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# EVALUATION OF HEATS AND ENTROPIES OF FUSION BY QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS METHOD

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## ABSTRACT

The technique of dynamic differential calorimetry is discussed as a method for the quantitative determination of several thermodynamic properties of crystals. Some results on heats and entropies of fusion of binary tetrahedral semiconductors are reported.

## INTRODUCTION

The method of dynamic differential calorimetry[1,2] has frequently been applied for the quantitative measurement of thermal effects in a great variety of both organic and inorganic materials. If a differential thermal analysis (DTA) apparatus is employed under standard conditions and accurately calibrated[3–7], several thermodynamic properties, namely heats of formation, allotropic and order–disorder transition energies, specific heats and heats and entropies of fusion, can be quantitatively evaluated. In several cases the accuracy of results can be compared with direct and indirect calorimetric measurements.

A detailed discussion of the more important factors affecting the quantitative DTA (i.e., particle size, heating rate, sample state, holder dimensions, etc.) was made by David[8] and some theoretical implications of the method were elucidated by Faktor and Hanks[9]. These authors suggested that heat changes can be determined with an experimental error of ±4–7%.

In this paper, as an introduction to the experimental problem of the connections between thermodynamic and bonding parameters[10], the method of dynamic differential calorimetry is described and preliminary results are reported on heats and entropies of fusion of some binary tetrahedrally coordinated compounds.

## TECHNICAL PROCEDURES AND CALIBRATION

The DTA apparatus consisted of a fully automatic standard thermoanalyser with operating range 25–1550 °C. Sample and reference material ($Al_2O_3$) were contained in two crucibles supported by a Pt–PtRh 10% differential thermocouple, which alternatively measured both differential e.m.f. and sample temperature. The entire assembly was enclosed in an alumina cup in order to obtain a uniform thermal field. Measurements were performed under standard conditions, i.e., linear heating rate of 5 °C min$^{-1}$, chart speed of 0.4 cm min$^{-1}$ and recorder sensitivity of 4 $\mu$V cm$^{-1}$, which allowed the detection of thermal effects involving temperature differences of about 0.3 °C.

Two different calibrations were obtained by using alumina crucibles (Fig. 1a) under reduced helium pressure (about 300 Torr) and vacuum sealed quartz ampoules (Fig. 1b), containing elements and substances with known heat of fusion, melting in the temperature range 150–1100 °C.

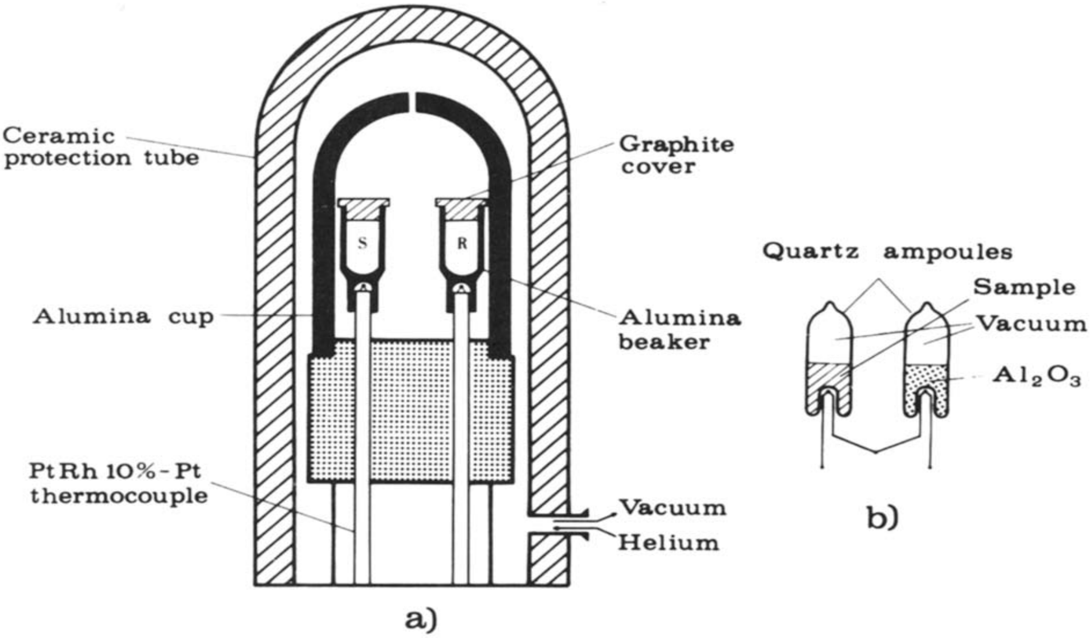

Fig. 1. Schematic DTA assembly for calorimetric measurements with alumina crucibles (a) and quartz ampoules (b).

If $\Delta H$ is the heat absorbed (evolved) during fusion (solidification) by $\mu$ moles of a given standard substance, then[11]:

$$\Delta H = K \int_0^t \Delta T \, dt$$

where $\int_0^t \Delta T \, dt = A$ is the peak area occurring in the time $(0, t)$ and $K$ the heat transfer coefficient of the system.

Generally $K$ increases with increasing temperature and a dependence-law $K \propto T^3$ has been suggested[9,12]. However, the uncertainties of literature data and experimental results in the calibration curve and the particular characteristics of the apparatus do not allow, in our opinion, the establishment of a rigorous analytical expression for the $K$ coefficients. The $K(T)$ function is, therefore, an empirical curve which must be experimentally determined for each single apparatus.

We found that within experimental errors our results can be fitted very well by the following linear relation

$$K = a + bT \text{ cal/cm}^2 \qquad (T \text{ in } ^\circ\text{C})$$

The constants $a$ and $b$, refined by the least-squares method, were found to be $a = 1.69$ and $b = 0.13 \cdot 10^3$ for the calibration with alumina crucibles (Table 1) and $a = 0.72$ and $b = 1.77 \cdot 10^3$ for the one with quartz ampoules (Fig. 2).

The calibration curves were drawn by means of the analysis of both heating and cooling thermograms (with an exception for antimony and tellurium which show supercooling), each point being the mean result of at least three different thermal cycles. Before each single run, the charges (0.5–1.5 g) were melted with a heating rate of 20 °C min$^{-1}$, in order to obtain massive ingots in crucibles.

As regards the measurements, we note that the uncertainty of the heats of fusion $\Delta H_F$ of standard substances and the systematic errors $\Delta A = \pm 0.1$ cm$^2$ and $\Delta K = \pm 0.08$ cal cm$^{-2}$ in computing the peak areas and the $K$ constants, respectively, allows us to calculate the $\Delta H_F$ values with an experimental error of ±6%. However, the mean variation in the results of Table 1 is only 2%. The large

TABLE 1

MELTING POINTS, EXPERIMENTAL AND CALCULATED VALUES OF HEATS OF FUSION OF STANDARD SUBSTANCES

| *Substance* | *Melting point, $T_F$ (°C)* | *Heat transfer coefficient, K (cal cm$^{-2}$)* | *Heat of fusion, $\Delta H_F$ (kcal mol$^{-1}$)* | | Δ % |
|---|---|---|---|---|---|
| | | | *Expt.* | *Calc.* | |
| In | 156.6 | 1.72±0.08 | 0.78±0.02[a,b] | 0.79±0.06 | +1.3 |
| Sn | 231.9 | 1.71±0.06 | 1.71±0.02[b] | 1.72±0.12 | +0.6 |
| Bi | 271.4 | 1.73±0.08 | 2.60±0.05[a,b] | 2.60±0.19 | 0 |
| Cd | 321.0 | 1.70±0.10 | 1.48±0.05[a] | 1.51±0.11 | +2.0 |
| Pb | 327.4 | 1.75±0.06 | 1.14±0.01[a] | 1.13±0.08 | −0.9 |
| Zn | 419.5 | 1.79±0.07 | 1.74±0.03[b] | 1.65±0.12 | −5.0 |
| Te | 449.6 | 1.74±0.10 | 4.18±0.13[a,b] | 4.20±0.30 | +0.5 |
| Sb | 630.5 | 1.74±0.05 | 4.74±0.01[a] | 4.82±0.34 | +1.7 |
| Al | 660.1 | 1.75±0.05 | 2.56±0.01[a] | 2.60±0.18 | +1.6 |
| KBr | 734 | 1.80±0.08 | 6.1 ±0.1[b] | 6.15±0.43 | +0.7 |
| NaCl | 801 | 1.81±0.10 | 6.7 ±0.2[b] | 6.61±0.46 | −1.3 |
| Ag | 960.8 | 1.86±0.10 | 2.78±0.08[a] | 2.72±0.19 | −2.2 |
| Au | 1063 | 1.81±0.11 | 3.05±0.10[b] | 3.08±0.21 | +1.0 |
| Cu | 1083 | 1.83±0.11 | 3.1 ±0.1[b] | 3.10±0.21 | 0 |

[a] Ref. 15. [b] Ref. 16.

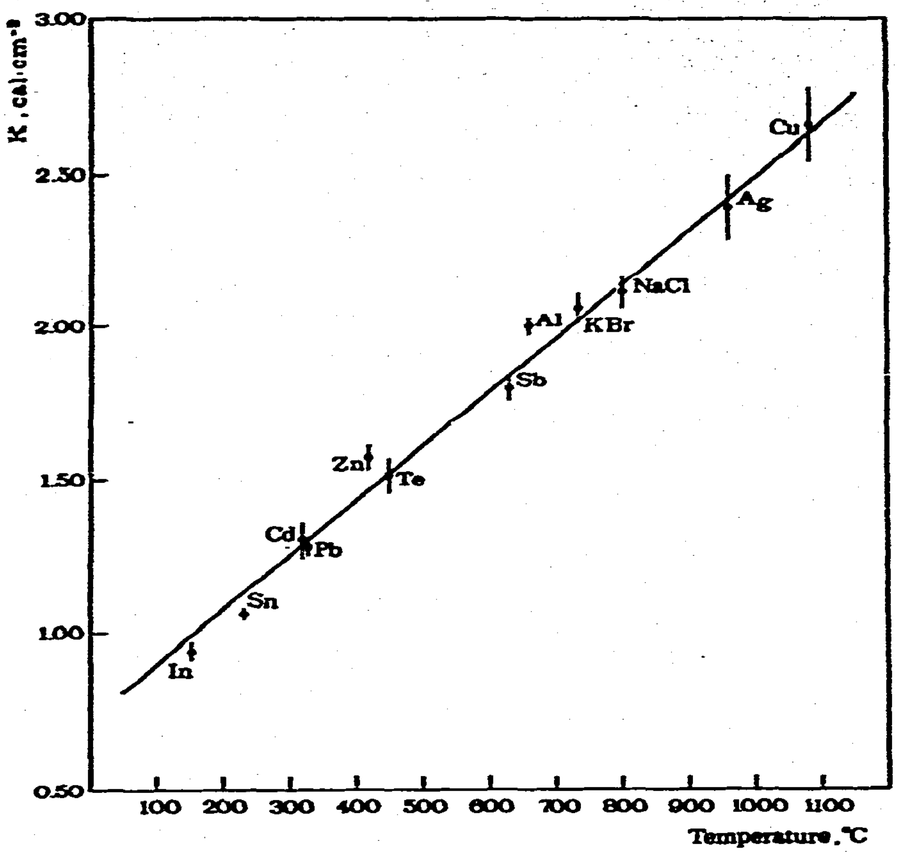

Fig. 2. Temperature variation of the heat transfer coefficient for the calibration with quartz ampoules.

discrepancy (5%) of zinc, observed in both calibrations, might be due to the too high value assumed for its heat of fusion. In fact, variation falls to 3% if Kelley's[13] value $\Delta H_F = 1.595$ kcal mol$^{-1}$ is adopted.

## EXPERIMENTAL RESULTS

We measured heats and entropies of fusion of the following tetrahedral semi-conductors with melting points below 1400 K: Ge, AlSb, GaSb, InSb, InAs, InP, CdTe, HgSe, HgTe, CuCl, AgI and $In_2Te_3$. Single crystals ($A^{III}B^{V}$ compounds) and powders ($A^{I}B^{VII}$ compounds) were employed as starting materials. Other samples were prepared in polycrystalline form by the direct synthesis method starting from stoichiometric amounts of "Specpure" elements (Johnson–Matthey) and checked with micrographic and röntgenographic examinations. For $In_2Te_3$, X-ray powder diffraction patterns belonging to an apparent zinc-blende-type structure, were obtained only after long annealing of the powders at about 550 °C. According to Thomassen et al.[14], a solid–solid phase transition of order–disorder type appears for this compound near the melting point. Other crystals showed the zincblende structure, with an exception for AgI, which changed form wurtzite to zincblende structure at 150 °C.

Calorimetric measurements were performed by both previously described methods with three different thermal cycles for each compound. Typical thermograms are reported in Fig. 3. The results of various runs were in excellent agreement and considerably within experimental errors.

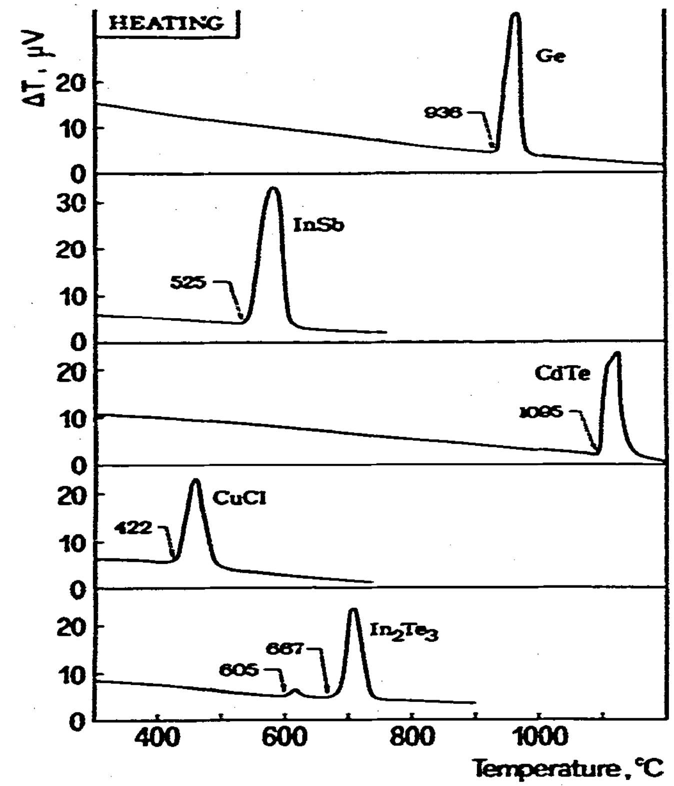

Fig. 3. DTA heating thermograms of some tetrahedrally coordinated semiconductors.

For AlSb, InAs, InP, CdTe, HgSe and HgTe the sealed tube technique only was employed. In fact, under normal helium pressure, large deviations of DTA curves from the base line were indicative of a loss of weight in the samples beginning below the melting point. In any case, in computing the peak areas, only the heating thermograms were considered.

The melting points of all compounds were determined by means of a careful calibration of the apparatus with standard elements. They agreed with the literature data with a mean accuracy of ±5 K.

The melting points, heats and entropies of fusion are in Table 2, and compared with the data obtained or estimated by other authors. The good agreement shows the validity of the method and its applicability to the study of these thermodynamic properties in more complex semiconducting compounds.

TABLE 2

MELTING POINTS, HEATS AND ENTROPIES OF FUSION OF SOME TETRAHEDRAL SEMICONDUCTORS

| *Crystal* | *Melting point,* $T_F$ *(K)* | *Heat of fusion,* $\Delta H_F$ *(kcal mol$^{-1}$)* | | *Entropy of fusion,* $\Delta S_F$ *(e.u. mol$^{-1}$)* |
|---|---|---|---|---|
| | | *Literature* | *This work* | |
| Ge | 1210 | $7.6^{a}$ $8.3^{b}$ $8.1^{c}$ $7.7^{d}$ | $8.2 \pm 0.5$ | $6.8 \pm 0.4$ |
| AlSb | 1330 | $14.2^{e}$ $19.0^{k}$ $16.9^{i}$ $10.6^{v}$ | $18.2 \pm 1.1$ | $13.7 \pm 0.9$ |
| GaSb | 980 | $12.0^{h}$ $14.6^{l}$ $15.6^{m}$ $18.8^{k}$ $12.3^{i}$ $15.6^{v}$ $16.0^{w}$ | $13.9 \pm 0.8$ | $14.2 \pm 0.9$ |
| InSb | 798 | $12.2^{h,m}$ $11.2^{p,w}$ $9.5^{q}$ $11.5^{5}$ $11.8^{l}$ $10.2^{k}$ $10.1^{i}$ $11.4^{v}$ $9.0^{o}$ | $11.6 \pm 0.7$ | $14.5 \pm 0.9$ |
| InAs | 1215 | $26.0^{o}$ $17.8^{m}$ $10.7^{k}$ $15.2^{i}$ $12.6^{q}$ $14.0^{r}$ $17.6^{z}$ $18.4^{w}$ | $14.8 \pm 0.9$ | $12.2 \pm 0.8$ |
| InP | 1330 | $12.0^{o}$ $19.7^{k}$ $16.6^{i}$ | $14.4 \pm 0.9$ | $10.8 \pm 0.7$ |
| CdTe | 1365 | | $5.8 \pm 0.4$ | $4.3 \pm 0.3$ |
| HgSe | 1072 | | $4.8 \pm 0.3$ | $4.5 \pm 0.3$ |
| HgTe | 943 | | $4.4 \pm 0.3$ | $4.7 \pm 0.4$ |
| CuCl | 702 | $2.45^{d}$ $2.62^{b}$ | $2.6 \pm 0.1$ | $3.7 \pm 0.2$ |
| AgI | 830 | $2.25^{d}$ | $2.1 \pm 0.1$ | $2.5 \pm 0.1$ |
| $In_2Te_3$ | 940 | | $12.8 \pm 0.8$ | $13.6 \pm 0.9$ |

[a] Ref. 15. [b] Values selected by Loebel, ref. 17. [c] After Wagman et al., ref. 18. [d] Ref. 16. [e] Ref. 19. [h] Ref. 20. [i] Values estimated by Sirota by taking $\Delta S_F = 12.5$ e.u. mol$^{-1}$, ref. 21. [k] Average values obtained over the liquides branches of $T$–$x$ phase diagrams, ref. 21. [l] Following Wade and Banister, ref. 22. [m] Ref. 23. [o] Ref. 24. [p] Ref. 25. [q] Ref. 26. [r] Ref. 27. [v] Ref. 28. [z] Ref. 29. [w] Ref. 20.

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