

## New correlative method of thermodynamic analysis of the inorganic compounds

V.P. Vasilyev<sup>1</sup>, A.F. Taldrik<sup>2</sup>, and N.I. Ilinykh<sup>3</sup>

<sup>1</sup>Chemistry Department, Moscow State University, Leninskiye Gory, Moscow 119992, Russia

<sup>2</sup>Institute of Superconductivity and Solid State Physics, Academician Kurchatov 1, Moscow 123098, Russia

<sup>3</sup>Ural Technical Institute of Telecommunications and Informatics, 15, Repin Str., Yekaterinburg 620109, Russia

### 1 Introduction

The present paper is the result of the fundamental thermodynamic study, which started with the experimental and review papers [1-5]. The main idea is based on the periodic law. The Russian scientist Kapustinsky established by calorimetry a linear relation between the enthalpies of formation and the logarithm of the total electrons' number of the compounds for the first time. He called this relation "the rule of thermochemical logarithmics" [6]. We developed this rule and established a strict relation between the enthalpies of formation, the melting temperatures and the sum of A and B atomic numbers for isostructural  $A^{III}B^V$  phases of sphalerite and wurtzite types [3, 5].

We applied our model to develop the thermodynamic calculation of the properties for isostructural compounds. Every binary system  $A^{III}-B^V$ , apart from B-As system, has only one compound  $A^{III}B^V$  with a congruent melting point. Most of the known  $A^{III}B^V$  compounds crystallize in a cubic system, of the ZnS type, except the nitrides of aluminum, gallium, indium and thallium, which have a hexagonal cell, ZnS wurtzite type. Boron nitride (hBN) is isostructural to graphite under normal conditions, and its high-pressure modification (cBN) is of blend ZnS type above 10 GPa.

The selection of  $A^{III}$  and  $B^V$  standard state is rather simple. Under standard conditions ( $P = 101325$  Pa) at  $T = 298$  K, all these elements are solid, but nitrogen which is a gas, while at some temperatures and pressures it may be solid. The experimental study of nitride systems is extremely complicated due to the fact that nitrogen gas is formed before its fusion. The liquidus curve depends on nitrogen pressure. It is necessary to maintain a nitrogen pressure between 6 and 10 GPa for nitrides [7]. It must be mentioned that nitrogen is solid at such pressures and at room temperature. The transition from solid to liquid takes place at  $T = 308$  K and  $P = 2.8$  GPa according to reference [8]. In view of the fact that phosphorus has ten forms allotropic forms [5] we selected the white phosphorus as standard state. According to obtained

results the white form is more suitable for our correlation model.

The relationship between the reduced enthalpies ( $\Delta_f H_{298}^o/T_m$ ), standard entropies ( $S_{298}^o$ ) and reduced Gibbs energies of formation ( $\Delta_f G_{298}^o/T_m$ ) of  $A^{III}B^V$  phases and the sum of their atomic numbers ( $Z_i = Z_A + Z_B$ ) was used to calculate the corresponding data of unknown phases. The method of similarity in the critical analysis of  $A_{0.5}^{III}B_{0.5}^V$  heats capacities is discussed and a set of equations  $C_p(T)$  is presented.

### 2 Correlations between the thermodynamic functions (enthalpies and Gibbs energy of formation) and standard entropies of the $A_{0.5}^{III}B_{0.5}^V$ phases and their melting points

#### 2.1 Enthalpy of formation ( $\Delta_f H_{298}^o$ ) of the $A^{III}B^V$ phases

The present investigation was initiated in [3-5], where the enthalpies of formation of  $A^{III}B^V$  compounds were reported. Data were normally given in kJ/mol-at ( $A_{0.5}^{III}B_{0.5}^V$ ). In this work we applied the new correlation approach between thermodynamic properties and melting point. Generally, the thermodynamic property optimisation for these binary systems includes modeling of the phase diagram. However, numerical results may be ambiguous; they depend on both the thermodynamic model and thermodynamic values selected for the optimization. As an example, the standard enthalpy of formation of  $Al_{0.5}Sb_{0.5}$  obtained from the optimizations performed by two different authors [9, 10] are -25.0 and -40.6 kJ/(K·mol-at), while for  $Ga_{0.5}As_{0.5}$ , the selected values by [9] and [11] are -37.7 and -44.4 kJ/(K·mol-at), respectively. A critical analysis and recommendations concerning the most realistic experimental and calculated data were reported in [3, 5]. The set of the

selected experimental values  $\Delta_f H_{298}^o$  reported in [3-5]

leads to a linear equation:

$$\Delta_f H_{298}^o = 14.78 - 0.0363 \cdot T_m; n=14; r = 0.999;$$

$$2\sigma = \pm 3 \text{ kJ/mol-at} \quad (1)$$

## 2.2 Correlation between the reduced enthalpies of formation and the sum of the atomic numbers

We used in [5] the criterion of mutual coherence for a set of thermodynamic properties of  $A_{0.5}^{III}B_{0.5}^V$  phases. Considering the reduced enthalpies of the formation  $\Delta_f H_{298}^o/T_m$  and the sum of A and B atomic numbers ( $Z_i$ ) in  $A_{0.5}^{III}B_{0.5}^V$ , a linear relation (2) is observed (Fig.1) and given in Table 1. As we clearly see, the correlation coefficient ( $r = 0.998$ ) is particularly high, so relation (2) may be used for analyzing isostructural phases thermodynamic.

$$\Delta_f H_{298}^o = (-36.055 + 0.1637 \cdot Z_i) \cdot T_m; n = 16,$$

$$r = 0.998, 2\sigma = \pm 0.37 \text{ kJ/mol-at} \quad (2)$$

The atomic number of an element is its main quantum number which characterizes its electron energy. The enthalpies of formation from relation (2) are reported in Table 1 together with the melting temperatures of the compounds. Using equation (2), it is possible to determine  $Al_{0.5}N_{0.5}$  melting temperature, which otherwise is unknown. From the enthalpy of formation  $\Delta_f H_{298}^o = 158.63 \pm 0.4 \text{ kJ/mol-at}$ , the obtained value is  $T_m = 4840 \pm 40 \text{ K}$ .  $Al_{0.5}N_{0.5}$  melting point must correspond to an nitrogen pressure in the range 6-10 GPa.

## 2.3 Correlation between standard entropies and sums of atomic numbers

The representation of  $S_{298}^o$  (J/(K·mol-at)) vs. sums of the atomic numbers  $Z_i$  is given in Fig. 2. For hexagonal nitrides  $A^{III}N$  (type  $P6_3mc$ ), we have:

$$1) S_{298}^o = 2.18 + 0.414 Z_i, r = 0.998 \quad (3)$$

And for cubic  $A^{III}B^V$  ( $F\bar{4}3m$ ), we obtain:

$$2) S_{298}^o = 15.41 + 0.274 Z_i, r = 0.96 \quad (4)$$

Although equation (3) gives  $-7.2 \pm 0.9 \text{ J/(K·mol-at)}$  for BN, we took  $7.4 \pm 0.2 \text{ J/(K·mol-at)}$  an experimental result [14, 15]. Equation (3) gives also thallium nitride standard entropy  $S_{298}^o = 38.6 \pm 1.0 \text{ J/(K·mol-at)}$ . The entropy of formation, (equation (5)) is as follow:

$$\Delta_f S_{298}^o = S_{298}^o(AB) - S_{298}^o(A) - S_{298}^o(B) \quad (5)$$

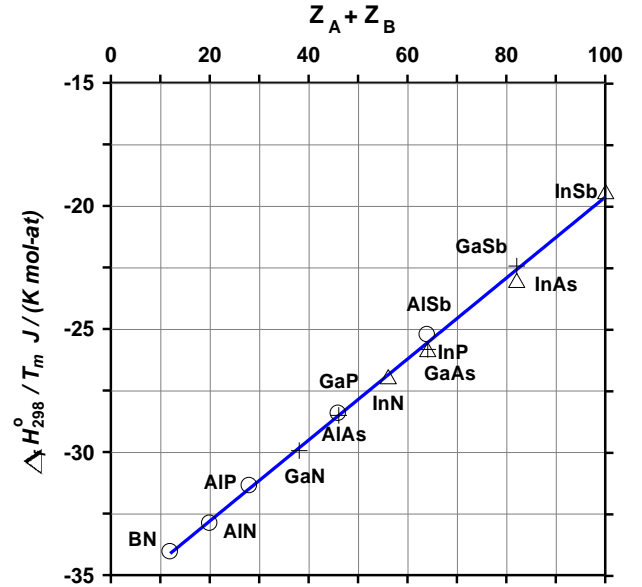


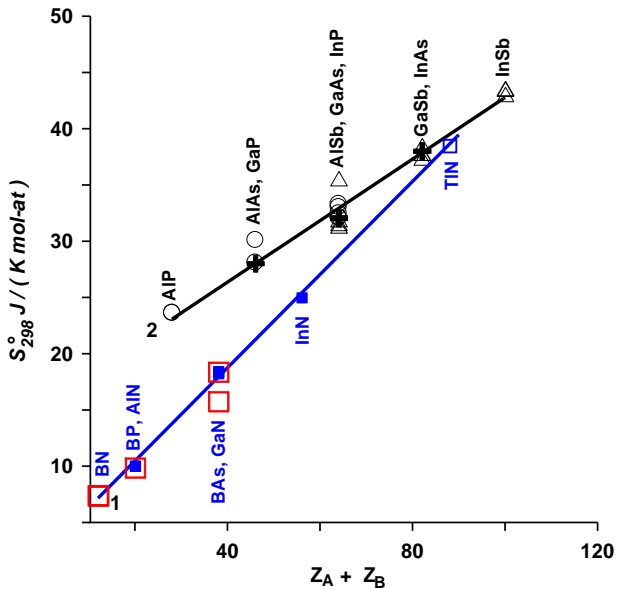
Fig. 1. Relationship between the reduced enthalpies of formation  $\Delta_f H_{298}^o/T_m$  and the sum ( $Z_i$ ) of the atomic numbers of A and B in  $A_{0.5}^{III}B_{0.5}^V$ .

Table 1: Optimized thermodynamic functions of  $A_{0.5}^{III}B_{0.5}^V$  compounds.

Phase	$T_m/K$	$-\Delta_f H_{298}^o$ kJ/mol-at	$S_{298}^o$ J/(K·mol-at)	$-\Delta_f S_{298}^o$ J/(K·mol-at)	$-\Delta_f G_{298}^o$ kJ/mol-at
$B_{0.5}N_{0.5}$ (12)	3730 $\pm 30$	127.13 $\pm 0.4$	7.4 $\pm 0.2$	43.4	114.2 $\pm 0.6$
$B_{0.5}P_{0.5}$ (20)	1655 $\pm 30$	54.24 $\pm 0.4$	10.4 $\pm 2$	13.1	50.4 $\pm 0.8$
$B_{0.5}As_{0.5}$ (38)	1343 $\pm 20$	40.06 $\pm 0.4$	17.9 $\pm 2$	2.8	39.2 $\pm 0.8$
$Al_{0.5}N_{0.5}$ (20)	4840 $\pm 30$	158.63 $\pm 0.4$	10.4 $\pm 0.4$	51.4	143.3 $\pm 0.6$
$Al_{0.5}P_{0.5}$ (28)	2793 $\pm 20$	87.89 $\pm 0.4$	23.1 $\pm 1$	11.2	84.55 $\pm 0.8$
$Al_{0.5}As_{0.5}$ (46)	2058 $\pm 10$	58.70 $\pm 0.4$	28.0 $\pm 1$	3.9	57.5 $\pm 0.8$
$Al_{0.5}Sb_{0.5}$ (64)	1328 $\pm 2$	33.97 $\pm 0.4$	32.9 $\pm 0.5$	4.1	32.7 $\pm 0.8$
$Ga_{0.5}N_{0.5}$ (38)	2620 $\pm 20$	78.16 $\pm 0.4$	17.9 $\pm 0.5$	50.5	63.2 $\pm 0.8$
$Ga_{0.5}P_{0.5}$ (46)	1790 $\pm 10$	51.05 $\pm 0.4$	28.0 $\pm 0.5$	13.3	47.2 $\pm 0.8$
$Ga_{0.5}As_{0.5}$ (64)	1511 $\pm 2$	38.65 $\pm 0.4$	32.9 $\pm 0.5$	5.4	37.1 $\pm 0.8$
$Ga_{0.5}Sb_{0.5}$ (82)	981 $\pm 2$	22.20 $\pm 0.4$	37.9 $\pm 0.5$	5.6	20.5 $\pm 0.5$
$In_{0.5}N_{0.5}$ (56)	2080 $\pm 20$	55.92 $\pm 0.4$	25.3 $\pm 0.5$	51.5	40.6 $\pm 0.8$
$In_{0.5}P_{0.5}$ (64)	1344 $\pm 2$	34.38 $\pm 0.4$	32.9 $\pm 1$	16.2	29.5 $\pm 0.8$
$In_{0.5}As_{0.5}$ (82)	1217 $\pm 2$	27.55 $\pm 0.4$	37.9 $\pm 0.5$	8.9	24.9 $\pm 0.8$
$In_{0.5}Sb_{0.5}$ (100)	799 $\pm 1$	15.73 $\pm 0.4$	42.8 $\pm 0.5$	9.1	13.0 $\pm 0.3$
$Tl_{0.5}N_{0.5}$ (88)	1018 $\pm 10$	22.04 $\pm 0.4$	38.6 $\pm 1.0$	41.5	9.7 $\pm 0.8$

$S_{298}^{\circ}$  and  $\Delta_f S_{298}^{\circ}$  from equations (3), (4) and (5) are given in Table 1.

Boron nitride has five polymorphic modifications [14, 15]. The hBP existing under normal conditions is not (P6<sub>3</sub>/mmc), it is  $F\bar{4}3m$  [16]. However, all nitride entropies ( $S_{298}^{\circ}$ ), as well as those of BP and BAs (also  $F\bar{4}3m$  space group), can be described by the linear approximation (3), which exhibits the wurtzite structure. The commonly accepted calculated values  $S_{298}^{\circ}$  for BAs (Table 1) differ from the experimental one by 2.2 J/(K·mol-at) [13]. This is probably related to the existence of polymorphic modifications, such as those in BN, or to some admixtures in it.



**Fig. 2.** Relation between  $A^{III}B^V$  standard entropies  $S_{298}^{\circ}$  and the sum of their atomic numbers ( $Z_A+Z_B$ ).  $\circ$  –  $Al_{0.5}B_{0.5}^V$  [13], [18], [22], [41];  $+$  –  $Ga_{0.5}B_{0.5}^V$  and  $\Delta$  –  $In_{0.5}B_{0.5}^V$  [11, 13, 18, 19, 21, 22, 41, 42];  $\square$  –  $B_{0.5}B_{0.5}^V$  [13]-[15], [22, 24];  $\blacksquare$  –  $A^{III}_{0.5}N_{0.5}$ , [18, 22, 24, 28];  $\square$  – TIN (evaluated in this work).

#### 2.4 Calculation of Gibbs energy $A_{0.5}^{III}B_{0.5}^V$ phases

$A_{0.5}^{III}B_{0.5}^V$  Gibbs energies were calculated using equation (2) and (6):

$$\Delta_f G_{298}^{\circ} = \Delta_f H_{298}^{\circ} - 298 \cdot \Delta_f S_{298}^{\circ} \quad (\text{kJ/mol-at}) \quad (6)$$

with  $\Delta_f H_{298}^{\circ}$  and  $S_{298}^{\circ}$  (from Table 1) for  $A_{0.5}^{III}B_{0.5}^V$  and pure elements  $S_{298}^{\circ}$  from [13]. The standard reduced Gibbs energy  $A_{0.5}^{III}B_{0.5}^V$  curves calculated from the sum of element atomic numbers of the elements  $Z_i$  is given in Fig. 3.

The linear equation (8), as well as the second order equations (7), (9) and (10) for the reduced Gibbs energy of  $A_{0.5}^{III}B_{0.5}^V$  compounds, are deduced according to Table 1. The equations (7)–(10) are represented in Fig. 3 by the curves 1-4, respectively. The two independent curves 1

and 4 in Fig. 3 overlap between BAs and AIAs compounds.

In general, Table 1 demonstrates the agreement of all recommended thermodynamics parameters within the limits of the accepted uncertainties in kJ/mol-at.

$$\Delta_f G_{298}^{\circ} = (-30.213 - 0.0596 \cdot Z_i + 0.00227 \cdot Z_i^2) \cdot Tm; n=3;$$

$$2\sigma = \pm 0.6 \quad (7)$$

$$\Delta_f G_{298}^{\circ} = (-35.484 + 0.2932 \cdot Z_i) \cdot Tm; n=7;$$

$$2\sigma = \pm 0.8; r=0.99; \quad (8)$$

$$\Delta_f G_{298}^{\circ} = (-35.207 + 0.1527 \cdot Z_i + 8.42 \cdot 10^{-4} \cdot Z_i^2) \cdot Tm; n=3;$$

$$2\sigma = \pm 0.8 \quad (9)$$

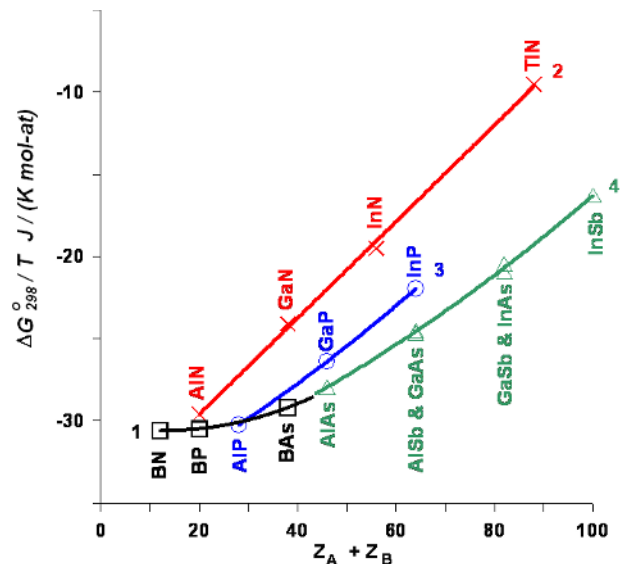
$$\Delta_f G_{298}^{\circ} = (-34.257 + 0.1006 \cdot Z_i + 7.90 \cdot 10^{-4} \cdot Z_i^2) \cdot Tm; n=6;$$

$$2\sigma = \pm 0.6 \quad (10)$$

#### 2.5 Method of similarity in the analysis of the heats capacities of $A^{III}B^V$ phases.

A critical analysis of heat capacities for  $A^{III}B^V$  phases was carried out for 16 compounds (which totaled at more than 1,200 points).

The experimental values are presented in Figs. 4-12, with the assumption that all the phases with the same sum of atomic numbers should be similar both at low and high temperatures. The experimental heat capacities data of  $A_{0.5}^{III}B_{0.5}^V$  phases before 1975 were published in the literature review [17]. More recent references exist in [19-43]



**Fig. 3.** Calculated reduced Gibbs energy curves for  $A_{0.5}^{III}B_{0.5}^V$  phases in standard conditions (Table 1) vs. of the sum of the atomic number of the elements ( $Z_A+Z_B$ ): nitrides ( $\square$ ), 2 - phosphides ( $\circ$ ), 3 - arsenides and antimonides of gallium and indium ( $\Delta$ ), borides ( $\square$ ) (equations 7-10). The two independent curves 1 and 4 have an overlap between BAs and AIAs compounds.

Lichter and Sommelet reported the similarity of heat capacities [18]. While studying two groups of phases with similar molecular masses (first AlSb, GaAs and InP; and second: GaSb and InAs), they noticed similar temperature dependencies for heat capacities vs. of  $A^{III}B^V$  molecular masses (at  $T > 298$  K). We have developed this rule and established that the experimental heat capacities of phases like BP and AlN ( $Z_i=20$ ), BAs and GaN ( $Z_i=38$ ), AlAs and GaP ( $Z_i=46$ ), AlSb, GaAs and InP ( $Z_i=64$ ), GaSb and InAs ( $Z_i=82$ ), i.e. having the same sums of atomic numbers of elements ( $Z_i$ ), are the same within all temperature ranges where the solid phases exist.  $A^{III}B^V$  molecular masses are related to the sum of A and B atomic numbers  $Z_i$ . In the present study, we show that all heat capacities isotherms have strict linear correlations vs. the logarithm of A and B atomic numbers sums for isostructural  $A^{III}B^V$  phases (both sphalerite and wurtzite types).

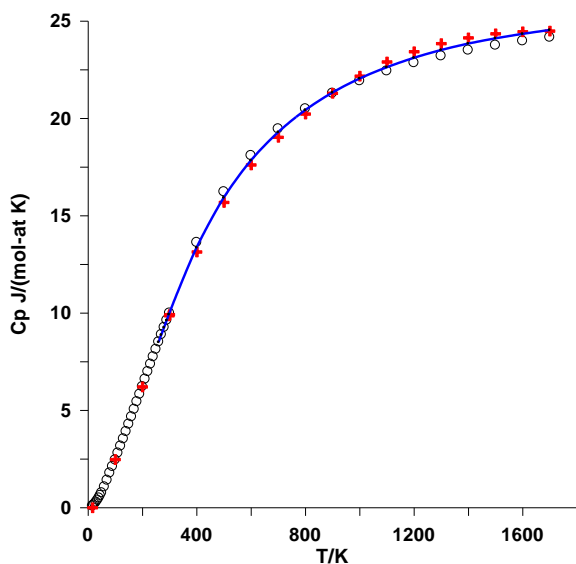


Fig. 4. Heat capacity of BN vs. temperature.  $\circ$ - [14, 15],  $+$ -[22]; — optimized values.

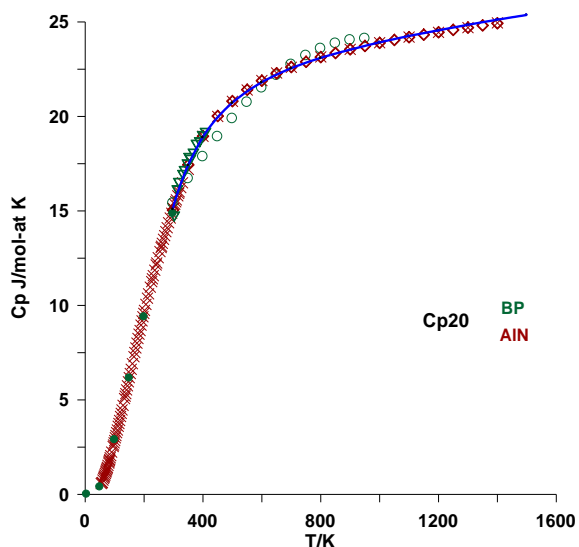


Fig. 5. Heat capacity of BP and AlN vs. temperature. BP:  $\bullet$ - [24] use only 5-298K;  $\circ$ - [25];  $\nabla$ -[26] use only 302.3-357.2K; AlN:  $\times$ - [24],  $\diamond$  - [27]; — optimized values.

Figures 4, 5, 8, 9, and 10 show that low-temperature heat capacities are in almost complete agreement within experimental errors. Therefore, we can assume that the behavior of specific heats at temperatures above room temperature will be similar to isostructural phases with the same of element atomic numbers.

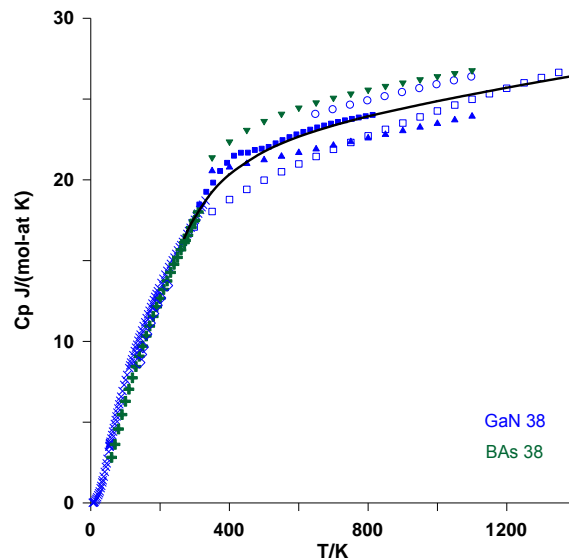


Fig. 6. Heat capacity of BAs and GaN vs. temperature. GaN:  $\times$  - [28];  $\circ$ - [29];  $\diamond$ -[30]-113-1100 use only 140-220K ;  $\blacktriangle$  -[22];  $\square$ -[31],  $\blacksquare$ -[32]; BAs:  $+$ - [24];  $\blacktriangledown$ -[22]; — optimized values.

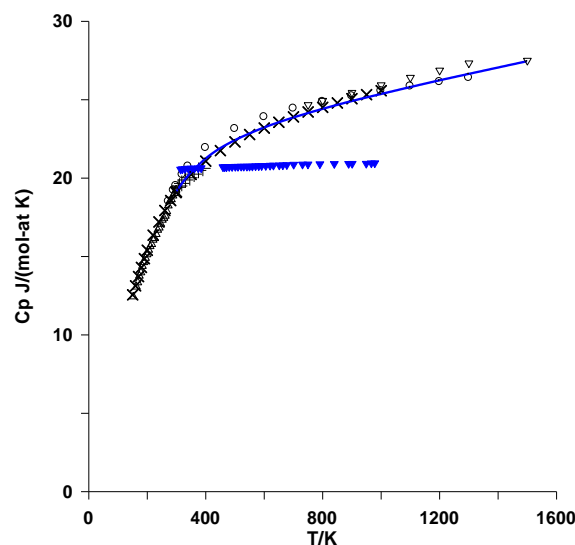
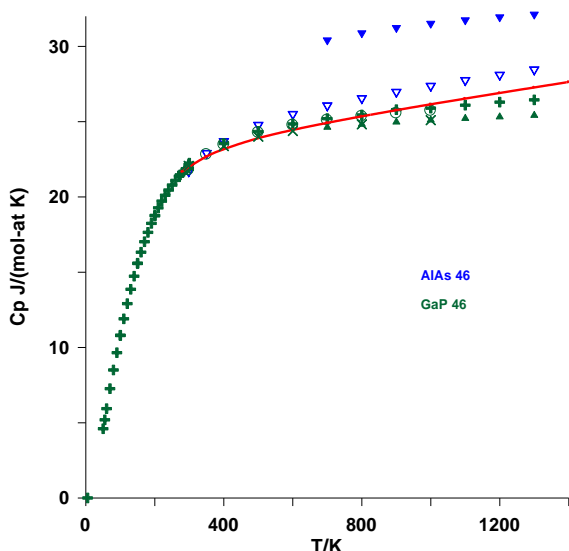
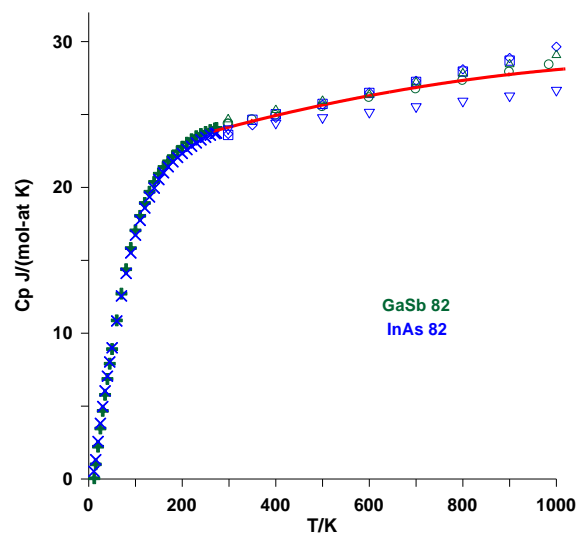


Fig.7. Heat capacity of InN vs. temperature.  $\nabla$  - [29];  $+$  - [35] exp.,  $\times$  - [35] calc,  $\circ$  - [36];  $\blacktriangledown$  - [33]; — optimized values.

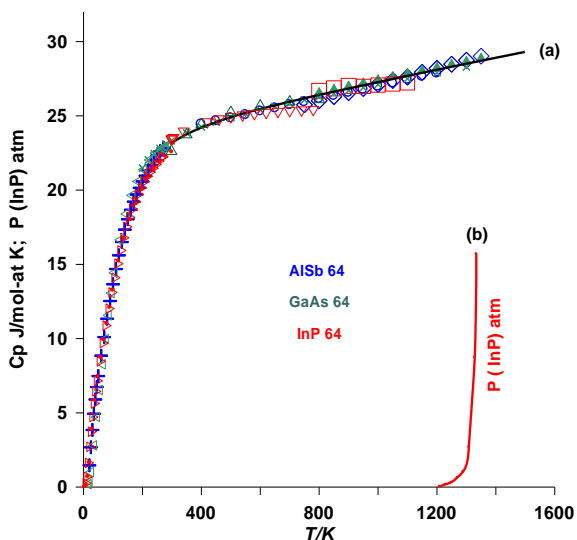
One of the biggest discrepancies in the previously reported specific heat ( $\pm 2$  J/(g-mol K)) is observed for GaN and BAs compounds ( $Z_i = 38$ ), as seen in Fig.6 above 300K. The variance of the data in the low-temperature region in Fig.6 is  $\pm 1$  J/(g-mol K). In the latter case, the discrepancy may be due to the presence in a BAs sample of other crystalline admixtures. For example, Gavrichev *et al.* have identified 4 crystalline modifications of boron nitride [14, 15].



**Fig. 8.** Heat capacity of AlAs and GaP vs. temperature: AlAs: ▽-[22], ▼-[29]; GaP: ▲-[29], +-[24]; ○-[40], ×-[19]; — optimized values.



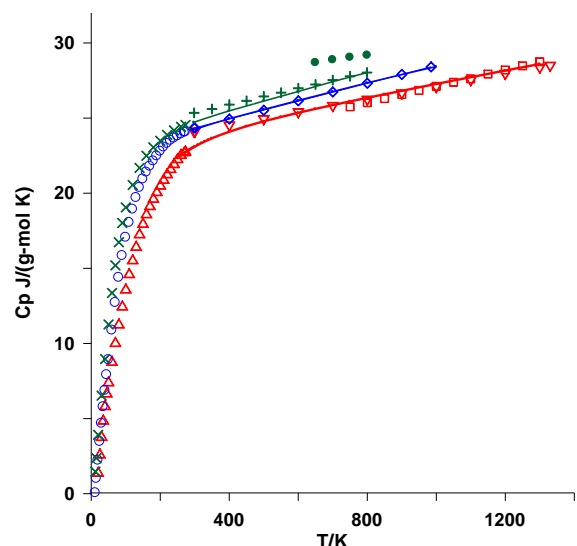
**Fig. 10.** Heat capacity of GaSb and InAs vs. temperature. GaSb: △-[22], ○-[18], +-[41]; InAs: ▽-[22], □-[18], ×-[41], ◇-[21]; — optimized values.



**Fig.9.** Heat capacity of AlSb, GaAs and InP vs. temperature: AlSb: ○-[18]; ◇-[29]; +-[41]; InP: △-[19], □-[29], ▷-[41], ▽-[40], ●-[42]; GaAs: ×-[19], ▲-[29], ◁-[41]; — optimized values.

The experimental heat capacities from references [29] (Fig.8, 11) and [33] (Fig.7) were not used in this study, since their uncertainties exceeded the confidence interval accepted for these compounds. For same reason the data [20] and [30] are used only in range 298-800K and 140-220K, respectively. At high temperatures, one faces problems of a different nature, i.e. those related to sample's volatility, decomposition, interactions with the container, and others that are often very difficult to account for.

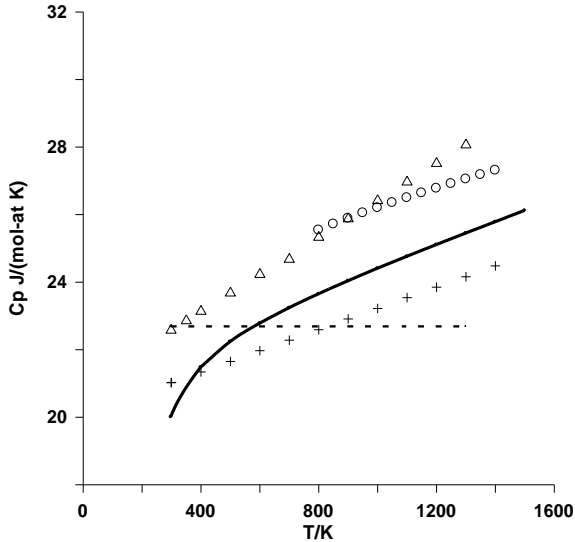
It is really necessary to take into consideration the significant vapor pressure of the group five elements (N, P, As, Sb) and their compounds with those of group three (B, Al, Ga, In), especially at high temperatures. Among the numerous A<sup>III</sup>B<sup>V</sup> phases analyzed in this study, the most contradictory thermodynamic data were reported for nitrides, phosphides and arsenides, this is directly related to the volatility issue.



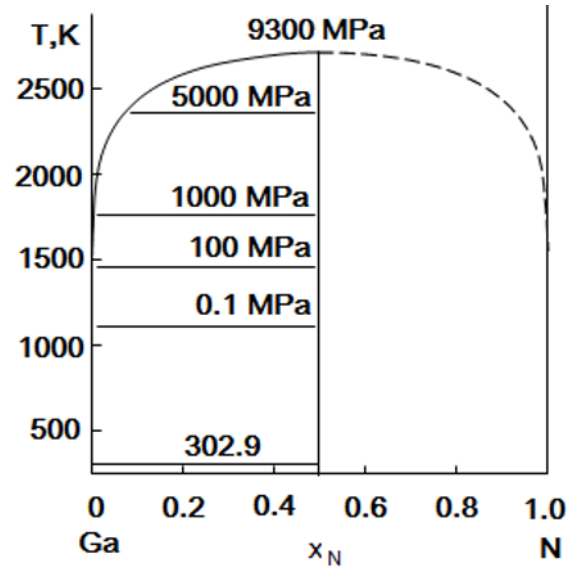
**Fig.11.** Heat capacity of antimonides of Al, Ga and In vs. temperature. InSb: ×-[41], +-[18], ●-[29]; GaSb: ○-[41], ◇-[18]; AlSb: ▽-[18], □-[29], △-[41]; — optimized values.

Phosphorus, arsenic and their compounds with the elements of subgroup B<sup>III</sup> are known to have high vapor pressures. The influence of decomposition and evaporation of phosphides and arsenides is considerable, especially at elevated temperatures. Figure 9 shows the vapour pressure of InP as a function of temperature (curve b). In addition some compounds, such as AlP and AlAs, are readily hydrolyzed in air.

It is necessary also to take into account the aggressive elements such as arsenic and phosphorus, which easily interact with almost all elements, especially at high temperatures.



**Fig.12.** Heat capacity of AlP vs. temperature. AlP 298-1500 K + - [22], o - [19], Δ- [29], - - - [44]; our prediction —



**Fig.13.** Calculated phase diagram of the Ga-N system and the nitrogen partial pressure [31].

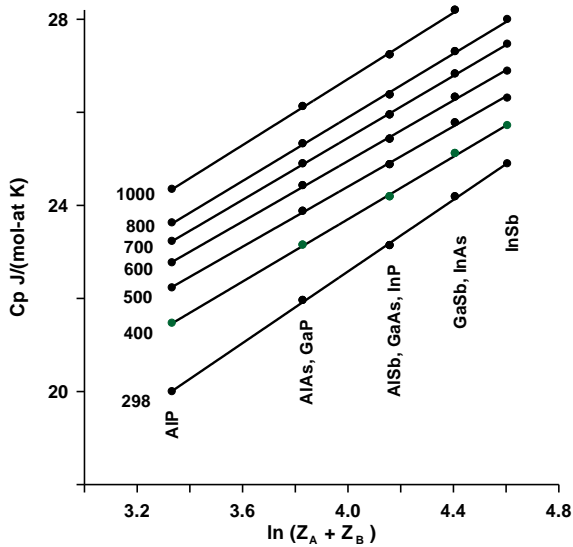
The group A<sup>III</sup> nitrides is known to losing nitrogen at temperatures well below their melting points, and therefore the liquidus curve in their *T-x* phase diagrams wander toward a nonvolatile component [31]. In a nitrogen system, nitride melting points must be determined at high nitrogen pressures from 6 to 10 GPa to avoid nitrogen evaporation. As an example, the Ga-N system was investigated and described by Unlande et al. [31], and results are presented in Fig.13.

The decomposition of indium nitride is clear in [33]. The heat capacity of InN is almost constant in the entire temperature range that was investigated. Indium nitride decomposition may occur at lower temperatures. At the same time, the data obtained by the same group of authors for gallium nitride [32] are consistent with the optimized values of the specific heat, even if they were not used in optimization procedure.

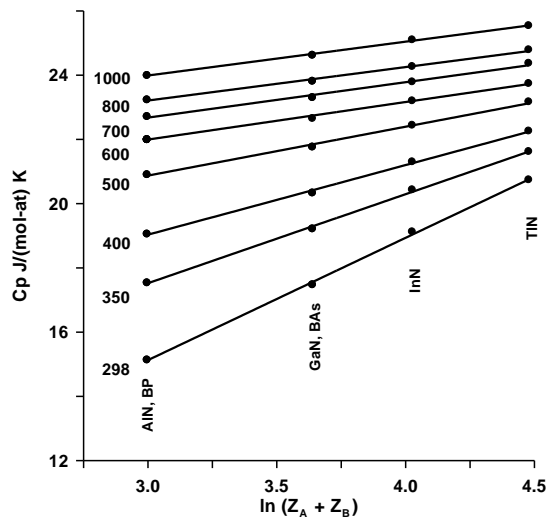
The aluminum phosphide heat capacity is practically unknown. There are conflicting evidences between [22, 29, 39], and [44]. Results [44] should be considered as estimates. As stated above, this compound is easily hydrolyzed in air and it is very difficult to obtain reliable experimental data. The equations in Table 2 were obtained by the least squares method. If we examine all the values  $C_p$  as a function of the sum of atomic numbers ( $Z_i$ ) of sixteen  $A_{0.5}^{III}B_{0.5}^V$  phases, two continuums of linear relations for every temperature of sphalerite and wurtzite forms were obtained. These relations are presented for some temperatures from 298 to 1000K in Fig.14 and 15. The equations of  $C_p(T)$  for AlP (3) and TiN (9) presented in Table 2 were obtained by extrapolating linear relations.

**Table 2.** Heat capacities of AIIIBV phases.

No	Phase and its melting point ( $T_m$ , K)	$Z_i$	$C_p = a + b \cdot 10^{-3} \cdot T - c \cdot 10^{-5} \cdot T^2 + d \cdot 10^3 \cdot T^{-1}$ ; J/(mol-at K)				Temperature range, K
			a	b	c	d	
1	BN <sub>hex</sub> (3720)	12	31.55	-1.093	-8.785	-9.300	260-1500
2	BP (1650); AlN (4840)	20	23.08	1.688	7.500		260-1500
3	AlP (2793)	28	21.34	3.239	1.838		260-1500
4	BAs (1343); GaN (2620)	38	22.53	2.621	5.181		260-1500
5	AlAs (2058); GaP (1790)	46	22.79	3.505	1.665		260-1500
6	InN (2080)	56	22.42	3.060	3.738		260-1500
7	AlSb (1328); GaAs (1511); InP (1344)	64	23.43	3.941	1.303		260 - $T_m$
8	GaSb (981); InAs (1215)	82	24.00	4.332	0.976		260 - $T_m$
9	TiN (1018)	88	22.49	3.331	2.473		260 - $T_m$
10	InSb (799)	100	23.44	5.774	0.394		260 - $T_m$



**Fig.14.**  $C_p(T)$  vs. logarithm of the sum of atomic numbers of elements for  $A^{III}B^V$  phases of the sphalerite type between 298-1000 K.



**Fig.15.**  $C_p(T)$  vs. logarithm of the sum of atomic numbers of elements for  $A^{III}B^V$  phases of the wurtzite type between 298-1000 K.

A similar  $C_p(T)$  dependency for AlP was obtained independently from literature data reported elsewhere [22], [29], [44]. Based on the above results, it is now possible to calculate all thermodynamic values for all the phases listed in Table 2 at high temperatures using the optimized values  $\Delta_f H_{298}^o$ ,  $S_{298}^o$ ,  $\Delta_f S_{298}^o$ , and  $\Delta_f G_{298}^o$  [5] and the well-known general thermodynamic relations previously given in [23].

$$\Delta_f G_T = \Delta_f H_{298}^o + \int_{298}^T \Delta C_p dT - T \Delta S_{298}^o - T \int_{298}^T (\Delta C_p / T) dT \quad (11)$$

The equation 7 in Table 2 has been obtained with the new data for indium phosphide [19]. New numerical

values of the heat capacity of AlSb, GaAs, and InP (Table 2) are not practically different from accepted in [5] without [19]:

$$C_p^o(T) = 23.09 + 4.275 \cdot 10^{-3} T - 1.173 \cdot 105 T^{-2} \text{ J/(K}\cdot\text{mol}\cdot\text{at)} \quad (12)$$

(260-1500K)

## Conclusions

A critical analysis of the thermodynamic properties of sixteen  $A_{0.5}^{III}B_{0.5}^V$  compounds was made by the method of correlative optimization. In this approach, the melting temperatures of isostructural phases and sums of atomic numbers ( $Z_i$ ) of these compounds are proved to be the important parameters for their thermodynamic analysis. The reduced thermodynamic parameters,  $(\Delta_f H_{298}^o / T_m)$  and  $(\Delta_f G_{298}^o / T_m)$ , obtained from the correlations are reliable for thermodynamics calculations, as they have the dimension of entropy J/(K·mol-at). These parameters are also easily transformed into dimensionless ones by dividing by R, the universal gas constant ( $R = 8.31447$  J/(K·mol-at)). It was established that the experimental heat capacity of phases like BP and AlN; BAs and GaN; AIAs and GaP; AISb, GaAs and InP; GaSb and InAs (i.e. having the same sum of element atomic numbers) are the same for all domains of solid phases existence within the limits of experimental errors. The proposed correlations can be used to evaluate some unknown thermodynamic properties for TiN, BP, BAs and AlP phases.

The results can be used for thermodynamic calculation of quasi-binary and quasi-ternary solid solutions on the base on  $A^{III}B^V$  compounds and used for thermodynamic handbooks. The proposed correlative method of thermodynamic functions can be also applied for other different groups of isostructural compounds. The knowledge of high temperature thermodynamic values gives way to optimizing the heat balance of single-crystal and epitaxial structure grows from gases phase in technology of optoelectronic materials.

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