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BASELINE INTERPOLATION IN DTA AND DSC QUANTITATIVE ANALYSIS OF SLOW PROCESSES

D. VUČELIĆ, A. STAMATOVIĆ* and U. TODORIĆ

Department of Physical Chemistry, Faculty of Sciences,
and Institute for Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia

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A simple method is described for use with the differential scanning calorimeter for baseline interpolation in continual processes over a wide temperature interval. For the process of water desorption from the synthetic zeolite LiA with the coverage $\theta = 1.5$, the measured heat of desorption was $Q = 11.2 \pm 0.5$ kcal/mole.

One of the basic conditions for DTA and DSC quantitative analysis is good baseline interpolation. In the case when the measured and the reference samples have similar thermal capacities the baseline is a linear function of the temperature, and quantitative analysis by one of the proposed methods [1–7] yields satisfactory results. In practice, however, the baseline is very often a curve, but for relatively fast processes or those taking place in a narrow temperature interval one can always find a reference substance of thermal characteristics such as to produce a linear baseline whose interpolation is not difficult. On the other hand, for processes taking place within wide temperature range, such as sorption–desorption, the quantitative thermal analysis does not give satisfactory results because the interpolation of the baseline is very difficult. Fig. 1a, curve I, shows the desorption of water from the synthetic zeolite LiA, obtained on the DSC-1B Perkin–Elmer calorimeter. The corresponding baseline in Fig. 1b, curve I, is complex not only for this sample but also for all others, so it is not suitable for routine linear interpolations.

For quantitative analysis in such cases, it is possible to record first a desorption curve for the zeolite with water and then after the water removal (at about 500°) to record a curve for the dry zeolite, under the same conditions and within the same temperature interval. The area under the peak, which represents the real process of water desorption, can be obtained from the difference between the curves either graphically or by a computer.

However, the problem can easily be solved if the output voltage from the DSC during the first run of the desorption curve is stored in some kind of memory, and during the second run of the dry zeolite, the difference of the two signals is plotted at the chart recorder. The curves obtained by this experimental procedure correspond to the existing process except that they are inverted because the process

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* Permanent address: Institute of Physics, Belgrade P. O. B. 57, Yugoslavia.

curves are subtracted from the background, but this can be overcome by simple inversion of the recorder leads.

Direct recording and play-back of the slowly changing DC signal is rather difficult. The problem can be solved by converting DC voltage into frequency, which can then be recorded on a tape recorder and during the play-back converted back

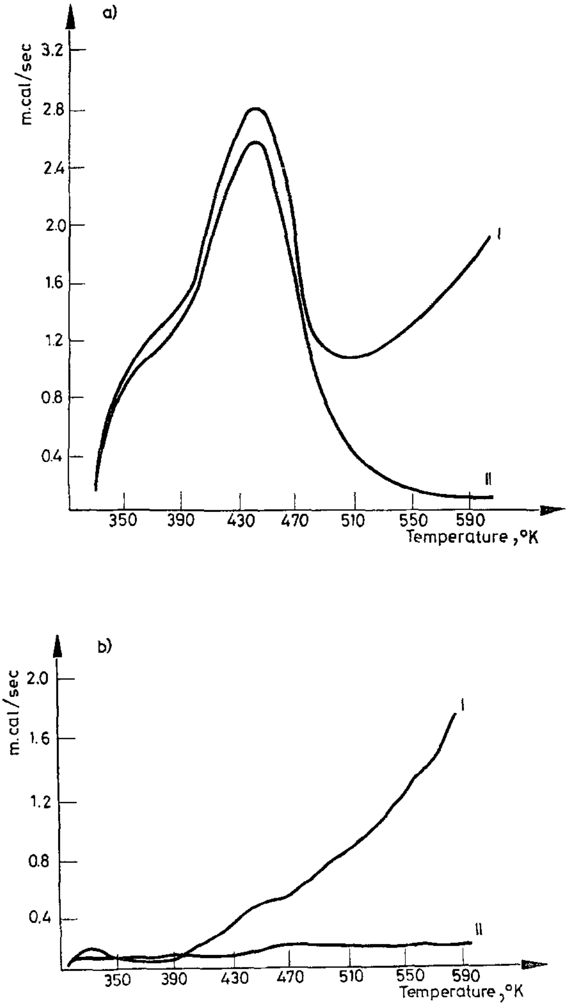

Fig. 1. Thermal analysis of water desorption from LiA zeolite (32.92 mg with 16.8% sorbed H_2O, scan speed 4°C/min). (a) Curve I — water desorption without compensation of the baseline; Curve II — desorption with compensation of the baseline. (b) Curve I — baseline of the measured sample (zeolite without water); Curve II — baseline after compensation of the signal from the DSC with the signal from the tape recorder

to DC signal by a simple frequency meter. A block diagram of such a supplement to the DSC apparatus is shown in Fig. 2. Fig. 2a shows a recording of the process curve in parallel with a chart recorder. Fig. 2b represents the difference of the voltage from a tape-recorded signal and the voltage signal from the dry zeolite. The results obtained with the DSC-1B Perkin-Elmer calorimeter, for which we have constructed the supplement, are shown in the same figure. In order to clarify the explanation, we have divided the whole process into three instead of two operations as described above.

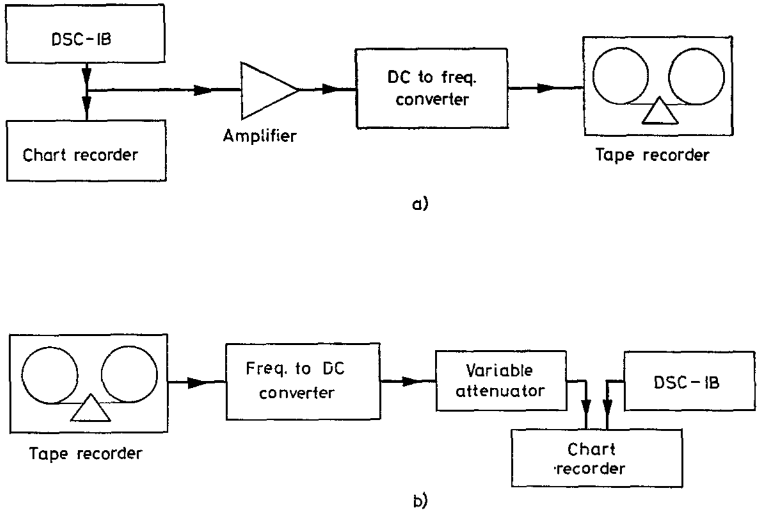

Fig. 2. Recording (a) and play-back (b) diagrams for baseline interpolation

The zeolite was pressed in an aluminium sample pan, placed on a quartz spiral and degassed in vacuum (10^{-3} torr) at 400°C for two hours. A fixed amount of water was then sorbed. The samples thus prepared were investigated within the temperature range 310–370°K (Fig. 1a, curve I). As can be seen, the baseline interpolation cannot be performed nor the desorption temperature heat determined from the area under the peak. Nitrogen was then passed through the DSC in order to remove the released water, and the sample was cooled to 310°K. The results are shown in Fig. 1b, curve I. Curve II in the same figure represents the baseline in play-back procedure when the recorded signal is counterconnected to the output of the DSC. It is clear that a fairly good baseline was obtained finally; the water was absorbed again on the same sample and the results of the thermal analysis, after coupling the supplement to the DSC, are shown in Fig. 1a, curve II. From the difference from curve I, the obtained curve II offers the possibility for quantitative analysis. Hence, the obtained value $Q = 11.2 \pm 0.5$ kcal/mole for LiA is in good agreement with $Q = 11.4$ kcal/mole for Li obtained with a classical Calvet type differential calorimeter, for the same coverage $\theta = 1.5$.

This modification of the DSC apparatus has been proved to be useful, and similar applications are possible in DTA as well as in other cases where a slowly changing signal has a considerable background masking of the basic process.

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