A HIGH TEMPERATURE DTA APPARATUS FOR LARGE AND HIGHLY CORROSIVE SAMPLES WITH HIGH VAPOUR PRESSURES.

W. Grob and R. W. Schmutzler

Physikalische Chemie Ia, Universität Dortmund, Postfach 500 500, D — 4600 Dortmund 50

SUMMARY

The paper describes the construction of a DTA apparatus for the temperature range up to 1100°C especially designed for large, strongly corrosive samples with high vapour pressures. Therefore tightly closed measuring cells and stirring of the samples is provided. A method for the determination of liquidus temperatures of mixtures from DTA measurements promising good reliability is proposed.

INTRODUCTION

Differential thermal analysis is a well established experimental technique for studying the phase behaviour of pure substances and mixtures. Modern instrumentation has been developped especially for high sensitivity, good dynamic behaviour to enable detection of closely neighbouring phase reactions and ease of handling for routine investigations, such as material characterization, quality control etc. .

There may however be experimental situations where special equipment for DTA investigations is needed. This can especially occur when the preparation of the samples results in large amounts without any practicable possibility to subdivide these samples subsequently, when the samples have high vapour pressures and/or are strongly corroded p.e. by air or humidity.

The purpose of this paper is to present a computer controlled DTA apparatus for temperatures up to 1100°C allowing for tightly closed sample cells with volumes up to 3 cm^3, which in addition allows stirring of the samples to enable fast temperature and composition equilibration in liquid and powdered samples.

CONSTRUCTION OF THE DTA APPARATUS

Measuring Cells

The sample cells are cylindrical containers with an inner diameter of 12mm, a wall thickness of 1mm and a length of 55mm. For our special application, the investigation of the ternary Cs/Au/CsBr system, they were made from pure sintered molybdenum, which proved to be sufficiently corrosion resistant. However, due to the strong reaction of Mo with oxygen above 400°C, the measurements had to be performed in vacuum or in an inert gas atmosphere. The measuring cells are tightly closed by molybdenum cones to avoid safely any evaporation of either Cs or CsBr at the high temperatures required (at least up to 1000°C). Sample and reference cell are two identical Mo containers. The reference cell is filled with Pb, the amount

of which is chosen to meet roughly the heat capacity of the filled sample cell.

Sensing Element for the Temperature Difference (Fig. 1)

The temperature difference between sample (1) and reference (3) cell is measured with a thermopile (2) consisting of 12 pairs of Pt10%Rh/Pt thermocouples, thus giving a signal of about $120\mu V$/deg. In addition, one of these thermocouples positioned with its welded tip at the middle of the sample cell is used to measure the temperature of the sample. The individual Pt and Pt10%Rh wires (ϕ 0.3mm) are insulated by alumina tubes (5). They are kept in position by grooves in a cylindrical body made of Stenan (Hoechst Ceramtec AG, Lauf/Pegnitz). This body (outer diameter 22mm, length 170mm) has bores of 14mm diameter to accomodate the cells.

Furnace, Vacuum Container and Stirring Mechanism

The main parts of our DTA apparatus are shown in fig. 1: Sample cell (1) and reference cell (3) are sticking in line in the thermopile (2), which fits into the furnace, consisting of a Mo tube (7) (22mm inner diameter, 6.5mm wall thickness and 200mm length) which supports 6 heating elements (6) (helices of 3mm diameter made from Alsichrom wire, 0.5mm ϕ (Thyssen, Düsseldorf)), electrically insulated by alumina tubes (4mm inner diameter, 5mm outer diameter, Friedrichsfeld, Mannheim). An additional NiCr/Ni thermocouple (4) used as sensing element for the temperature program controller (Eurotherm, Limburg) is placed in the center of one of these heating elements. The whole furnace is suspended horizontally by three tungsten sticks (8) of 2mm diameter and 300mm length between two Mo flanges in the axis of a vacuum container (fig. 2, (A)) made out of an aluminum tube (inner diameter 140mm, outer diameter 176mm length 530mm) and closed at both ends by flanges made from brass. Thermal insulation is provided by heat shields made from stainless steel and by filling the free space by fibrous ceramics (Kerlane 60, SEPR Savoie Feuerfest, Düsseldorf).

One of the brass flanges contains all electrical connections for the thermopile, the thermocouples and the furnace. The other one contains a rotatable vacuum connection. The whole vacuum container is supported by ball bearings. It can be rotated about its horizontal axis, thus providing a simple but efficient possibility of stirring the large samples. To avoid disturbances of the measurements by changes of the room temperature, the whole container is kept at $50^{0}C$ by a thermostated water bath.

During the measurements a constant He pressure of 10 ± 2mbar was maintained, which proved to be low enough to avoid disturbances due to gas convection and sufficiently high to provide good thermal contact between the heating elements and the Mo tube (7).

Computer Control

The whole apparatus is controlled by an IBM compatible personal computer (D). For this purpose it is connected via an IEEE 488 interface bus to a scanner and a digital multimeter (E) (Keithley, München) of high sensitivity and resolution. In order to check any severe malfunctioning of the apparatus it is furthermore connected via a bidirectional userport (C) to
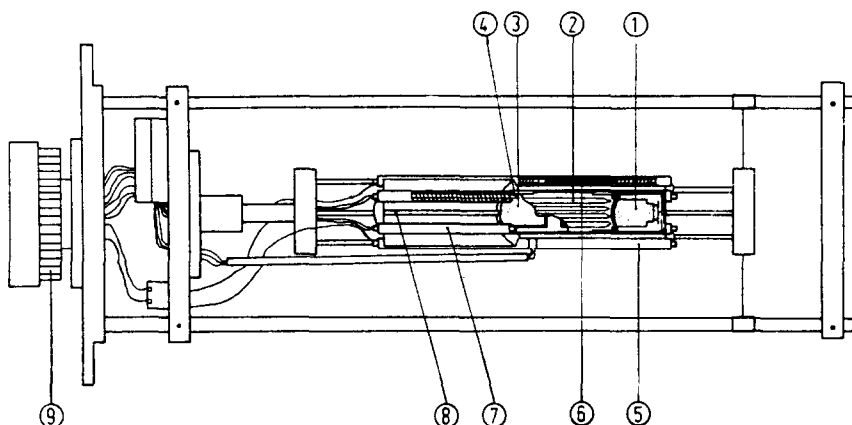
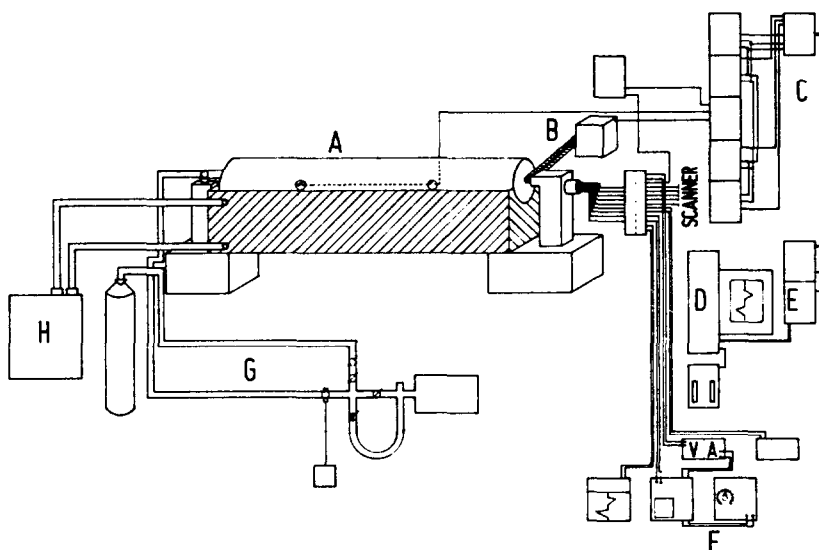Fig. 1: Schematic drawing of the inner DTA – assembly

Fig. 2: General lay–out of the DTA – Apparatus

all essential components of the apparatus. During the measurements the computer undertakes the following tasks: It initiates every 20 seconds a measuring cycle consisting of reading via scanner and multimeter the sample temperature, the signal of the thermopile and the temperature feeded into the temperature program controller (F). These data are formatted, indicated on the monitor, send to a line printer and to a data file on a floppy disc. Between every two measurements the pressure is adjusted and the correct functioning of the thermopile and the thermocouple needed for temperature control of the furnace and temperature determination of the sample is checked as well as the temperature of the water bath.
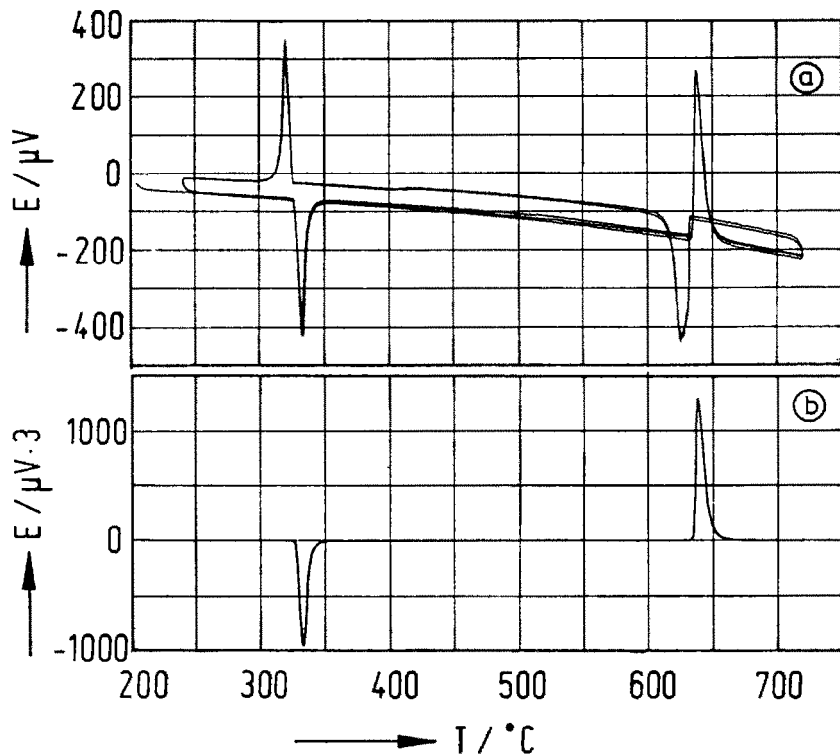
Fig. 3: Uncorrected thermogram for three heating and cooling cycles (a) and corrected
thermogram after data processing (see text) (b)

RELIABILITY AND SENSITIVITY

The thermogram in fig. 3a shows the uncorrected measuring curves for three heating and
cooling cycles of a sample containing 4.40 g CsBr with a reference cell containing 12.44 g Pb
at a heating rate of 3K/min. As can be seen from the figure, there is some slight drift of the
base line and a hysteresis between heating and cooling curve corresponding to a ΔT of
0.6–0.7°C. However the curves are quite reproducible and the base line passes smoothly
through the peaks, thus enabling a sensible correction of its drift. Fig. 3b shows the same
results after summing up the heating curves of the 3 runs and subtracting the base line fitted
as usual to a polynomial of fifth order.

Fig. 4b shows the dependence of the melting peak of CsBr on the heating rate from
1K/min to 10K/min. The inset proves a nice linear dependence of the onset temperature and
the temperature at the peak maximum on the heating rate. Extrapolation of the onset
temperature to zero heating rate gives a melting point of CsBr (purity 99.5%, Merck AG,
Darmstadt) of 633°C which compares quite well with literature data (636°C (ref.1)). An even
better agreement is obtained for the melting point of Pb, which is obtained from the onset
temperature of its melting peak in fig. 3b at 327.4°C (literature value (ref.2) 327.4°C) thus

indicating the quality of the calibration of the thermocouples used. In addition fig. 4a shows that neither onset temperature nor the temperature of the peak maximum depends appreciably on the sample mass. After the complection of the phase transition, the signal of the thermopile decays exponentially with time with a time constant of about 1.8min. Thus good resolution of closely neighbouring thermal events is guaranteed.
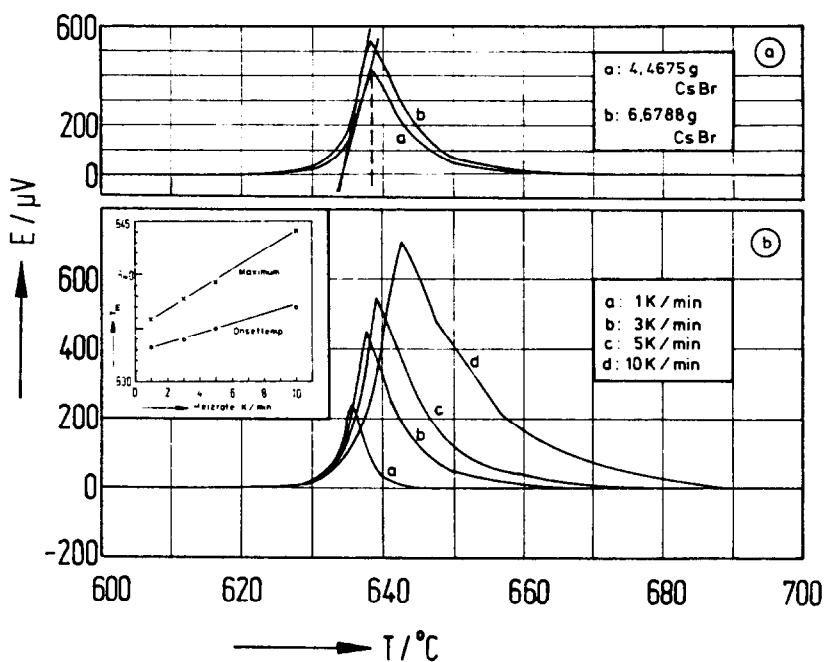

Fig. 4: Effect of sample mass (a) and heating rate (b) on the melting peak of CsBr

DETERMINATION OF LIQUIDUS TEMPERATURES OF MIXTURES

The transition temperatures of invariant phase equilibria such as — in constant pressure experiments — first order phase transitions of pure substances, eutectic or peritectic reactions in binary mixtures etc. are precisely determined by DTA as the onset temperatures of the corresponding peaks of the heating curves. These are obtained in the usual way (ref.3) from the intersection of the tangent to the ascending side of the peak at its inflection point with the base line, extrapolated to zero heating rate. The determination of liquidus temperatures in binary mixtures however needs a different procedure, since the melting process in this case may extend over a very wide temperature range and the "true" onset of the freezing peak in the cooling curve is very often obscured by strong supercooling. Here the afore mentioned exponential decay of the thermopile signal at the end of a thermal event allows the determination of that particular time (and the corresponding temperature), where the decay with the already determined time constant begins. To obtain the true liquidus temperature, the temperature thus determined must still be corrected for the dynamic behaviour of the
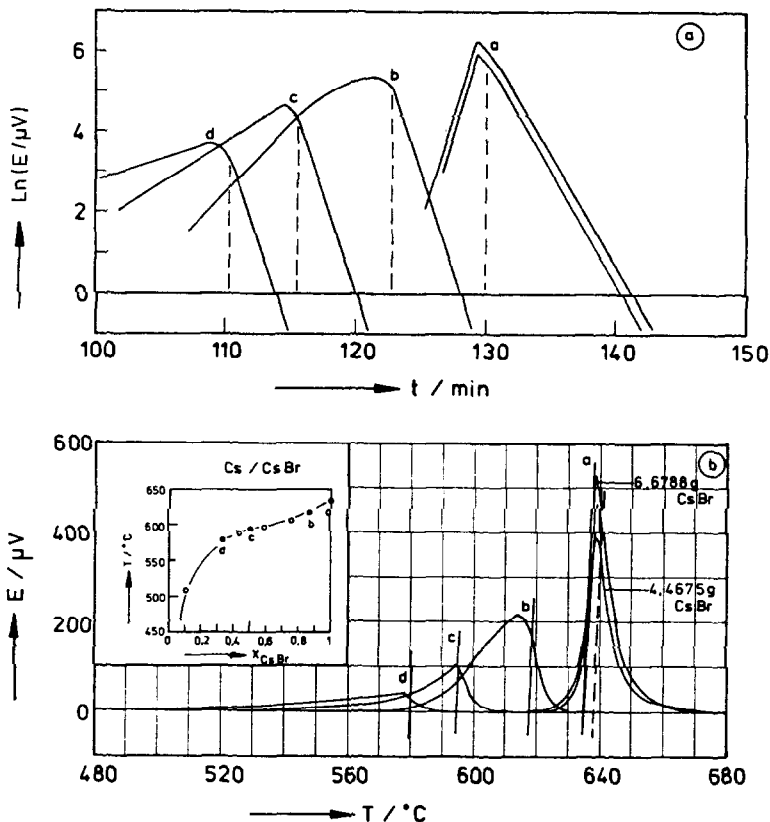
Fig. 5: Determination of the time constant for the decay of the melting peak CsBr (peak a in (a)) and determination of the phase diagram of CsBr/Cs mixtures (see text) (a), (b)

DTA apparatus (ref.3). This method promises good reliability even in the case of liquidus lines with strong curvatures. Fig. 5 visualize its application to the determination of the phase diagram of the Cs/CsBr system, which has been measured with the DTA apparatus already described (ref.4).

ACKNOWLEDGEMENT

REFERENCES
(1)   A. Klemm "Transport Properties of Molten Salts" in: Molten Salt Chemistry, ed. M. Blander, Interscience Publishes, John Wiley & Sons, New York 1964
(2)   S. Allard, ed., Int. Tables of Selected Constants 16, Pergamon Press, Oxford, N.Y., Paris, Braunschweig (1969)
(3)   H. K. Cammenga, W. Eysel, E. Gmelin, W. Hemminger, G. C. Höhne, this volume
(4)   W. Grob and R. W. Schmutzler, Ber. Bunsenges. Phys. Chem. 93 (1989) 1078