Thermochimica Acta, 90 (1985) 9–14
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EXPERIMENTAL STUDY ON BASELINE DRIFTS OF A TIAN–CALVET TYPE CALORIMETER

A. SANAHUJA

Department de Termologia, Facultat de Fisica, Universitat de Barcelona, Diagonal 645, 08028 Barcelona (Spain)

(Received 28 January 1985)

ABSTRACT

The stability of a Tian–Calvet type calorimeter used in enthalpy of solution determinations has been analysed. The mechanical action necessary for starting the solution process causes a permanent drift on the baseline. The influence on the total energy involved in a solution process has been quantitatively determined by a series of blank experiments (without real solution process). As a result of this experimental study a baseline correction method is proposed.

INTRODUCTION

Tian–Calvet type calorimeters [1] have been used for the measurements of partial molar enthalpy, enthalpy of formation, enthalpy of solution, enthalpy of mixing and enthalpy of adsorption.

A Tian–Calvet type calorimeter was built in our laboratory to measure the enthalpy of a solution as a function of temperature at low concentrations. In this calorimeter, before the solution was established, the sample placed in one of the calorimetric cells is allowed to reach thermal equilibrium and a stable baseline is obtained. When heat is evolved by a solution process the thermopiles register the change in temperature between the calorimetric cell and the isothermal block. Since heat is transferred to the block, the output peak decays to the original baseline. The total energy is obtained from the area of the thermogram. Thus, the baseline stability is of great importance for accurate measurements, principally at low values of the heat involved.

Previous analysis of the baseline fluctuations in these calorimeter types [2] indicated three possible factors.

(1) Unequal thermal contacts of the thermopiles between the two calorimetric units.

(2) Thermal and electrical noise through the thermopiles.

(3) Temperature fluctuations of the isothermal block due to imperfect control and changes of room temperature.

0040-6031/85/$03.30

The mechanical action necessary to start the solution process can also produce baseline drifts.

In this paper these factors are analysed and different correction methods for baseline drift are discussed.

EXPERIMENTAL

The calorimeter used is of Tian–Calvet type which is described in detail in a previous work [3]. It was adapted for working at different temperatures. The uncertainty of the temperature determinations was ±0.005 K. A test of stability shows that the temperature was kept constant within ±0.005 K over 12 h. In order to avoid errors which are related to the manipulation process, an electrical calibration is carried out before and after each measurement. Before the solution was performed the sample was located in two stainless-steel cylinders which were closed with two teflon plugs. Each plug had an O-ring that fitted perfectly into the cylinder and prevented the sample from humidifying. Plugs and the sample were dropped into the solvent by a piston pressed by a 1 rpm synchronous motor. The effect of the plugs was measured previously by blank experiments.

The calorimeter response (thermogram), pre-amplified, was measured on a microprocessor based on a digitial voltmeter.

The experimental system was located in a room with a temperature fluctuation of ±0.5 K.

ANALYSIS OF THE BASELINE STABILITY

After the calorimeter had reached thermal equilibrium, the electrical and thermal noise (short-time noise [1]) was ±0.1 μV. Short-time noise was obtained from peak to peak on the output signal at 10-min intervals. The baseline had a repeatability (long-time noise [1]) of ±0.2 μV over 12 h. Long-time noise was calculated as the difference between the means of output signal over successive 10-min intervals.

The repeatability of the baseline before and after measurements of a heat flux by means of an electrical heater (i.e., electrical calibration) was within ±0.1 μV. This type of the baseline "drift" must be assigned to the category of long-time noise and limits the calorimeter resolution to ±0.01 J.

When measuring the heat involved in a real solution process the observed behaviour of the baseline became worse. The baseline drifts increased to 1–4 μV in a systematically endothermic sense. Therefore, the resolution decreases from ±0.1 to ±0.5 J. The same baseline behaviour was observed in blank experiments where only plugs were dropped into the solvent. Therefore, the baseline drifts were caused by mechanical action.

BASELINE CORRECTION

In order to obtain accurate measurements of the enthalpy of solution, it is principally necessary to correct the baseline at low concentrations. The two standard possibilities are:

(1) a linear correction;

(2) a Heaviside correction.

The first possibility was more suitable when the effect that produced the baseline drift remained throughout the total measurement time, i.e., differential scanning calorimeters where the temperature was varied linearly with time [4–6], or when the heat of stirring and constant heat leaks to or from the outside cause the baseline to drift steadily [7].

For flux calorimeters in isothermal mode, where the temperature of the block was controlled to a constant value and baseline drifts were produced by a short-time effect, corrections by a Heaviside function were more appropriate.

The experimental information provides a possible alternative for correcting the baseline. The thermogram of a blank experiment is shown in Fig. 1. z_i and z_f are the baseline values before and after plugs have been dropped into the solvent. $\Delta z = z_f - z_i$ represents the drift. The striped area is proportional to the energy E' which is related to the thermal and mechanical effects of the plugs. Plots of $E'_{1,2}$ vs. Δz for each one of two set of plugs are shown in Figs. 2 and 3, respectively. One can assume a linear relationship between $E'_{1,2}$ and Δz

$$E'_{1,2} = A_{1,2} + B_{1,2}\Delta z$$

where $A_{1,2}$ represents the thermal effect of the plugs.

The slopes and intercepts of the plots have been calculated by the least-squares linear regression method. The results of such a calculation are reported in Table 1 with the calculated values of the error. r is the correlation coefficient and N is the number of experimental data. The relative error does not exceed 2% in the determination of $B_{1,2}$. The relative error of $A_{1,2}$ is very high, exceeding 30%. This shows that the thermal effect of plugs is poorly reproducible. The error in $A_{1,2}$ can be represented as an

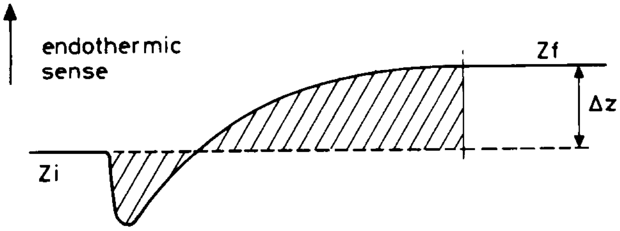

Fig. 1. Thermogram of a blank experiment.

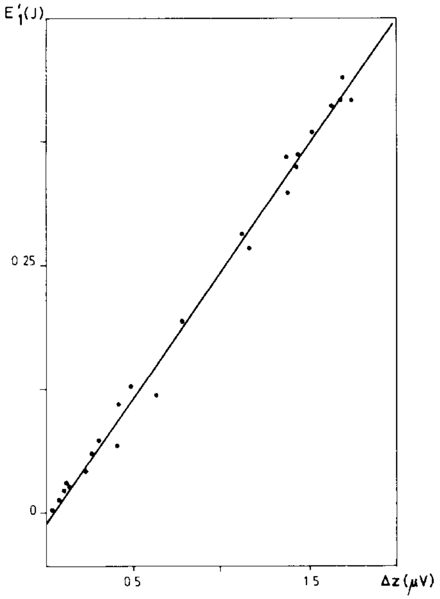

Fig. 2. E_1' values vs. Δz obtained in a series of blank experiments.

intrinsic noise of the system which limits its sensitivity and the accuracy of calorimetric measurements.

The thermogram of a solution process is shown in Fig. 4. The thermal and

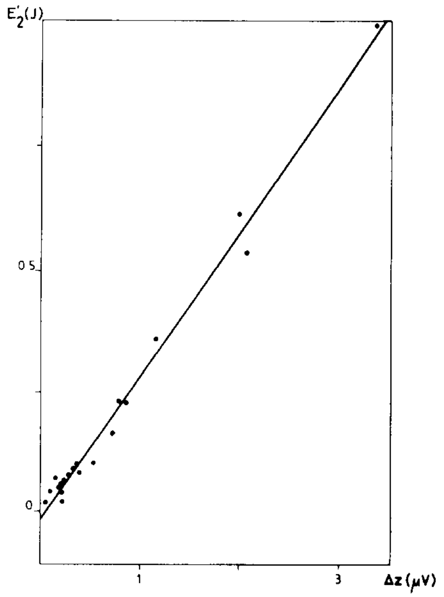

Fig. 3. E_2' values vs. Δz obtained in a series of blank experiments.

TABLE 1

Constants for the least-squares fit of the experimental data obtained in blank experiments

	N	$B_{1,2}$ (J μV^{-1})	$A_{1,2}$ (J)	r
1	24	-0.012 ± 0.005	0.225 ± 0.005	0.993
2	25	-0.016 ± 0.005	0.263 ± 0.005	0.995

mechanical effects of plugs can be simultaneously corrected. Area I (discontinuous outline) is proportional to the energy E'' which is related to the heat involved in the solution process and plug effects. Area II (dotted area) is proportional to the energy E which is related to the enthalpy of solution. E can be obtained by subtraction of E'' and $E'_{1,2}$.

Two examples of calorimetric molar enthalpies of solution of NaCl in water at 313.15 K corrected by the three methods are reported in Table 2. We have accepted for the enthalpy of solution at the given molality the value obtained by the third correction type.

All figures given in this paper obviously only relate to our system. They will be different for another system of the same kind with any mechanical action used to start the solution process [8]. The relationship between E' and Δz must be determined, therefore, for each system by previous blank experiments.

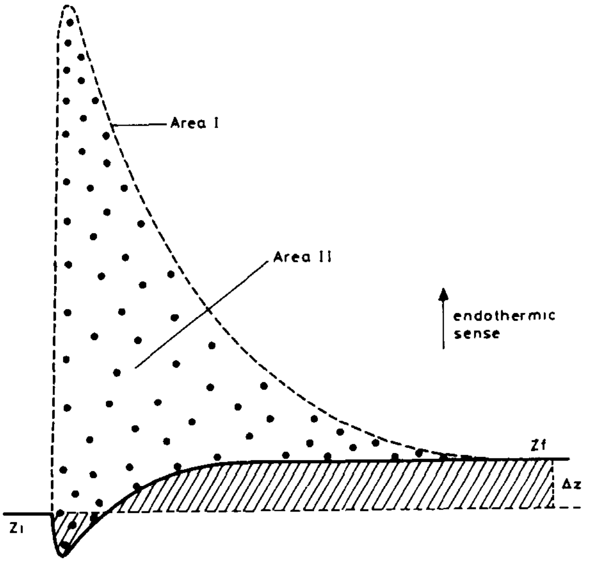

Fig. 4. Thermogram of a solution process (discontinuous outline). The continuous line represents the baseline evolution determined in previous blank experiments.

TABLE 2

Calorimetric molar enthalpies of solution of NaCl in water at 313.15 K corrected by a linear function, a Heaviside function and the proposed method

Correction method	m (mol kg^{-1})	n_s (mol)	Δz (μV)	E (J)	$\Delta \bar{H}_s(m, 313.15)$ (cal mol^{-1})
Linear	0.0352	1.20968 10^{-3}	1.1	3.23	638
Heaviside				3.12	616
Proposed				3.07	607
Linear	0.0435	1.51404 10^{-3}	4.0	4.85	766
Heaviside				4.38	691
Proposed				4.11	648

ACKNOWLEDGEMENT

The author acknowledges financial support of this work from the Department of Education of "Generalitat de Catalunya".

REFERENCES

1 W. Hemninger and G. Höhne, Calorimetry, Verlag Chemie, Weinheim, 1984.
2 H. Inaba, S. Takahashi, T. Mima and K. Naito, J. Chem. Thermodyn., 16 (1984) 573.
3 A. Sanahuja and E. Cesari, J. Chem. Thermodyn., 16 (1984) 1195.
4 Ch.M. Guttmam and J.H. Flym, An. Chem., 45 (1973) 408.
5 J.B. Ott, J.R. Goates and D.L. Cardon, J. Chem. Thermodyn., 8 (1976) 505.
6 Y.P. Handa, R.E. Hawkins and J.J. Murray, J. Chem. Thermodyn., 16 (1984) 623.
7 E.M. Arnett, W.G. Bentrude, J.J. Burke and P.McC. Duggleby, J. Am. Chem. Soc.,, 87 (1965) 1542.
8 M.V. Kilday, J. Res. Natl. Bur. Stand., 85 (1980) 449.