

# DETERMINATION OF STANDARD HEATS OF POLYMORPHIC TRANSFORMATIONS AND MELTING OF SOME MONOVALENT METAL HALIDES BY THE DTA TECHNIQUE

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Received September 11th, 1975

The standard heats of polymorphic transformations and melting of silver, mercury(I), thallium, and copper(I) halides were determined by the differential thermal analysis using an apparatus of own construction. The apparatus makes it possible to follow thermal processes in static or controlled atmosphere up to 800°C, and the DTA curves can be recorded so as to allow quantitative evaluation. The experimental values of the standard heats are compared with tabulated values, determined mostly by calorimetric measurements.

The standard heats of polymorphic transformations ( $\Delta H_p$ ) and melting ( $\Delta H_m$ ) are important physico-chemical constants. Their calorimetric determination is in fact more accurate than the determination based on the DTA method, but from the DTA curve we are able to study the behaviour of the substance during controlled heating or cooling in a wide temperature range. The thermal behaviour of silver, mercury(I), thallium, and copper(I) halides is only sporadically mentioned in the literature<sup>1</sup>, and even more rarely is found a quantitative evaluation of their DTA curves<sup>2</sup>. The experimental results reported in this paper are compared with available tabulated values, which have been mostly measured calorimetrically<sup>3-5</sup>.

## EXPERIMENTAL

### Chemicals

Substances used for the calibration of the DTA apparatus as well as thallium bromide, thallium chloride, and mercury(I) chloride were commercial chemicals, reagent grade purity. The other compounds to be measured were prepared in the Institute of Physics of Solids of Czechoslovak Academy of Sciences, their purity was better than reagent grade. As the standard for the DTA technique served freshly annealed aluminium oxide for chromatography.

### Apparatus

The apparatus for differential thermal analysis was of own construction<sup>6</sup>; it consists of the apparatus itself, a programmed temperature controller, recorder, and integrator. In the apparatus,

the sample and the standard are placed in thin layers in platinum crucibles, which bear precisely on the base of the sample holder. The difference between the temperature of the sample and that of the standard is measured by means of AuPd-PtRh thermocouples, the sample temperature by means of a Pt-PtRh thermocouple. The programmed increase and decrease of temperature is provided by a linearly programmed unit (manufactured at the Development workshop, Faculty of Natural Sciences), which is controlled by the input signal from the AuPd-PtRh thermocouple. The unit allows the option of the heating rate from 0.16 deg/min to 60 deg/min. After the preselected temperature is reached, the direction of the course is reversed, so that cyclic scanning (heating-cooling) is possible. The recorder unit consists of two line compensation recorders EZ 2. To the recorder which gives the temperature difference ( $\Delta T$ ), and integrator IT 1 (Laboratorní přístroje, Prague), whose numerical reading is proportional to the area of the effect followed, is connected over a transmitting potentiometer. The other recorder is employed to measure the sample temperature.

### Measurement Procedure

A weighed sample of a selected grain size is rammed by a defined pressure in a platinum crucible. The values of the grain size and the ramming pressure were equal for all the measured and reference substances. The crucible is placed on the sample holder and the DTA curve is recorded with the heating rate of 5 deg/min; simultaneously the integrator records the area of the thermal effects. The function of the apparatus was tested first by model experiments with calibration substances ( $\text{NH}_4\text{NO}_3$ ,  $\text{KNO}_3$ , and  $\text{NaNO}_3$ ) whose  $\Delta H_p$  and  $\Delta H_m$  values are tabulated<sup>1,3,7</sup>. The weights of the batches of the calibration substances lay in the span of 14.5–15.5 mg. Based on the known weight  $M$  of the batch, the area  $S$  of its thermal effects, and tabulated standard heat  $\Delta H$ , the calibration factor  $A$  occurring in the relation

$$S = \Delta H \cdot M/A$$

was calculated. For measurements in static atmosphere we found the value  $A_1 = (12.5 \pm 1.8) \cdot 10^{-4} \text{ J mm}^{-2}$ , for measurements in inert atmosphere provided by argon stream we found  $A_2 = (13.6 \pm 1.8) \cdot 10^{-4} \text{ J mm}^{-2}$ . From the DTA curves (14 calibration substances<sup>6</sup>) and tabulated values of temperatures of polymorphic transformations and melting we plotted a working curve in the range of 32–770°C for reading the instantaneous temperature. The temperatures of the various effects were determined graphically according to Šesták and Bergreen<sup>8</sup>.

The monovalent metal halides mentioned were investigated employing the heating rate of 5 deg/min, the weights of the batches lay in the range of 19.5–20.5 mg. The thermal behaviour of mercury(I), thallium, and silver halides was studied on air, that of copper(I) halides in inert atmosphere. The standard heats  $\Delta H_m$  and  $\Delta H_p$  were determined with the accuracy of 2.38%, the temperatures with the accuracy of  $\pm 2.5^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The technique of determination of the temperatures and standard heats of the processes studied was tested on the apparatus described by a series of measurements, which confirmed the reproducibility of the results. The differences between the measured temperatures of three determinations were low enough for the calculation of their arithmetic means, as given in Table I as the experimental results. The deviations

from the arithmetic means were usually lower than 1%, only in two cases they attained 1.5%. The analogous deviations for the standard heats (also averages of three determinations) lay usually between 1 and 3%, sometimes even below 1%; only in two cases, deviations as high as 5% were obtained. The integrator was found to yield results one order more accurate than as could be obtained by techniques of empirical integration (planimetric technique or weighing of the area enlarged photographically); it gives, however, accurate data only in case that the points of the start and the end

TABLE I

Comparison of Experimental Temperatures and Standard Heats of Thermal Processes with Tabulated Data

Thermal processes: P polymorphic transformation, M melting, S sublimation.

Substance	Process	Temperature, °C				Standard heat, kJ mol <sup>-1</sup> <sup>a</sup>			
		exp.	ref. <sup>3</sup>	ref. <sup>4</sup>	ref. <sup>5</sup>	exp.	ref. <sup>3</sup>	ref. <sup>4</sup>	ref. <sup>5</sup>
AgF	P	79	—	—	—	6.4	—	—	—
	P	250	—	—	—	1.6	—	—	—
	M	425	435	—	—	9.4	—	—	—
AgCl	M	442	455	455	455	14.2	13.0	13.2	13.2
AgBr	M	420	430	424	430	9.4	9.2	8.8	9.1
Hg <sub>2</sub> F <sub>2</sub>	P	159	—	—	—	9.2	—	—	—
	P	260	—	—	—	11.1	—	—	—
	P	305	—	—	—	23.5	—	—	—
	P	550	—	—	—	37.3	—	—	—
Hg <sub>2</sub> Cl <sub>2</sub>	S	222	—	—	—	139.9	—	—	—
Hg <sub>2</sub> Br <sub>2</sub>	S	212	—	—	—	124.9	—	—	—
Hg <sub>2</sub> I <sub>2</sub>	S	179	—	—	—	96.7	—	—	—
TlCl	M	428	429	—	427	16.8	15.9	—	17.8
TlBr	M	450	460	—	460	19.9	16.3	—	25.0
TlI	M	418	440	—	440	16.5	14.6	—	13.0
CuCl	P	410	—	408	—	2.3	—	4.0	—
	M	425	430	424	429	5.8	10.2	10.3	10.9
CuBr	P	390	380	388	—	3.8	5.9	8.9	—
	P	460	465	470	—	8.9	2.9	1.6	—
CuI	M	479	488	489	487	3.9	9.6	7.2	9.6
	P	371	—	372	—	8.2	—	8.2	—
CuI	P	379	—	—	—	2.7	—	—	—
	P	405	—	403	—	0.4	—	—	—
	M	575	588	600	587	11.0	10.9	8.3	10.8

<sup>a</sup> The values of the standard heats reported in kcal mol<sup>-1</sup> were recalculated according to the relation 1 kcal = 4.187 kJ.

of the thermal effect lie in the so-called zero band of the integrator. This condition was met during each measurement by switching the integrator in immediately before the thermal effect occurred, so that the drift of the base line in the temperature region up to the start of the thermal effect was not recorded. The comparison of the experimental temperatures and standard heats of the processes followed with tabulated values is given in Table I.

*The authors wish to thank Professor M. Ebert for valuable comments and interest devoted to this work, Dr M. Smíšek and Mr M. Dušek for manufacturing the linearly programmed unit, and Dr M. Lébl for providing us with the substances measured.*

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Translated by P. Adámek.