9, 7286.7, 7287.1, 7286.6, 7287.4. Mean value of the voltage is 7287.3 μV, standard deviation 1 μV. Similar results were obtained for the other studied systems. However, it should be pointed out that higher sensitivity of the discussed method (which can be further enhanced using more sensitive voltmeter and higher frequency of sampling) can be utilized only if the whole experiment is carried out very carefully.

References

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