Thermochimica Acta, 77 (1984) 375–382
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A SIMPLE DTA APPARATUS FOR TEACHING PURPOSES TESTED BY THE EXAMPLE OF THE DEHYDRATION OF $BaCl_2 \cdot 2\ H_2O$

E. WIEDERHOLT and M. PLEMPEL

Bergische Universität-Gesamthochschule Wuppertal, D-5600 Wuppertal 1 (West Germany)

(Received 26 January 1984)

ABSTRACT

The design and construction of a simple DTA apparatus for teaching purposes with an electric soldering pot as oven are described. The efficiency of the apparatus is demonstrated by the dehydration of $BaCl_2 \cdot 2\ H_2O$. Upon rapid heating of the oven (ca. 30 K min^{-1}) there are two slightly overlapping endothermic peaks, while at a slower heating rate (ca. 4 K min^{-1}) four endothermic peaks can be detected. The apparatus thus proves to be quite sensitive despite its simple construction.

INTRODUCTION

Until now thermoanalytical methods have assumed no particular importance in instructional courses in the natural sciences. The main reasons are:

(1) only rarely do chemistry teachers become acquainted with thermoanalytical methods during their studies, since they are not always part of a chemist's curriculum;

(2) because of their low production number the selling price of a thermoanalytical apparatus is so high that schools cannot afford them, and hence they are not even available for teaching purposes at most universities;

(3) well-known companies with the relevant know-how are neither able nor willing to bring a simple and economical teaching apparatus onto the market, since the service costs would be relatively high and at the same time there would be a danger that the simple apparatus would become competitive with those presently produced for scientific purposes.

During the past few decades modern instrumental analytical methods have had an essential influence on chemistry. Hence, there is an undeniable need to present and apply these methods within school courses.

The discussion of modern methods and techniques in course-work can be recommended, if the following criteria are fulfilled:

(1) the student must be able to understand the principle of a given method;

(2) this principle must be demonstrable by a simple apparatus;

(3) the method must allow for the solution of chemical problems relevant to school courses.

0040-6031/84/$03.00

These criteria are valid, for example, for DTA [1], one of the important thermoanalytical methods.

In previous work the construction of a simple DTA apparatus has been discussed which uses an electric soldering iron as oven [2]. In this report a still more convenient DTA apparatus is described that can be easily constructed by a student and can be operated very easily.

THE CONCEPTION OF A DTA TEACHING APPARATUS

An apparatus for teaching purposes has to satisfy different requirements other than a scientific one. First, a self-constructable DTA model for teaching purposes must be inexpensive. It must also be sturdy enough to resist damage caused by faulty operation. It should not be simply a black box, but rather its construction should be evident to the student.

It should be assembled from parts which are readily available commercially, or which can easily be produced without a great deal of mechanical skill. In order to design a DTA experiment which lasts for only a few minutes, the apparatus should have variable heating rates of up to ca. 30 K min^{-1}.

Linear heating and cooling rates — normal for scientific apparatus — are not necessary. However, its results have to be reproducible. It must also be possible to use the apparatus more than once in a given lab. session, and, therefore, the oven has to cool down quickly after each experiment.

A DTA experiment for teaching purposes has to demonstrate first and foremost whether a substance exhibits a physical change and/or a chemical reaction upon varying the temperature. The construction of a classical DTA apparatus following Roberts–Austen is simpler then the Boersma-technique common today. The classical technique, however, allows only a qualitative determination of the heat change as being either endo- or exothermic.

In order to record the ΔT and T signals with small effort, a simplified connection of the thermocouples is used. The resulting errors in determining the absolute temperature can be neglected in most cases.

As display and recording apparatus a y/t plotter is used. In most cases a signal field width of 2–5 mV is chosen. The apparatus has to be easily serviceable and should be frequently applicable in a variety of experiments during the lab. course, not just once for the sole purpose of demonstrating the methodology.

Figure 1 shows an apparatus fulfilling these given criteria. The parts needed for its construction will be described below. By now the complete apparatus is produced and distributed by Mauer *.

* Mauer Lehrmittel + Labortechnik GmbH, Postfach 20, D-6238 Hofheim am Taunus 7, West Germany. Nr. 275 500.00 Differenzthermoanalyse-Lehrgerät Modell DTA 8307.

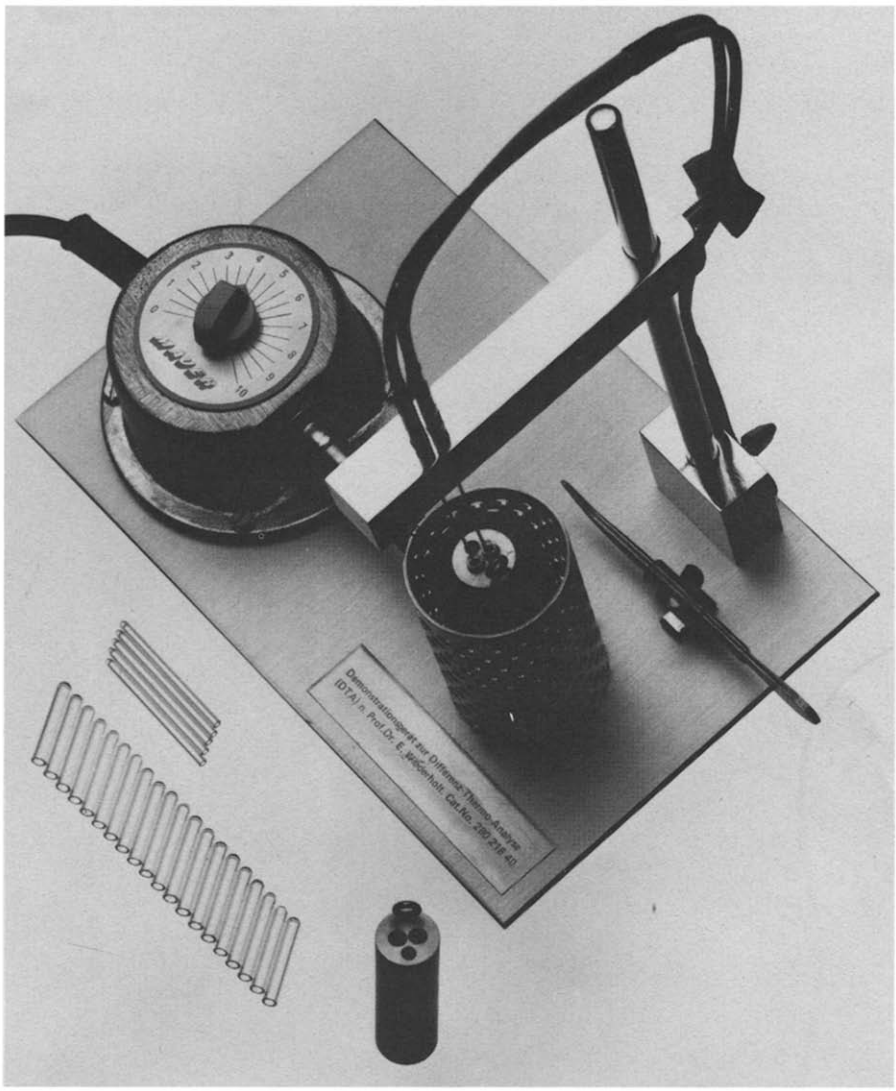

Fig. 1. The DTA apparatus for teaching purposes (photograph reproduced with permission from Mauer).

EXPERIMENTAL

Parts

For the oven. Electric soldering pot: 0–120 W; 220 V; volume, 20 cm^3; 200 mm ID; 60 mm deep; Model ZWMS or ZWMS-R with additional electronic power control. (Zeva-GmbH, D-3548 Arolsen 1, West Germany.)
For control of the oven. Electronic power control or (better): variable transformer that can be better controlled: 220 V connection, 5 A, range 0–260 V.

As insert to the oven. Aluminum cylinder, 19.5 mm ID, height 60 mm, with three symmetrical borings (5.2 mm ID and 30 mm deep) on the top surface, to take samples and, eventually, an additional temperature sensitizer (self-constructable).
As sample holder. Glass tubes, one end sealed, 5 mm ID, height ca. 35 mm.
As temperature sensitizer. Two mantel thermocouples, Cromel–Alumel, 1 mm ID, Nr. 4AD 100/2000 (Philips).
Holder for the thermoelements. Rack (self-constructable).
As display and recording apparatus. Two channel y/t plotter Linoscript Nr. 2388 (Linseis, D-8672 Selb, West Germany).

Construction and execution of the experiment

The aluminum cylinder is placed in the electric soldering pot. The crucible tubes are filled with aluminum oxide (as reference) and the sample to be examined, and these are placed into the aluminum cylinder. The two thermocouples are held by a rack so that they are immersed into the two substances. The thermocouples are connected to the two-channel y/t plotter as shown by the simplified diagram (Fig. 2). Paper transport of the plotter and heating of the oven are begun.

Pre-Experiment

In order to test the apparatus a measurement of Al_2O_3 under conditions to be applied later is recommended.
Parameters. Operating voltage of the oven, 67 or 100 V; reference substance, γ-Al_2O_3, ca. 100 mg; sample, γ-Al_2O_3, ca. 100 mg; surrounding atmosphere, Air, static; two-channel plotter, ΔT signal field width, 1 mV; T signal field width, 10 mV; paper speed, 100 mm h^{-1}.

Discussion

The DTA curve of Al_2O_3 (Fig. 3) as sample and reference substance shows only small deviations ($< \pm 0.25$ K) from the zero line. This demonstrates the good thermic symmetry of the oven and DTA insert.

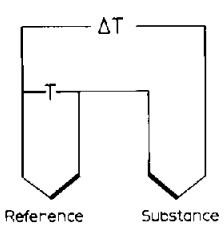

Fig. 2. Simplified mimic diagram for DTA.

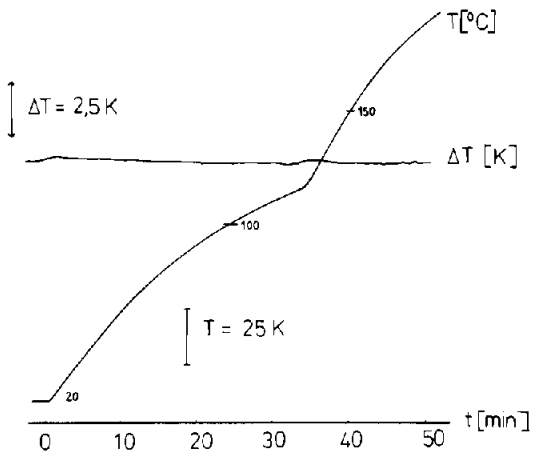

Fig. 3. DTA curve of aluminum oxide.

The temperature curve of the non-regulated oven follows a straight line only in the lower part. In order to get a slow increase in temperature at the beginning and a similar one for higher temperatures, the operating voltage is increased from 67 to 100 V after ca. 35 min. By regulating the oven voltage more frequently a practically linear increase in temperature can be obtained, but this capability is not required for a teaching apparatus. For these DTA measurements a constant oven voltage is generally sufficient.

The temperature curves obtained are reproducible. With a variable transformer of 0–220 V it is possible to regulate temperature curves of any given slope more precisely than can be done by a thyristor.

The electric soldering pot model has the following advantages:

(1) the aluminum insert can easily be taken out of the oven and thus both can be cooled down quickly, and a new measurement can be performed after only a few minutes have passed (a ventilator can be used to accelerate the cooling process);

(2) the aluminum insert is practically unoxidized by heating, while the cut copper top of the soldering iron has to be rebored quite frequently and replaced from time to time;

(3) the handling of the electric soldering pot, which can be purchased with a power-control, is much more convenient.

The only disadvantages of the soldering pot are its slightly higher price and the fact that the maximum attainable temperature is "only" about 550 °C.

DTA INVESTIGATION OF $BaCl_2 \cdot 2\ H_2O$

The sensitivity and efficiency of a DTA apparatus can be demonstrated by the dehydration of $BaCl_2 \cdot 2\ H_2O$, which has been examined by numerous

researchers. In their famous study Borchardt and Daniels [3] also investigated $BaCl_2 \cdot 2\ H_2O$, detecting two endothermic peaks as a result of the dehydration. The same result was obtained by Paulik et al. [4] and Liptay [5] with a derivatograph. They detected from room temperature up to 300 °C two slightly overlapping endothermic peaks, which they characterized as resulting from the successive loss of two molecules of water. Wendlandt and Simmons [6] found two DTA peaks in their DTA and TGA measurements for the loss of the first water molecule and two (possibly three) further peaks for the loss of the second.

The first two steps are quite certain

$$BaCl_2 \cdot 2\ H_2O(s) \rightarrow BaCl_2 \cdot H_2O(s) + H_2O(l)$$

$$H_2O(l) \rightarrow H_2O(g)$$

Based on a more recent investigation by Lutz et al. [7] the following additional reactions are also assumed to play a role:

$$BaCl_2 \cdot H_2O(s) \rightarrow BaCl_2 \cdot 0.5\ H_2O(s) + 0.5\ H_2O(g)$$

$$BaCl_2 \cdot 0.5\ H_2O(s) \rightarrow BaCl_2(s) + 0.5\ H_2O(g)$$

Parameters

Metal salt hydrate sample. Finely ground $BaCl_2 \cdot 2\ H_2O$ of analytical reagent grade quality is used in this investigation. Dried γ-Al_2O_3 is used as reference substance.

There have been four DTA investigations of $BaCl_2 \cdot 2\ H_2O$ performed with different operating voltage of the oven and sensitivity of the plotter. A plotter signal field width for T with 10 mV maximum and a paper-advance speed of 200 mm h^{-1} were held constant.

Experiment 2.1. Operating voltage 220 V, ΔT signal field width 10 mV.
Experiment 2.2. Operating voltage 130 V, ΔT signal field width 2 mV.
Experiment 2.3. Operating voltage 100 V, ΔT signal field width 2 mV.
Experiment 2.4. Operating voltage 67 V, increased to 100 V after 35 min, ΔT signal field width 2 mV.

RESULTS AND DISCUSSION

The DTA curve of $BaCl_2 \cdot 2\ H_2O$ in Fig. 4 shows two slightly overlapping endothermic peaks. In the lower part the curve looks similar to the figure in the Liptay Atlas [5]. The advantages of the present method are the small amount of time (less than 10 min) needed for the measurement, the practically linear increase in temperature up to 250 °C using normal 220 V voltage and the possibility of working in a relatively insensitive recording interval which often is the only one available on a school plotter.

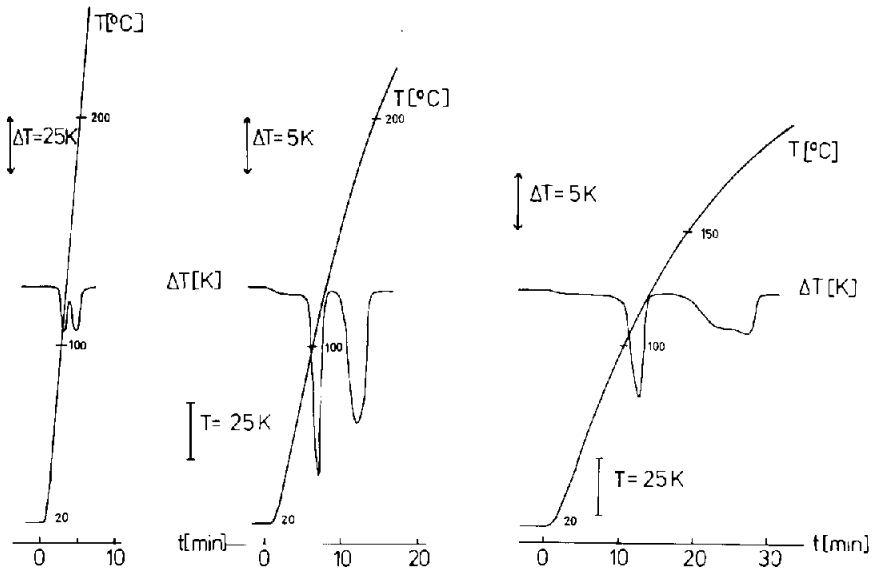

Fig. 4. DTA curve of $BaCl_2 \cdot 2\ H_2O$, soldering pot 220 V, ΔT signal field width 10 mV.

Fig. 5. DTA curve of $BaCl_2 \cdot 2\ H_2O$, soldering pot 130 V, ΔT signal field width 2 mV.

Fig. 6. DTA curve of $BaCl_2 \cdot 2\ H_2O$, soldering pot 100 V, ΔT signal field width 2 mV.

The DTA curve of $BaCl_2 \cdot 2\ H_2O$ in Fig. 5 with a smaller operating voltage of 130 V and an increased sensitivity of the ΔT signal shows a complete separation of the two endothermic peaks. The second peak is asymmetric and there may be a shoulder, but the increase in temperature is no longer linear. The duration of the DTA experiment has increased thereby to just over 20 min.

The DTA curve of $BaCl_2 \cdot 2\ H_2O$ in Fig. 6 shows that at an operating voltage of 100 V the second endothermic peak is split. This suggests that $BaCl_2 \cdot 0.5\ H_2O$ may be an intermediate compound. The time needed increases to ca. 30 min.

The DTA curve of $BaCl_2 \cdot 2\ H_2O$ in Fig. 7 shows that by decreasing the operating voltage to 67 V the first endothermic peak is also split, as already observed by Wendlandt and Simmons [6]. As a result it can also be demonstrated with the teaching apparatus that the following reaction steps occur

$$BaCl_2 \cdot 2\ H_2O(s) \rightarrow BaCl_2 \cdot H_2O(s) + H_2O(l)$$

$$H_2O(l) \rightarrow H_2O(g)$$

The final temperature that can be obtained with this voltage is not sufficient, however, to split off the second molecule of crystalline water. Consequently the operating voltage is increased to 100 V after ca. 35 min.

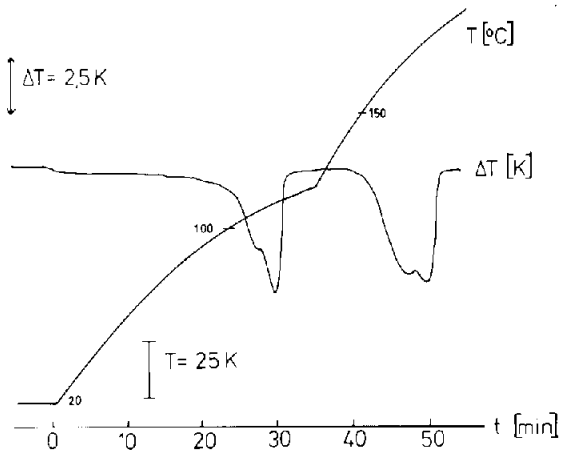

Fig. 7. DTA curve of $BaCl_2 \cdot 2\ H_2O$, soldering pot 67 V and 100 V, ΔT signal field width 2 mV.

The procedure results in four endothermic effects in a single plot. Apparently the following reactions occur

$$BaCl_2 \cdot H_2O(s) \rightarrow BaCl_2 \cdot 0.5\ H_2O(s) + 0.5\ H_2O(g)$$

$$BaCl_2 \cdot 0.5\ H_2O(s) \rightarrow BaCl_2(s) + 0.5\ H_2O(g)$$

CONCLUSIONS

The investigation of $BaCl_2 \cdot 2\ H_2O$ in a simple teaching DTA apparatus demonstrates that reasonable results can be obtained even by simple means. To the authors it seems more important, however, that the student has the opportunity in school to become acquainted with thermoanalytical methods, which he may eventually apply in science or technology at a later time using higher-quality commercial equipment.

REFERENCES

1 E. Wiederholt, Differenzthermoanalyse (DTA) im Chemieunterricht, Aulis, Köln, 1981.
2 E. Wiederholt, J. Chem. Educ., 60 (1983) 431.
3 H.J. Borchardt and F. Daniels, J. Phys. Chem., 61 (1957) 917.
4 F. Paulik, J. Paulik and L. Erdey, Anal. Chim. Acta, 41 (1968) 170.
5 G. Liptay, Atlas of Thermoanalytical Curves, Vol. 1, No. 22, Akademiai Kiado, Budapest, 1971.
6 W.W. Wendlandt and E.L. Simmons, Thermochim. Acta, 3 (1972) 171.
7 H.D. Lutz, W. Becker, Ch. Mertins and B. Engelen, Z. Anorg. Allg. Chem., 457 (1979) 84.