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# CALORIMETRIC STUDIES OF THE HEATS OF FORMATION OF IIIB–VB ADAMANTINE PHASES

S. MARTOSUDIRDJO* AND J. N. PRATT

*Department of Physical Metallurgy & Science of Materials, University of Birmingham, Birmingham (England)*

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## ABSTRACT

The techniques of precipitation calorimetry and solution calorimetry, with molten tin as the solvent medium, have been used to measure the heats of formation of six IIIB–VB semiconductor compounds. Standard heats of formation at 298 K obtained from these measurements are: AlP (−17.41), AlAs (−14.43), AlSb (−5.97), GaP (−12.49), GaAs (−9.76) and InP (−6.75) −*k* cal g atom$^{-1}$. These and other data are used to examine the validity of published theoretical estimates of the heats of formation of these phases. The interrelation of their heats of atomization and energy band gaps is briefly discussed.

## INTRODUCTION

Thermodynamic properties of semi-conducting phases are of both practical and theoretical interest. Technologically, these data are relevant to the design and control of the processing of such materials for the manufacture of electronic devices. At the same time, they are of fundamental significance in attempting to further the understanding of the interrelation of bond character, structural stability and energy band gaps of such phases. Since they include several of the technologically most important semi-conductor compounds, the classic IIIB–VB adamantine structures have been the subject of many physical and chemical studies. Nevertheless, the heats of formation of most of these have previously not been well established. Published data reveal considerable discrepancies; the majority of suggested values are derived from vapour phase equilibria or e.m.f. measurements or are estimates based on phase boundary analyses or empirical models. Some have been examined by combustion or acid-solution calorimetry, but very few have been investigated by liquid-metal calorimetry, despite its particular suitability for the study of alloy phases. The technique of tin-solution calorimetry was, however, applied to the study of IIIB–VB compounds by Schottky and Bever[1]. These workers successfully measured the heats of formation of InSb, GaSb and InAs by this means, but were unable to obtain satisfactory values for

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*On study leave from Indonesian Institute of Sciences (LIPI).

(Note: Throughout this paper 1 cal = 4.184 J)

GaAs, InP and AlSb owing to the relative insolubility of these compounds in liquid tin at the calorimeter temperatures. This problem has been circumvented in the present studies by using a precipitation technique and this has enabled satisfactory measurements of the heats of formation of AlP, AlAs, AlSb, GaP, GaAs and InP to be made.

## EXPERIMENTAL

The method of precipitation calorimetry relies on the ability to induce precipitation of the phase under investigation by the addition of one of its components to a *dilute* solution of the other component in a liquid metal solvent. The procedure requires the separate measurement of the heat of solution of the component predissolved in the solvent and of the heat of precipitation when the second pure component is introduced. Basic requirements for the successful application of the precipitation technique have been discussed in an earlier publication[2].

In the present case, molten tin (Pass S grade, 99.999% purity) was used as the solvent and samples were introduced from a dispenser at near room temperature. Denoting the dispenser temperature by $T_i$ and the tin-bath temperature by $T_f$, the steps involved in deriving the heat of formation of the compound may be summarised as:

$$\langle \mathrm{A}\rangle_{T_i} \rightarrow \{\mathrm{A}\}^{\mathrm{Sn}}_{T_f}, \qquad \Delta H_1 \text{ (dissolution)} \tag{1}$$

$$\langle \mathrm{A}\rangle_{T_i} \rightarrow \langle \mathrm{A}\rangle_{T_f}, \qquad \Delta H_2 = \int_{T_i}^{T_f} Cp_{\mathrm{A}} \cdot \mathrm{d}T \tag{2}$$

$$\langle \mathrm{B}\rangle_{T_i} + \{\mathrm{A}\}^{\mathrm{Sn}}_{T_f} \rightarrow \langle \mathrm{AB}\rangle_{T_f}, \qquad \Delta H_3 \text{ (precipitation)} \tag{3}$$

$$\langle \mathrm{B}\rangle_{T_i} \rightarrow \langle \mathrm{B}\rangle_{T_f}, \qquad \Delta H_4 = \int_{T_i}^{T_f} Cp_{\mathrm{B}} \cdot \mathrm{d}T \tag{4}$$

$$\langle \mathrm{A}\rangle_{T_f} + \langle \mathrm{B}\rangle_{T_f} = \langle \mathrm{AB}\rangle_{T_f}, \qquad \Delta H_{\mathrm{AB}} \text{ (formation)} \tag{5}$$

$$\Delta H_{\mathrm{AB}} = \Delta H_1 - \Delta H_2 + \Delta H_3 - \Delta H_4$$

To obtain meaningful data, reaction (1) should correspond to infinite dilution conditions, while "complete" (i.e. >99%) precipitation of B as the compound AB must be achieved by reaction (2). Experimental bath temperatures and solute concentrations were therefore selected to meet these conditions and also, as far as possible, to give fast rates of precipitation and return of the calorimeter to equilibrium. The measurements were performed using an isoperibol calorimeter normally used for solution calorimetry. No modification of the apparatus or basic evaluation procedure was involved and a description of these may be found elsewhere[3]. The calorimeter was calibrated by the drop technique, using approximately 0.5 g samples of tin initially at room temperature; the associated heat effect was calculated using Hultgren et al.'s[4] assessed data for this element. During each series of experiments, a calibration drop was made after every two experimental specimens and the calibration value ($C_c$) used for individual specimens was interpolated from the observed slow linear variation of $C_c$ with increasing bath content.

The Al, Ga, In, As and Sb used in the experiments were all 99.999% "Specpure" materials supplied by Johnson-Matthey and Co. and the red P, of similar purity, was obtained from British Drug Houses Ltd. In the normal procedure, the VB element involved was pre-dissolved in the tin-bath and the less volatile and more easily handled element was added as the precipitating agent. With AlSb, however, this sequence proved unsatisfactory, since the rate of compound precipitation at feasible bath temperatures was restricted by the slow solution of Al at low temperatures; good results were obtained by pre-dissolving the Al and adding Sb to complete the precipitation. The solubility of InP in liquid tin is such that either the precipitation technique or solution calorimetry would appear to be applicable. In initial experiments the former method was attempted, but the precipitation proved to be weak and inconsistent. Measurements on this compound were therefore made by orthodox tin-solution calorimetry; a sample of InP was provided for this purpose by the Materials Division, Royal Radar Establishment, Malvern.

Calorimeter specimens were introduced in the form of wire, chips or coarse powder, depending on the material involved. The more finely divided samples were enclosed in small pure tin capsules, of known weight, before loading into the calorimeter and the observed heats were corrected for the effect of the capsules.

## RESULTS

The required values of the isothermal heats of solution of the elements, at or sufficiently close to the appropriate temperatures, were taken mainly from previous studies made in the authors' laboratory[5,6] or elsewhere[7,8]. New measurements were made, in the course of the present investigation, of the heat of solution of aluminium at 727 K; the results showed good consistency with values previously observed at higher and lower solution temperatures. The element heat of solution values used in the heat of formation calculations are shown in Table 1.

TABLE 1

HEATS OF SOLUTION OF ELEMENTS IN TIN (cal g atom$^{-1}$)

| *Element* | $\Delta\bar{H}$ | *T (K)* | *Reference* |
|---|---|---|---|
| Al | +6081 | 727 | Present work |
| | +6195 | 750 | 7 |
| | +5984 | 656 | 5 |
| P | +5821 | 750 | 8 |
| As | +2993 | 750 | 8 |
| Sb | +3720 | 750 | 8 |
| In | −154 | 656 | 6 |

Except for red phosphorus, in the case of which the $C_p$ equation from Kubaschewski et al.[9] was used, the changes of heat content of the pure components between drop and bath temperatures ($\Delta H_2$ and $\Delta H_4$ above) were evaluated using Hultgren et al.'s assessed data for the specific heats of the elements[4]. The heats of formation of the compounds, at the various experimental temperatures, yielded by the present precipitation or solution (InP) calorimetry are assembled in Table 2; Shottky and Bever's[1] published values for GaSb, InAs and InSb have been included to complete the series.

TABLE 2

HEATS OF FORMATION OF IIIB–VB COMPOUNDS (kcal g atom$^{-1}$)

Reference states: solids; P(red).

| | | |
|---|---|---|
| *AlP*[a] | *AlAs*[a] | *AlSb*[a] |
| $-17.684 \pm 0.205$ | $-14.712 \pm 0.146$ | $-6.046 \pm 0.09$ |
| 582 K (12 meas.) | 670 K (19 meas.) | 527 K (7 meas.) |
| *GaP*[a] | *GaAs*[a] | *GaSb*[c] |
| $-12.660 \pm 0.108$ | $-9.845 \pm 0.159$ | $-4.97 \pm 0.04$ |
| 582 K (11 meas.) | 523 K (21 meas.) | 273 K (12 meas.) |
| *InP*[b] | *InAs*[c] | *InSb*[c] |
| $-6.778 \pm 0.131$ | $-7.40 \pm 0.12$ | $-3.47 \pm 0.07$ |
| 333 K (13 meas.) | 273 K (14 meas.) | 273 K (12 meas.) |

[a] Precipitation calorimetry. [b] Solution calorimetry. [c] Solution calorimetry (Schottky and Bever)[1].

TABLE 3

COMPARISON OF EXPERIMENTAL AND THEORETICAL HEATS OF FORMATION OF IIIB–VB COMPOUNDS (kcal g atom$^{-1}$)

| *Compound* | *Theoretical* | | | *Experimental* |
|---|---|---|---|---|
| | *Ref. 26* | *Ref. 27* | *Ref. 18* | $\Delta H^0_{298}$ |
| AlP | −12.4 | −12.1 | — | −17.41 |
| AlAs | −8.7 | −8.7 | −20.8 | −14.43 |
| AlSb | −5.5 | −10.2 | −8.6 | −5.97 |
| GaP | −8.7 | −12.4 | — | −12.49 |
| GaAs | −5.5 | −8.2 | −8.3 | −9.76 |
| GaSb | −3.1 | −4.8 | −3.9 | −4.97 |
| InP | −5.5 | −10.2 | — | −6.76 |
| InAs | −3.1 | −5.8 | −4.6 | −7.40 |
| InSb | −1.4 | −4.5 | −1.8 | −3.47 |

In order to facilitate discussion and comparison with other data, standard heats of formation at 298 K have been derived from the experimental values and may be found in Table 3. For these computations the specific heats of the elements were taken from the sources already indicated; $C_p$ values for AlSb, GaP and GaAs, respectively, were taken from Hultgren et al.[4], Pankratz[10], and Cox and Pool[11], while

Piesbergen's[12] estimates were used for AlAs and InP. In the absence of direct information, it was assumed that $C_p$ values for the compound AlP approximate those of the isoelectronic adamantine element and data for silicon were therefore used[4].

## DISCUSSION

### *Aluminium phosphide*

The value of −17.41 ± 0.22 kcal g atom$^{-1}$ for the standard heat of formation may be considered to be well established by the present work. It is in substantial agreement with the estimate of −18 ± 1.5 derived by Panish et al.[13] from the liquidus of the Ga–Al–P system. A slightly higher value of −19.75 ± 0.25 kcal g atom$^{-1}$ was reported earlier by Kischio[14], but, being obtained by acid solution calorimetry, may be subject to greater uncertainties than the present technique owing to the larger individual heats of solution involved.

### *Aluminium arsenide*

Kischio[15] has also previously reported a heat of formation for this compound, on the basis of studies of the reaction of arsenic–saturated hydrogen with molten aluminium. He obtained a value of −13.9 ± 1.0 kcal g atom$^{-1}$ which provides support for the more precisely defined value of −14.43 ± 0.15 which is now obtained. The very substantial agreement between these two investigations thus appears to invalidate the higher value of −17.7 ± 1.6 kcal g atom$^{-1}$ indicated by the high temperature Knudsen effussion measurements of Hoch and Hinge[16].

### *Aluminium antimonide*

No experimental measurement of the heat of formation of this compound has been reported previously. The value of −5.97 ± 0.1 kcal g atom$^{-1}$ now obtained shows that the most commonly accepted previous estimates of −11.5 (ref. 17) and −12.5 (ref. 18) are most probably too high. It is noteworthy, however, that the present experimental value is in very close agreement with the value (−6.0 kcal g atom$^{-1}$) estimated more recently, by Marina and Nashel'skii[19], from heats of atomisation of other III–V compounds.

### *Gallium phosphide*

The present calorimetrically obtained value for this compound, −12.49 ± 0.11 kcal g atom$^{-1}$, again agrees well with the estimate of −13.1 made, as above, by Marina and Nashel'skii[19]. It is also in very satisfactory agreement with that computed by Thurmond[20] from phase diagram and vapour pressure studies (−12.2 ± 1.25). The slightly lower values of these three studies would therefore appear to be preferable to that (−14.55 ± 1.25) found by Ermolenko and Sirota[21] by means of oxygen bomb calorimetry.

### *Gallium arsenide*

Present precipitation calorimetry has yielded a heat of formation of −9.76 ±0.16 kcal g atom$^{-1}$ for this phase. This suggests that previous values arising from phase equilibria studies (−8.85; Thurmond[20]) or mass spectrometry (−9.0 (ref. 22)) are too low, while that selected by Sirota[18] (−10.48), on the basis of galvanic cell and bomb calorimetry studies, is slightly high. The heat of formation derived by Abassov et al.[23] from e.m.f. studies (−9.7) is, however, in excellent agreement with the present value.

### *Indium phosphide*

The heat of formation of −6.76±0.13 kcal g atom$^{-1}$, found for this phase by the present tin-solution calorimetry, again differs substantially from previously published values. Sharivov and Gadzhiev[24], studying the thermal decomposition of the compound in a calorimetric bomb, obtained a standard heat of −10.5±1 kcal g atom$^{-1}$. Criticism of the accuracy of that study has been made by Sirota[18], who has himself reported a value of −10.75±0.75 after using combustion bomb calorimetry. Similar values are suggested by high temperature mass spectrometric studies[22]. However, strong support for the validity of lower values, such as indicated by the present work, is provided by an independent tin-solution calorimetric study by Pool[25], who has obtained a value of −7.25±0.22 kcal g atom$^{-1}$ at 273 K.

### *Theoretical estimates of heats of formation*

It is of interest to examine the predictions of various theoretical models in the light of the experimental values now established; three main approaches to the calculation of the heats of formation of these compounds may be considered. In terms of the well-known Pauling model[26], the heat of formation will reflect the amount of ionic character, in the otherwise covalently bonded material, and this will be indicated by the differences in the thermochemically defined electronegativities of the components. The heat of formation is thus given by the relation

$$\Delta H(\mathrm{AB}) = -23{,}060(x_{\mathrm{A}}-x_{\mathrm{B}})^2 \text{ cal g atom}^{-1}$$

where $x_{\mathrm{A}}$ and $x_{\mathrm{B}}$ are the Pauling electronegativities. An alternative to the Pauling model is represented by Phillips and Van Vechten's[27] calculation of the heats of formation of tetrahedrally co-ordinated semiconductors, using spectroscopically derived ionicity values to define the ionic and covalent parts of the tetrahedral bonds. They have established a formula

$$\Delta H(\mathrm{AB}) = \Delta H_0(a_{\mathrm{Ge}}/a_{\mathrm{AB}})^S[1-b(E_2/\bar{E})^2]\,f_{\mathrm{i}}(\mathrm{AB})$$

where $a_{\mathrm{Ge}}$ and $a_{\mathrm{AB}}$, respectively, are the lattice constants of Ge and the compound, $f_{\mathrm{i}}$ (AB) is the fractional ionicity of bonding, $E_2$ and $\bar{E}$ are determined from the absorptive part of the dielectric constant spectrum of the compound, and the remaining terms are empirically established constants. Finally, Sirota[18] has attempted to estimate the heats of formation of some IIIB–VB compounds, from experimental electron distribution data, by using statistical atomic theory as the basis for his bond energy calculations. The various theoretical estimates, together with the experimental values, are compared in Table 3. Whilst, with a few exceptions, general trends are reasonably predicted, it is clear that none of the theoretical models yields consistently reliable values. The greatest degree of success is shown by the Phillips and Van Vechten treatment, which would thus appear at present to offer the most useful method of estimating the heats of formation of such structures.

### *Heats of atomization and band gaps*

Since the discovery of the semiconducting properties of $M^{III}X^{V}$ compounds by Welker[28], and his postulation of the energy gap's dependence on binding energy and effective ionic charges, numerous attempts have been made to establish working empirical relationships between band gaps and various experimental parameters which are directly or indirectly connected with the binding or lattice energy. Among these, Ruppel et al.[29] and Pigón[30] have considered heats of formation and Sirota[18] the heats of atomization per mole; Manca[31] has used single bond energies, calculated using Pauling's equation, and also heats of atomization per mole; Klein[32] has used ionization energies; Sclar[33], ionic and covalent radii, and Pearson[34] the average principal quantum numbers and electronegativity differences. More recently, Vijh[35] and Pratt and Chua[36], by considering heats of atomization per equivalent or per bond, have suggested single correlations applicable to a wide variety of structural types and bond character; a linear relationship approximating to $Eg(\mathrm{ev}) = -2.84 + 0.074 \times \Delta H^{\mathrm{at}}$ (kcal $\mathrm{mol}^{-1}$ $\mathrm{bond}^{-1}$) has been proposed by the latter authors. The validity of these relations to describe adequately the characteristics of low ionicity compounds is, however, not well established; data are scattered and lack reliability in many cases. By combining with the heats of vapourisation of the elements[4], the present improved heats of formation of the IIIB–VB compounds have therefore been used to re-derive

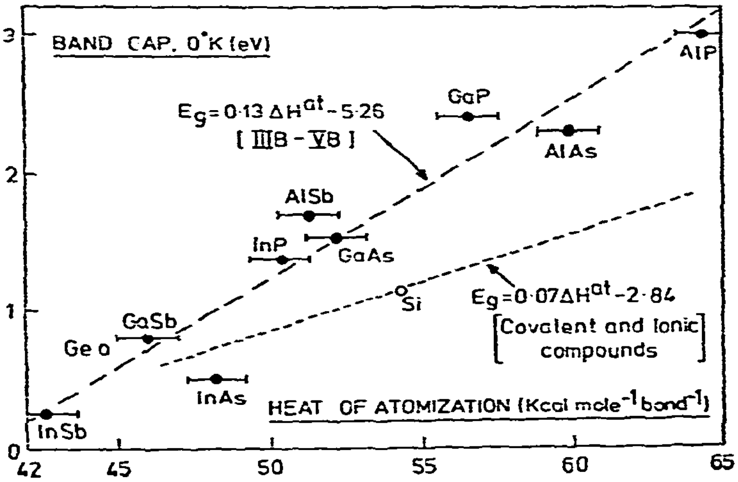

Fig. 1. The interrelation of band gaps and heats of atomization of IIIB–VB adamantine phases.

their heats of atomisation. The interrelation of these and the respective band gaps at 0 K are re-examined in Fig. 1. While a clear dependence of band gap on heat of atomization is confirmed, it is seen to differ significantly from the above relation, which is strongly influenced by the data for highly ionic compounds. It is thus evident that for the accurate prediction of band gaps of the more covalent materials a more discriminating analysis is essential and, in this connection, further similar calorimetric studies of heats of formation of related adamantine phases will be of considerable interest.

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