

Electrical calibration and testing of calorimeters with simulated, time-variable reaction power¹

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Abstract

For calorimetric investigations where the reconstruction of the real heat-flow rate during the experiment is required, the usual electrical calibration with constant power is often not sufficient. However, the use of a chemical calibration is limited by the number of suitable and certified reactions showing a known dynamics of the heat-flow rate. Therefore, a computer controlled electrical calibration unit was developed capable of duplicating any simulated reaction power–time curve in the calorimetric cell. The calibration unit consists of a universal simulation software with an interface to a programmable precision current supply connected to the calibration heater inside the calorimetric vessel. The reliability of the electrical calibration was proved with a continuous titration calorimeter using different recommended test reactions (TRIS+HCl, dilution of aqueous KCl, NaCl and urea solutions).

In order to test the electrical calibration procedure in the dynamic mode the heat-flow rate of a first-order equilibrium reaction during a continuous titration experiment was simulated. It is demonstrated that the combination of simulation software and electrical calibration hardware provides a very close adaptation of calibration and experiment, allows a more reliable estimation of experimental uncertainties, simplifies the verification of complex data analysis procedures and opens up new possibilities for the optimization of experimental parameters. © 1998 Elsevier Science B.V.

Keywords: Calibration; Calorimetry; Equilibrium constant; Error analysis; Titration calorimetry

1. Introduction

The accuracy of calorimetric measurements is essentially determined by the reliability of the calibration procedure. The most common way to calibrate a calorimeter is to generate a precisely known quantity of energy by electrical heating (usually at constant

power) with a built-in resistance heater. But the need for the highest comparability between calibration and experiment is often ensured only by using a suitable chemical test reaction with a well-known enthalpy of reaction [1]. Especially for thermokinetic studies or the application of continuous titration calorimetry for the determination of equilibrium constants, where a reconstruction of the time dependence of the real heat-flow rate during the experiment is required, the electrical calibration with constant heat power is not sufficient. However, the application of chemical calibration is limited by the number of suitable and

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certified test reactions showing a reproducible dynamics of the heat-flow rate [1–3].

Therefore, a unit for computer controlled electrical calibration was developed making possible the simulation of any reaction power–time curve and the output of the appropriate electrical power to the calibration heater located in the calorimetric vessel, respectively. The calibration unit was tested with a titration calorimeter based on a heat conduction microcalorimeter of the Calvet-type. The reliability of the electrical calibration of the instrument used has been proved by comparison of the calibration constants determined electrically or chemically using different recommended test reactions (TRIS+HCl, dilution of aqueous KCl, NaCl and urea solutions) [1,3,4].

In order to test the electrical calibration unit in the dynamic mode the simulation of the heat-flow rate of a first-order equilibrium reaction ($A+B \rightleftharpoons AB$) during a continuous titration experiment was chosen. It is demonstrated that apart from a very close adaptation of the conditions of a real experiment the calibration unit opens up more remarkable possibilities for the evaluation and optimization of calorimetric experiments.

2. Experimental

2.1. Titration calorimeter

Calorimetric measurements were performed by means of a twin heat conduction microcalorimeter of the Calvet-type (DAK 1A-1, Russia). The sensitivity of the differential thermopile was approximately 0.18 V/W. Typical signal noise and drift were $<0.5 \mu\text{W}$ (point to point) and $<1 \mu\text{W/h}$, respectively. A home-made titration insertion cell (Fig. 1) with a built-in calibration heater was used for all experiments. Reagents were injected by means of a Hamilton syringe (1 cm^3) mounted on a step-motor driven precision syringe pump (SP250i, WPI, USA). A thin stainless steel tube (i.d. 0.2 mm), connected to the syringe, reached directly into the calorimetric vessel. In order to minimize temperature differences between the reagent and the solution in the vessel, the injection tube is wound to a coil embedded in a heat exchanger before entering into the vessel. The calorimetric vessel (i.d. 9 mm) is made from acid-proof steel, gold-plated

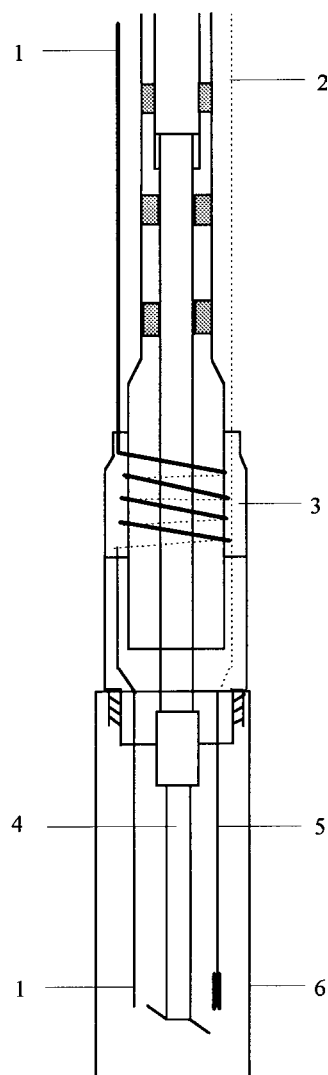


Fig. 1. Construction of the titration insertion cell, (1) injection capillary, (2) copper leads for calibration heater, (3) heat exchanger, (4) stirrer, (5) calibration heater, (6) stainless steel vessel.

inside and can be filled with 2 to 6 cm^3 of solution. The calibration heater is placed symmetrically to the end of the injection tube near the stirrer ensuring a sufficient equivalence between chemical reaction and electrical heating. The heater ($R=50 \Omega$) was manufactured from 0.04 mm insulated aurotan wire wound on a thin stainless steel capillary and is connected to 0.07 mm copper leads inside the capillary. Both heater and capillary were gold-plated by

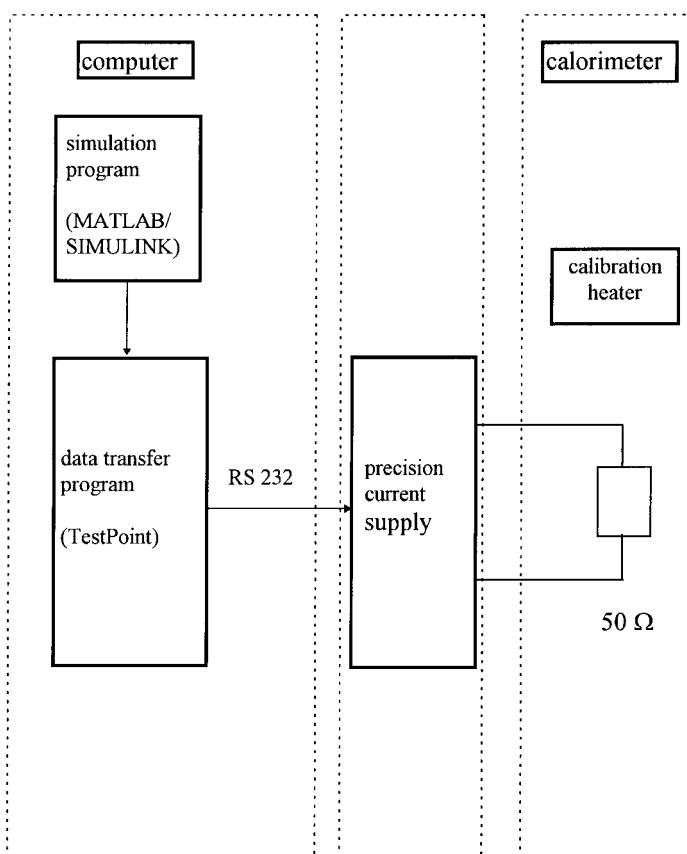


Fig. 2. Scheme of the electrical calibration unit.

electrolysis after varnishing with conductive silver paint. This treatment guaranteed a high heat conductivity and chemical resistance of the heater as well. The stirrer is located in the centre of the vessel and is driven by an electronically controlled motor which is mechanically separated from the stirrer by a magnetic coupling. An optimal mixing was achieved at a stirring rate of 150 rpm.

The calorimetric signal was recorded by means of a computerized data acquisition system after pre-amplification (20000x) inside the calorimeter. All experiments have been performed at $25.00 \pm 0.02^\circ\text{C}$.

2.2. Calibration unit

The calibration unit consists of several software and hardware components and is schematically shown in Fig. 2. A universal simulation program developed on the MATLAB[®]-SIMULINK[®] platform (MathWorks

Inc., USA) produces an output file containing the power–time data for the calibration experiment. SIMULINK[®] as a block oriented, graphical programming interface provides the necessary flexibility and easy operation for the simulation of different reaction types (equilibria or non-equilibria) with variable input parameters. The output data of the simulation are converted and transferred to a programmable precision current supply, connected to the calibration heater, by another program developed with the TestPoint[®] software package (Keithley Instruments, USA). The current values at the output correspond to the input data with a maximum relative deviation of 0.1%.

2.3. Reagents

The following reagents were used for the chemical calibration experiments after drying at 100°C to con-

stant weight: potassium chloride (suprapure, Merck, Germany); sodium chloride (suprapure, Merck, Germany); urea (p.a., Merck, Germany); and tris(hydroxymethyl)aminomethane (TRIS) (p.a., Merck, Germany). Hydrochloric acid was prepared volumetrically from a Merck standard solution (Titrisol). All solutions were prepared using ultrapure water (Milli-Q Plus, Millipore Corp., USA).

3. Results and discussion

Before testing the calibration unit with time-variable signals, normal calibration experiments with constant power were performed in order to check the accuracy of the electrical calibration set-up in comparison to the chemical test reactions. The identity of the calibration constants defined by

$$S = \frac{\text{energy released}}{\text{signal area}} = \frac{\text{heat flow rate}}{\text{signal height}} \quad (1)$$

was used as a criterion. Several electrical calibration experiments at different power, heating time and amount of water in the calorimetric vessel resulted in a calibration constant of $265.25 \pm 0.75 \mu\text{W/V}$, independent of the different conditions. This finding also proved the linear operation of the calorimeter.

Chemical calibrations were performed using the reaction of 0.1 mol/l TRIS solution with hydrochloric acid and the dilution with pure water of 1 mol/kg KCl, NaCl and urea solutions, respectively. All measurements were carried out by continuous injection of 1 cm³ of reagent during 1 h. The overall heat released were calculated using the recommended enthalpy of reaction of -47.44 kJ/mol for the protonation of TRIS [4,5], dilution enthalpy data for KCl and NaCl reported by Parker [6] and Tachoire [7] and compiled dilution data for urea published by Marsh [1]. Table 1 reports the calibration constants determined with these test reactions and their relative deviation from the electrical calibration constant demonstrating a sufficient accuracy of the electrical calibration procedure, temporary without considering dynamic parameters of the calorimeter. In the next step, the reliability of electrically determined time constants of the calorimeter was studied by comparing deconvoluted calorimetric curves (real heat-flow rates) to heat-flow rates calculated from the appropriate reference data of the

Table 1

Deviation of the chemical calibration constant from the electrically determined calibration constant

System	S ($\mu\text{W/V}$)	Deviation (%)
NaCl–H ₂ O	266.91 ± 0.15	0.63
KCl–H ₂ O	267.09 ± 0.34	0.69
Urea–H ₂ O	266.96 ± 0.19	0.64
TRIS–HCl	267.22 ± 0.22	0.74

test reactions. Therefore, the calorimetric curve, recorded after switching off the current to the calibration heater, was analysed in order to identify the best model for describing the dynamics of the calorimeter and to compute the appropriate parameters (time constants). It was found that a first-order model using one time constant (equivalent to the Tian equation) provided the best fit of the experimental curves. The deconvolution of the curves measured during a titration experiment additionally required the consideration of the variation of the time constant with increasing volume of liquid in the calorimetric vessel. Therefore, a modified Tian equation as suggested by Tachoire and Torra [8],

$$P'(t) = P(t) + \tau(v) \frac{dP(t)}{dt} \quad (2)$$

with

$$\tau(v) = \tau_0 + av, \quad (3)$$

was applied to deconvolute the calorimetric curves. $P'(t)$ the reconstructed heat-flow rate, $P(t)$ is the calorimetric signal, τ_0 the time constant of an empty cell, and v denotes the volume of liquid in the vessel. The validity of the approximation (3) was proved by a linear regression analysis of time constants measured at different volumes of water in the vessel. It is worth mentioning that the resulting slope a corresponded very well to the estimated value calculated taking into account the heat capacity change only. As a conclusion from this result, an electrical calibration have to be performed at least before and after a titration in order to determine the parameters of Eq. (3). This procedure was applied to the dilution experiments of KCl and NaCl. The results of the deconvolution are illustrated in Fig. 3 for the dilution of 2 cm³ KCl-solution ($m=1 \text{ mol/kg}$) with water. Fitting of the reconstructed heat-flow rates to the data calculated

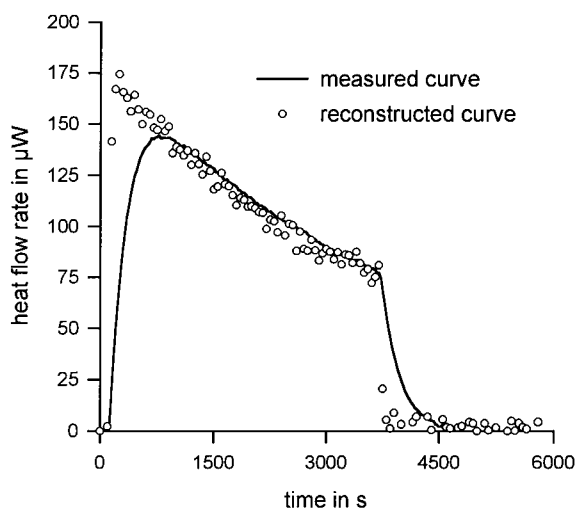


Fig. 3. Results of a potassium chloride ($m=1$ mol/kg) dilution experiment.

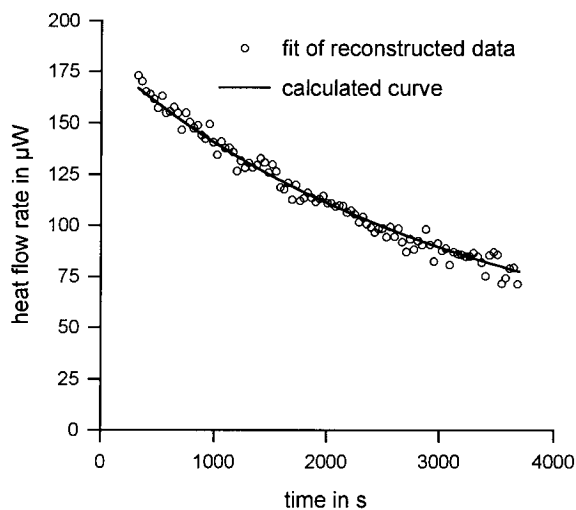


Fig. 4. Fit of the reconstructed experimental heat-flow rates to calculated data for KCl dilution ($m=1$ mol/kg).

from the reference data of Parker [6], using Eq. (1) with the calibration constant as adjustable parameter, gave a very good adaptation (Fig. 4). The resulting calibration constant corresponds to the value reported in Table 1 (based on the integral procedure) within 0.2%.

These results prove the accuracy of the electrical calibration set-up and of the deconvolution procedure

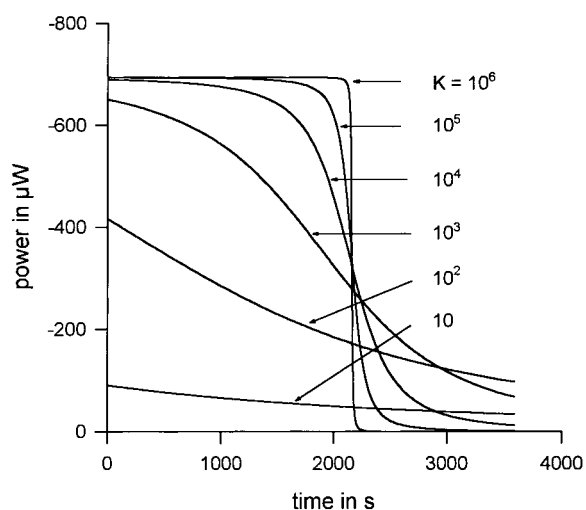


Fig. 5. Simulated reaction power curves for a first-order equilibrium reaction using different equilibrium constants K ($c_A=0.015$ mol/l, $c_B=0.05$ mol/l, $\Delta H=-50$ kJ/mol, injection rate= 1 cm³/h).

under static as well as dynamic conditions which was the prerequisite for using an electrical duplication of time-variable heat-flow rates for the calibration of a calorimeter.

Finally, the new calibration unit was tested with simulated heat-flow rates of a simple first-order equilibrium reaction of the form $A+B \rightleftharpoons AB$. Different theoretical reaction power-time curves were calculated with varying equilibrium constants and fixed values for the concentrations ($c_A=0.015$ mol/l, $c_B=0.05$ mol/l), the titration rate (1 cm³/h of B) and the reaction enthalpy ($\Delta H=-50$ kJ/mol) using the MATLAB/SIMULINK based simulation software. The results are shown in Fig. 5. Afterwards, the simulated data were transferred to the programmable precision current supply and the appropriate electrical power was released in the calorimetric cell. The resulting measurement curves were deconvoluted using the model described above. Fitting of Eq. (1) also resulted in calibration constants which were in excellent agreement with the electrical calibration constant of the integral measurements. In addition, the equilibrium constants K as well as the reaction enthalpy were recomputed by a usual least-squares analysis of the deconvoluted data [9,10]. The relative deviations of the fitted values from the exact input values are shown in Fig. 6. Obviously, the message of

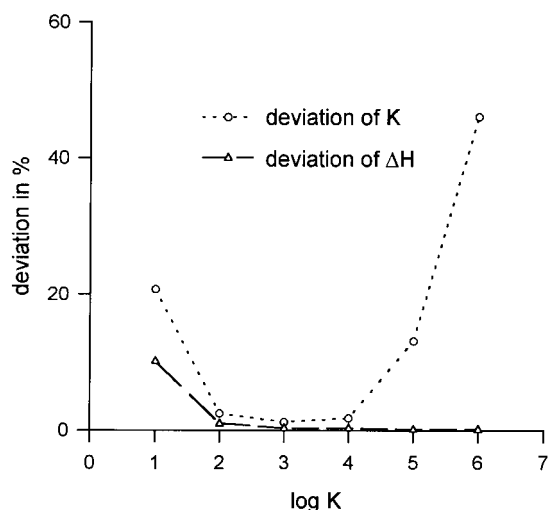


Fig. 6. Relative deviations of recomputed K and ΔH values from the given input data.

the diagram is similar to the results of error analysis reported by Christensen [11] or Olier [12] which are based on simulation calculations with estimated errors of input data (concentrations etc.). The important advantage of the new results is the fact that the error curves in Fig. 6 represent the real experimental error caused by the calorimetric measurement and by the data analysis procedure, respectively. Therefore, the described calibration method allows a more objective estimation of the limits of the calorimetric determination of equilibrium constants as well as optimization of the experimental parameters like concentration range, injection rate etc. Furthermore, comparing the input data of the simulation with the recomputed values of ΔH and K is a good possibility to check the correctness of the complex data analysis procedure.

4. Summary

A new electrical calibration arrangement capable of duplicating any simulated reaction power–time curve in the calorimetric cell was described and successfully tested. A crucial prerequisite for the application of this calibration method was a sufficient similarity of the heat conduction conditions between the energy released electrically and chemically, which was proved by comparison of static and dynamic para-

meters of the calorimeter determined by chemical and electrical calibration experiments, respectively. The following advantages have been described:

- The calibration unit enables an optimal adaptation of calibration and experiment.
- The application of time-variable power significantly improves the characterization of the dynamic properties of a calorimeter.
- Simulated input data with exactly known parameters are very useful for the verification of complex data analysis procedures.
- The combination of simulation software and calibration hardware allows a more reliable and easy estimation of the experimental uncertainties and limits and opens up new possibilities for the optimization of experimental parameters.

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