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An isoperibol drop calorimeter[1]

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Abstract

An isoperibol calorimeter is described. Its operation involves the drop of a sample from temperatures up to 1373 K into a metal block at 298.15 K. By this method the enthalpy contents of the samples can be measured. The calibration factor, obtained by electrical and drop calibrations, had a reproducibility of ±0.11%. The calorimeter was tested by determining the enthalpy of silver; agreement with the data of Barin was within a range of ±1%.

Keywords: Drop calorimeter; Calorimetry; Heat content

1. Introduction

Binary and ternary chalcogen systems have been investigated in our group for the last 20 years. These systems are of special interest, because their compounds have electrical and optical properties for possible technical applications. The knowledge of their thermodynamic data would not only allow calculations to optimize their binary phase diagrams but would enable calculation of multicomponent systems. In this connection high temperature enthalpy data are lacking for many compounds in chalcogen systems. Therefore we have built a modified isoperibol drop calorimeter. The equipment described is a development of a calorimeter used by Southard [1]. It has an improved system to maintain an isothermal zone in the furnace. The data registration, storage and handling are performed with a personal computer.

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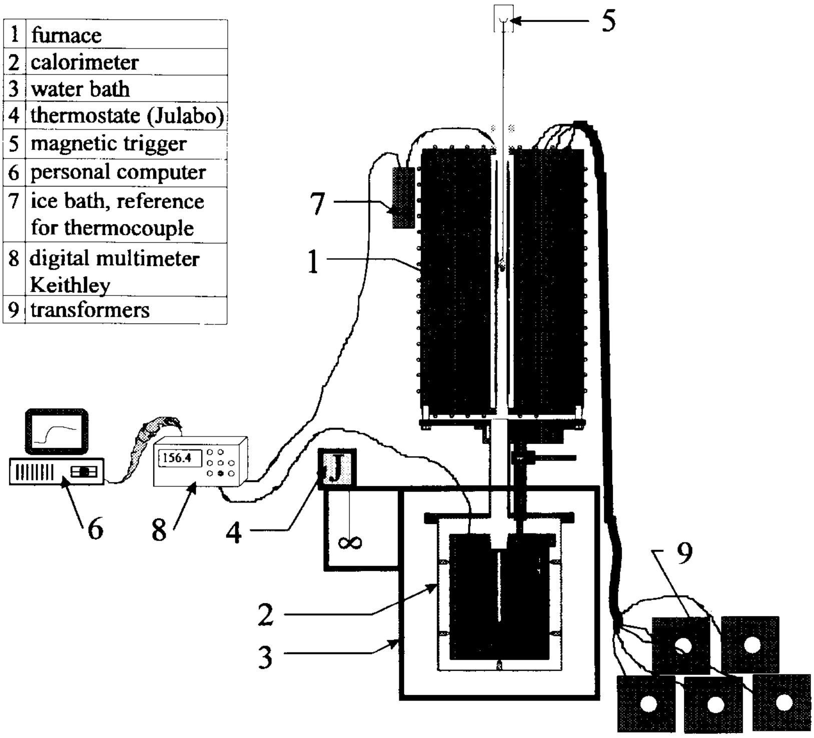
2. Description of the calorimeter

The cross section of the drop calorimeter is shown in Fig. 1. The apparatus consisted of three main units, the furnace (1), the calorimeter (2) and the water bath. (3).

The furnace is shown in Fig. 2. It consisted of three concentric alumina tubes (1) of 60 cm length and a water cooled brass jacket (2) which was insulated from the heating system by Al_2O_3 powder. The furnace was heated by five Kanthal (A, B, C, D and E) heaters (Table 1). One heater was wound on an outer alumina tube of 15 cm o.d., two heaters were fixed on the middle tube (7.5 cm o.d.) and two were mounted on the inner tube (3 cm i.d.). Power for the heaters was supplied through a 1.25 kW voltage stabilizer, stable to 220 V ± 0.5%. The power of each heater was adjusted separately by a transformer (Fig. 3). The temperature distribution in the tube was such that a 20 cm length was isothermal to 0.3 K. This length was sufficient to hold the sample. The temperature of the furnace was measured by a Pt–Pt10Rh thermocouple (Figs. 2, 4), the junction of which was within the isothermal zone. The thermocouple was calibrated, using the melting temperatures of ice ($T = 273.15$ K), lead ($T = 600.65$ K), antimony ($T = 903.65$ K) and silver ($T = 1234.93$ K).



1	furnace
2	calorimeter
3	water bath
4	thermostate (Julabo)
5	magnetic trigger
6	personal computer
7	ice bath, reference for thermocouple
8	digital multimeter Keithley
9	transformers

Fig. 1. The calorimeter assembly.

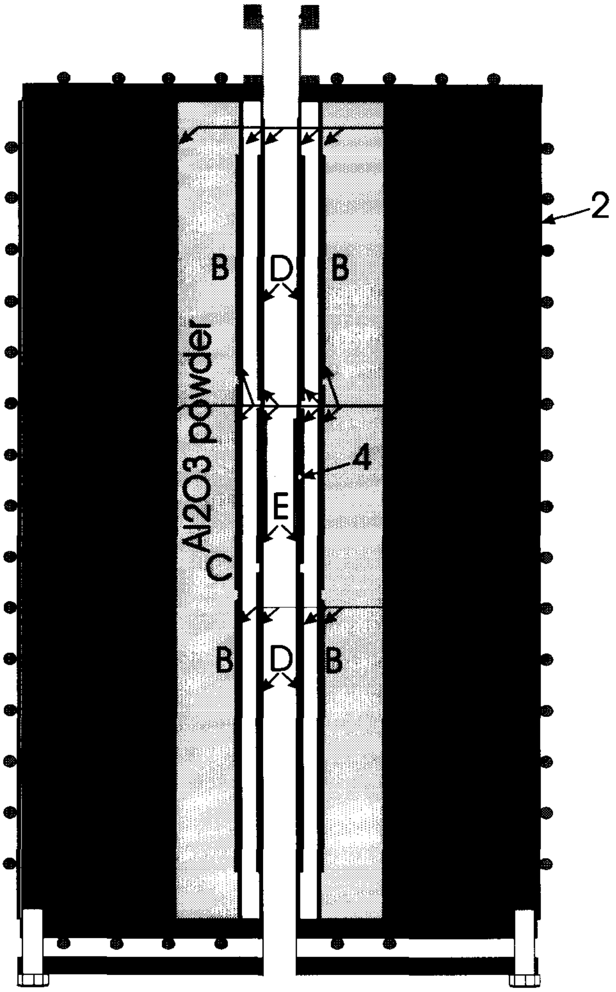


Fig. 2. The furnace.

The samples were suspended into the furnace by a nickel alloy wire. The wire was led out through a hole in the top of the furnace and fastened by a trigger-relais. The furnace had another hole at the bottom as outlet for the sample. Furnace and calorimeter block were separated by a water cooled gate. This device makes the heat exchange between furnace and calorimeter virtually zero.

The calorimeter (Fig. 4) was fixed to the furnace by screws which were insulated electrically and thermally from the calorimeter. The calorimeter proper consisted of a central cylindrical copper block (12 cm i.d. and 19 cm height), which rested on insulating Plexiglas knife edges (1) in a brass vessel (2) (14 cm o.d. and 25 cm height, weight

Table 1
Kanthal wires

Wire	Diameter/mm	Resistance/Ω
A	1.2	31.71
B	0.8	46.70
C	0.8	20.73
D	0.6	54.23
E	0.6	18.77

19 kg). Parts of the central block were a cylindrical outer copper jacket (3), an inner copper block (4) with two conical cavities, the upper one containing a conical tube (5), the lower one was closed by a conical copper plug (6). The receiving cavity of the conical tube was protected by a copper crucible (7), which could easily be removed when ampoules with samples were accidentally broken.

The inner calorimeter block had a hole for a platinum (Pt1000) and a NTC 150 resistance thermometer (8).

The calorimeter assembly was immersed in a water bath (50 l) and maintained at a temperature of 298.15 K by a thermostat (Julabo). Removal of the whole unit from the water bath was made possible by two steel wires with balanced counter weights, which were fastened to the wall. The temperature of the water bath was measured by an NTC 150. The fluctuations of the temperature during a run (1 h) were ±0.0014 K, during a period of 50 h ±0.0034 K. The temperature fluctuations in the calorimeter block were ±0.0007 K in a period of 1 h, ±0.002 K in a period of 50 h.

The calorimeter was calibrated electrically by measuring the temperature increase of

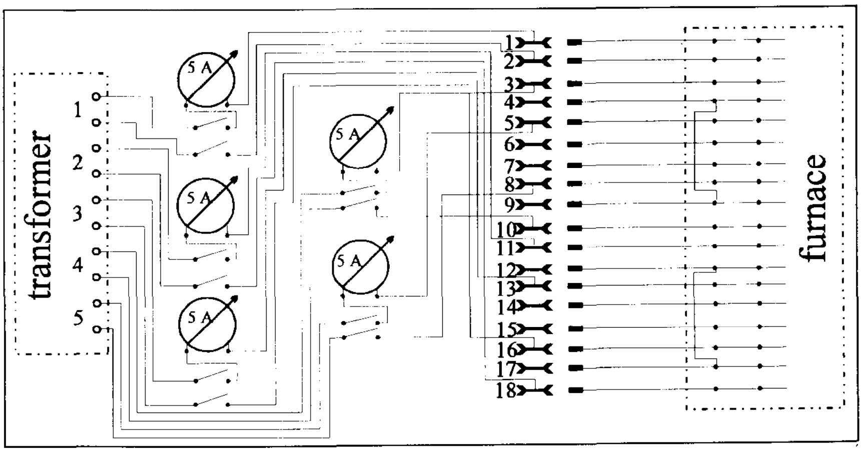


Fig. 3. Electrical connection of the heaters.

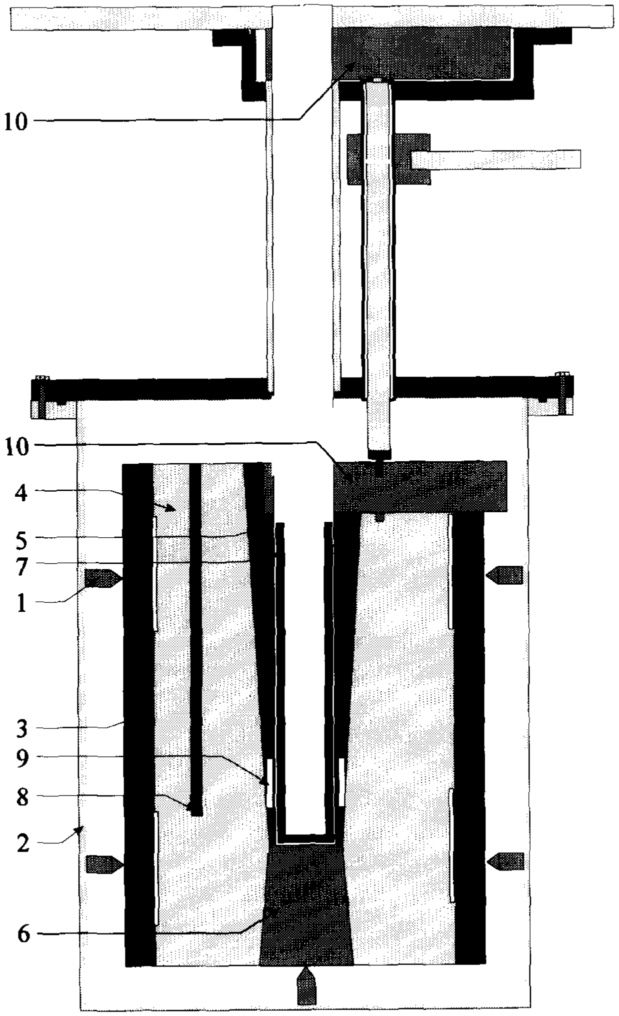


Fig. 4. The calorimeter.

the calorimeter achieved by the input of a known amount of electrical energy. The calibration heater (9) (resistance 90 Ω, oxidized Konstantan) was wound on a groove of the conical tube in the central calorimeter block. Adequate insulation of the calibration heater was achieved by thermal resistant insulating coating (Cramolin). The voltage was measured with a digital voltmeter (DMM 192, IEEE interface, Keithley) with a precision of ±1 μV, the current with a digital voltmeter (M-4650CR, RS232 interface, Metex) with a precision of ±1 mA. The input of electrical energy was timed by a Casio precision stopwatch which permitted reading to ±0.01 s. The DC current was supplied by a DC source (LNG 50-4 , Heinzinger).

Table 2

Accuracy of DMM 192 multimeter

Location	Detector	Measuring range	Resolution	ΔT/K
Furnace	Pt–PtRh10	0.2 V	1 μV	0.1
Calorimeter	Pt1000	2 kΩ	10 mΩ	0.0026
Calorimeter	NTC 150	200 kΩ	100 mΩ	0.00012
Water bath	NTC 150	200 kΩ	100 mΩ	0.00012

3. Experimental procedure

The samples were encapsulated in silicon ampoules of 15 mm o.d. and 50 mm length and sealed under vacuum. They were heated to a given temperature in the furnace. The average specimen contained between 1 and 15 g substance.

Temperatures of the furnace and of the calorimeter were measured with the aid of a Keithley DMM 192 multimeter, which had an IEEE interface to transfer the data to an IBM PC. Registration, storage and processing of the data were made by means of a TURBO Pascal program. The sensitivity of the various measuring devices are given in Table 2.

The sample was held in the furnace for 4 h to obtain constant temperature. When the temperature of the calorimeter block was constant and near 298.15 K, the temperature of the calorimeter was registered for 375 s in intervals of 1 s. The gates (Fig. 4: 10) were opened. The sample was dropped into the calorimeter by operating the magnetic trigger and the gates closed. After the drop, the temperature of the calorimeter block was registered for 2225 s in intervals of 1 s. All data were stored in an ASCII file.

The heat of the content of the quartz, used for the ampoules, was determined in separate experiments. The values were in good agreement with the data given by Barin [2,3].

The increase in the temperature of the calorimeter was determined from the registered temperatures by the Regnault-Pfaundler equation, using a TURBO Pascal program.

The enthalpies of the substances were fitted by a curve of the form

$$Q = d + (aT) + (bT^2) + (cT^{-1}) \tag{1}$$

The heat capacities were given by

$$c_p = a + (2bT) - (cT^{-2}) \tag{2}$$

The calorimeter was calibrated electrically from 20 calibrations (Table 3), which gave a calibration factor $K = 7382.7 \pm 8.2$ J K^{-1}. The calorimeter was also calibrated by dropping a known amount of α-Al_2O_3, encapsulated in a silica ampoule, into the calorimeter, using the $\Delta H(T - 298.15\ \mathrm{K})$ data of α-Al_2O_3, given by Barin [2,3]. In addition the reproducibility was tested. In this case the furnace temperature was held at 750 K. If necessary, the enthalpy values were corrected to 750 K for small deviations from the temperature (Table 4). By the drop method $K = 7379.7 \pm 3.2$ J K^{-1} (Table 3) was obtained.

Table 3

Calibration of the calorimeter; calibration factor in J K^{-1}

No.	Calibration by α-Al_2O_3	Electrical calibration	No.	Calibration by α-Al_2O_3	Electrical calibration
1	7374.3	7388.4	12	7383.8	7390.3
2	7382.3	7371.7	13	7382.8	7386.1
3	7385.5	7399.8	14	7380.0	7379.8
4	7375.5	7387.0	15	7377.4	7386.9
5	7383.2	7392.0	16	7378.7	7391.0
6	7382.4	7375.7	17	7376.9	7388.7
7	7380.1	7377.0	18	7377.7	7379.2
8	7374.3	7373.9	19	7380.0	7374.9
9	7377.5	7369.0	20	7382.5	7384.5
10	7381.7	7370.6	K	7379.7	7382.7
11	7377.4	7387.5	σx	±3.19	±8.19

The standard deviation was calculated by the equation

$$\sigma x = \sqrt{\frac{\sum x^2 - n\bar{x}^2}{n}} \tag{3}$$

The accuracy of the calorimeter was checked by dropping a silver rod (99.995% purity, 98.2829 g; Heraeus). The results are listed in Table 5.

The errors of the enthalpy contents, measured in the calorimeter, can be separated into systematic and random errors. Systematic errors arise mainly from:

(a) the uncertainty of the reported heat capacity of silica glass (±0.5%),
(b) the heat loss of the sample during the drop (estimated error <0.02%),
(c) ageing of the thermocouple (calibration must be performed every month).

Random errors are due to the following factors:

(a) the corrected value of ΔT, the temperature increase of the calorimeter; sample: α-

Table 4

Reproducibility, ten runs with α-Al_2O_3, encapsulated in a silica ampoule

No.	Furnace temperature in K	ΔT calorimeter in K	Q_{sample} in J $ampoule^{-1}$	No.	Furnace temperature in K	ΔT calorimeter in K	Q_{sample} in J $ampoule^{-1}$
1	750	1.3893	10256.5	8	750	1.3897	10259.5
2	750	1.3907	10267.1	9	750	1.3907	10267.5
3	750	1.3803	10190.3	10	750	1.3901	10262.9
4	750	1.3921	10277.7	x	750	1.3884	10250.0
5	750	1.3885	10251.0	σx		±0.003	±25.0
6	750	1.3884	10249.8	%		±0.2	±0.2
7	750	1.3840	10217.7				

Table 5
Enthalpy of silver

T/K	This calorimeter $\Delta H(T-298.15\text{ K})$ in kJ mol^{-1}	Barin $\Delta H(T-298.15\text{ K})$ in kJ mol^{-1}	Deviation $\Delta H(T-298.15\text{ K})$ in kJ mol^{-1}	Deviation ΔH in %
756.8	12.163	12.168	0.005	–0.04
794.0	13.067	13.210	0.143	–1.0
814.5	13.721	13.790	0.069	–0.5
1042.3	20.454	20.475	0.021	–0.1
1048.2	20.933	20.632	0.301	+1.4
1052.6	20.645	20.765	0.120	–0.6
1053.0	20.803	20.778	0.025	+0.1

Al_2O_3 in a silica ampoule; $m_{\text{ampoul}} \cong 15$ g ($T_0 = 750$ K; $\Delta T = 1.3884$ K; error = ±0.2%),

(b) the initial temperature T_0 (furnace $T_0 = 400$ K; maximum error = ±0.025%) (furnace $T_0 = 1350$ K; maximum error = ±0.007%),

(c) the equilibrium temperature of the calorimeter block (1 h; 298.15 K; $\Delta T = \pm 0.0007$; maximum error = ±0.0005%),

(d) the weights of the substance and the silica ampoule (±0.1 mg; error = ±0.001%),

(e) the uncertainty of the calibration factor ($K = 7382.7$; ±8.2 J K^{-1}; error = ±0.11%).

The main error arises from the scatter in the heat capacity of silica glass. The total error decreases with increasing temperature differences between furnace and calorimeter.

Acknowledgements

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