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Thermochemical Constants of $A^{III}B^{V}$ Compound Semiconductors, and Approximate Methods of Calculation

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Published data on the phase diagrams and on the nature of melts in the A^{III}-B^{V} system and on the thermochemical constants of $A^{III}B^{V}$ semiconducting compounds are reviewed. Approximate methods of calculating thermochemical constants are suggested: they are based on summing the constants of the elemental semiconductors whose atomic weights add up to the molecular weight of the compound. 128 references.

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I. INTRODUCTION

$A^{III}B^{V}$ compounds, composed of elements of Groups III and V of the Periodic Table, have recently attracted a great deal of attention from physicists, chemists, and device technologists because of their semiconductor properties [1]. The properties of $A^{III}B^{V}$ compounds have increased our understanding of semiconductors, and have given rise to new applications in different branches of electronics: in semiconductor electronics (by virtue of the properties of their crystal lattice), in molecular electronics (by making possible new solid-state circuits), and in quantum electronics (which relies on quantum phenomena within the atoms and molecules of the material).

A knowledge of the thermochemical properties of $A^{III}B^{V}$ compounds (or III–V compounds) is essential to the full understanding of their nature and properties, and also for the development of apparatus and techniques for preparing these compounds and for producing devices from them. The constants which must be known to solve the first problem include the enthalpy and entropy of formation of the compound, the free energy of the formation reaction, the heat of atomisation, the absolute entropy, etc. The second and the third problem cannot be solved without a knowledge of the phase diagrams of the individual components and of the compound, of the vapour pressure of the volatile component at the melting point, of the specific heat, heat of melting, etc.

Many of the above constants have been determined experimentally for the compounds which can be prepared relatively easily. Some of these compounds, however, have high melting points and high vapour pressures of the volatile component at their melting point: most of the physicochemical constants which are available for these compounds were obtained by calculation and are only tentative. In many cases data are altogether lacking.

This review attempts to systematise the thermochemistry of III–V compounds by a critical discussion of published methods of evaluating physicochemical constants by approximate calculations.

II. PHASE DIAGRAMS AND NATURE OF MELTS IN A^{III}–B^{V} SYSTEMS

With the exception of boron-containing systems, the phase diagrams of A^{III}–B^{V} systems (plotted as T against x, where T is temperature and x is the composition in at.%) are all of the same type [2]. They all include one congruently melting compound (of 1 : 1 atomic composition) whose melting point is much higher than the melting points of the components (Fig. 1). The eutectic on the side of the A^{III} component is degenerate. The other eutectic, on the right-hand side of the diagram, usually lies at high concentrations of the B^{V} component. An analysis of these phase diagrams suggests that only the compound can have semiconductor properties in these binary systems.

As the atomic weight of the component atoms increases, the shape of the phase diagram for the binary system changes, indicating a change in the type of interaction between the elements. In the heaviest systems the phase diagrams no longer show a 1 : 1 compound (see, for example, the rare earth element–bismuth systems). The new compounds have neither a tetrahedral structure nor semiconductor properties.

The semiconducting phases in the binary systems belong to the type known as linear phases, in which the solubility of the components is very low. Mironov and Borisova [15] have discussed deviations from stoichiometry in the III–V semiconductors and the methods used to study these deviations.

Thermodynamic arguments based on the free-energy curves for the crystal and the melt in a binary system which forms a compound semiconductor have shown that the maximum melting point (the distectic point) of the compound does not coincide with the stoichiometric composition. The phase diagram of the binary system in the region of the compound takes the form shown in Fig. 2. Crystals grown from a melt lying in the composition region *3* contain an excess of component B, those grown from region *1* contain an excess of component A. A crystal of exactly stoichiometric composition can be grown only from a melt of composition *Q*.

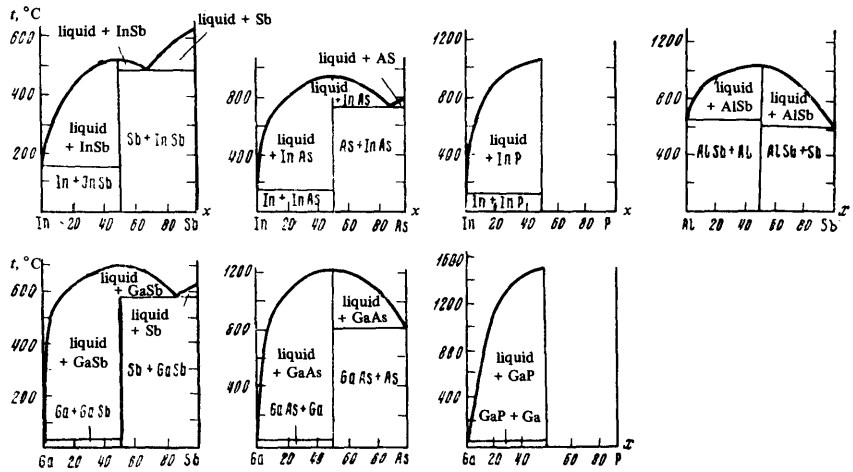


Figure 1. Phase diagrams of some $A^{III}-B^{V}$ systems in $T-x$ coordinates: In–Sb,[3,4] In–As,[5,6] In–P,[6,7] Al–Sb,[8,9] Ga–Sb,[10,11] Ga–As,[6,11] Ga–P.[12,14]

However, in most III–V compounds the deviations from stoichiometry arising from the solubility of an excess of the components in the compound are not detectable by precision X-ray, chemical, or mass-spectroscopic analyses. $A^{III}B^{V}$ semiconductors can be prepared with such a low concentration of current carriers (under conditions leading to mutual compensation of impurities and native defects) that the presence of a stoichiometric excess of one of the components is inconceivable. GaAs and GaSb are exceptional in this respect: a shift of their maximum melting point towards the gallium-rich side has been detected by an indirect method [16,17].

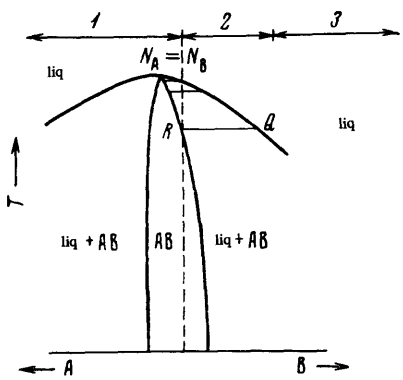


Figure 2. Part of the phase diagram in the region of the compound semiconductor, illustrating the deviation of the maximum melting point from the stoichiometric composition [15].

The most likely source of deviations from stoichiometry in III–V compounds are lattice defects and impurity atoms. The latter can displace normal atoms from lattice sites or, if they are not too large, they can reside in interstitial sites. In either case, the conductivity type of the compound is affected. Atom displacements (or substitutions) in the lattice of a III–V compound can produce point defects of various types: vacancies at the normal lattice sites, interstitial atoms surrounded by four atoms of the same kind or of the opposite kind, and the substitution of atoms of one kind by atoms of the other kind [18].

These structural defects appear to be the only mechanism by which the composition of III–V compounds can deviate from stoichiometry. Many attempts at inducing non-stoichiometry by adding an excess of one of the components to the melt, by diffusion of the vapour of the volatile component into the solid compound, or by other methods, were unsuccessful. The conclusion, which is extremely important in the technology of III–V compounds, is that small variations in the composition of the melts used to grow single crystals of the compounds have a negligible effect on the physical properties of the crystals.

Equilibrium in the A–B systems involves four phases: component A(sol), component B(vap), a solution of component A(liq) in B(liq), and the compound AB(sol). This equilibrium corresponds to a quaternary point in the $p-T-x$ diagram (where p is pressure) at the intersection of four lines characterising the corresponding three-phase equilibria [19]. In unstable III–V compounds the quaternary point lies in the region of low pressures, at temperatures close to the melting point of component A, and consequently at low concentrations of component B in solution.

An analysis of all possible phase equilibria indicates that, for all practical purposes, the most important equilibrium is

$$\text{AB(sol)} \rightleftharpoons \text{solution of B in A(liq)} \rightleftharpoons \text{B(vap)} \ .$$

Three-phase equilibria in binary systems are monovariant ($v = 3$, $F = 1$). Hence, this equilibrium is described on a $p-T-x$ diagram by a curve terminated at one end by the quadruple point and at the other end in one of a number of ways [20,21], depending on the type of interaction between the components A and B.

The binary phase diagram for an involatile (A) and a volatile (B) component which react to give a semiconducting

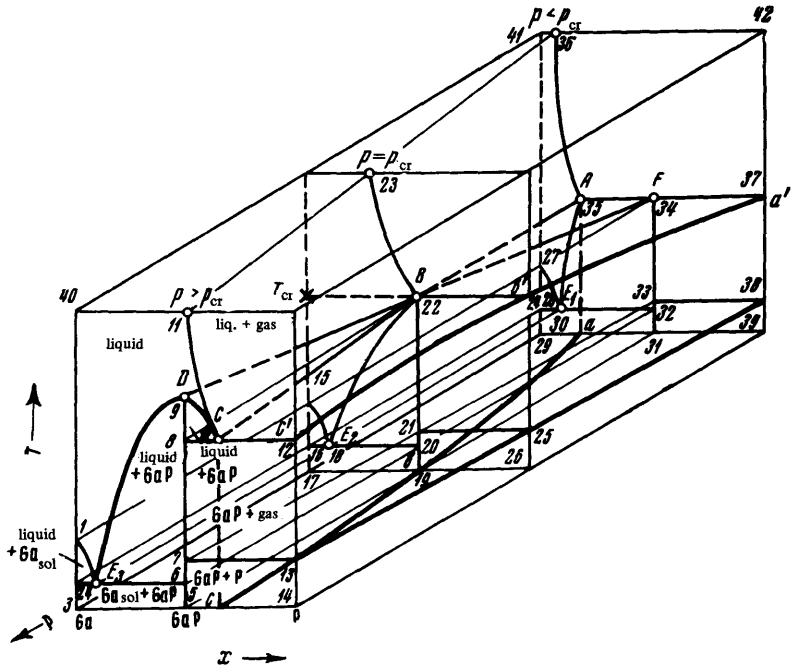


Figure 3. Hypothetical three-dimensional phase diagram for the gallium–phosphorus system [12].

compound at low pressures is of the peritectic type. Unstable compound semiconductors are almost completely dissociated below the melting point when heated under normal conditions, and therefore their liquidus curve does not show a maximum.

However, when the pressure is raised, the regions of the phase diagram are displaced towards the point where the liquid phase composition is the same as that of the compound, and the solid phase begins to take part in the transformations [22,23]. On further raising the pressure the peritectic phase diagram is converted into a phase diagram with a normal maximum [24].

The transition from one type of phase diagram to the other under the influence of external pressure is illustrated by the hypothetical three-dimensional phase diagram for the Ga–GaP system shown in Fig. 3. The diagram includes the following regions and equilibrium lines:

Two-phase regions: *1–2–3–18–30–27–28–16–15–1* (melt + Ga crystals); *2–3–5–6–20–16–17–19–31–32–28–29* (GaP crystals + Ga crystals); *5–7–13–14–26–19–21–25–38–39–31–32* (GaP crystals + P crystals); *6–4–9–6–20–32–34–22–35–30–18–4* (melt + GaP crystals); *9–22–10–8* (melt + GaP crystals).

Single-phase region: *40–41–36–28–11–10–9–41–27–30–35–36* (melt).

Two-phase equilibrium lines: *BD* (GaP crystals + melt); *a'b'c'* gives the temperature variation of the vapour pressure of liquid P; *1–15–27* gives the pressure dependence of the melting point of Ga; *13–25–38* gives the temperature dependence of the vapour pressure of solid P.

Three-phase equilibrium lines: *ABC* (melt + GaP crystals + vapour); $E_1E_2E_3$ (melt + GaP crystals + P crystals); *BF* (melt + GaP crystals + vapour). *B* is the point corresponding to the four-phase equilibrium (melt + GaP crystals + liquid P + P vapour).

The three-phase equilibrium of interest (compound AB(sol)–solution of component B in A(liq)–component B(vap)) is shown by the line *CBA* in the three-dimensional diagram (see Fig. 3). The projections of this line are shown on the three coordinate planes: *cba* on plane p–x, $c'b'a'$ on plane p–T, and E_3D on plane T–x.

Fig. 4 shows a series of consecutive isobaric sections of the three-dimensional phase diagram, drawn by Folberth [25] to demonstrate the shift of the point representing the three-phase equilibrium line on the T–x plane (points *1–5* in Fig. 4*a*–4*e*) caused by an increase of pressure. The point goes through a maximum (Fig. 4*f*).

Wagner [26] has discussed the general case of equilibrium between liquid and solid phases in a binary system containing a compound. The liquidus curve (Eqn. (1)) was derived without making allowance for the temperature dependence of the energy of mixing ω ($\omega = \omega_{AB} - (\omega_{AA} + \omega_{BB})/2$, where ω_{AB}, ω_{AA}, and ω_{BB} are the interaction energies between unlike and like atoms) or for the difference in specific heat between the solid and the liquid phase of the compound:

$$\omega = \frac{RT}{2(x-0.5)^2}\left[\ln\frac{1}{4x(1-x)} - \frac{\Delta S_f}{R}\left(\frac{T_f}{T}-1\right)\right], \qquad (1)$$

where ΔS_f and T_f are the entropy and the temperature of fusion of the compound, x is the atom fraction of component B in the melt, and R is the gas constant.

Eqn. (1) was applied to InSb and GaSb by Schottky and Bever [27], who postulated that melts of these compounds are regular solutions with an entropy of melting equal to the ideal entropy of mixing. Experimentally, gallium antimonide melts were found to behave like ideal solutions whereas indium antimonide melts gave negative deviations from ideality.

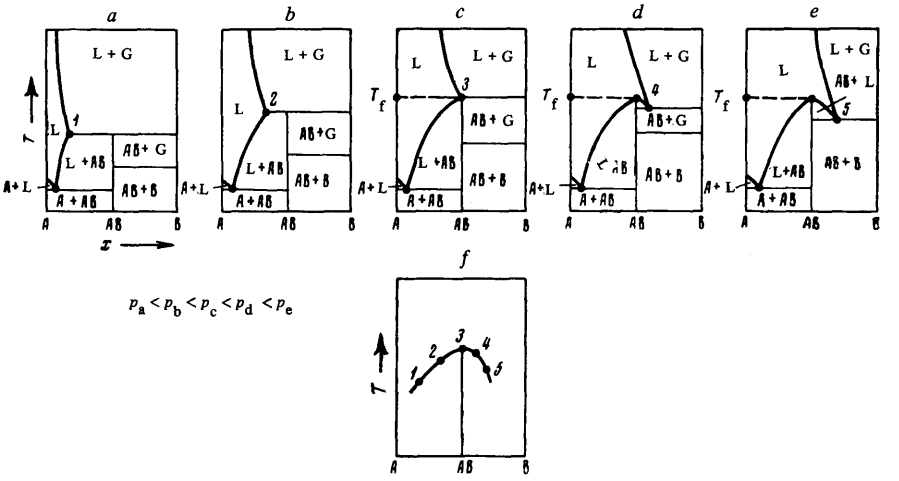


Figure 4. Isobaric sections of the phase diagram for a binary system consisting of an involatile component A and a volatile component B and forming a semiconducting compound AB: *a*)–*e*) isobaric sections; *f*) projections of the three-phase equilibrium point (AB_{sol}–solution of B in A_{liq}–B_{gas}) on the T–x plane (liquidus line).[25]

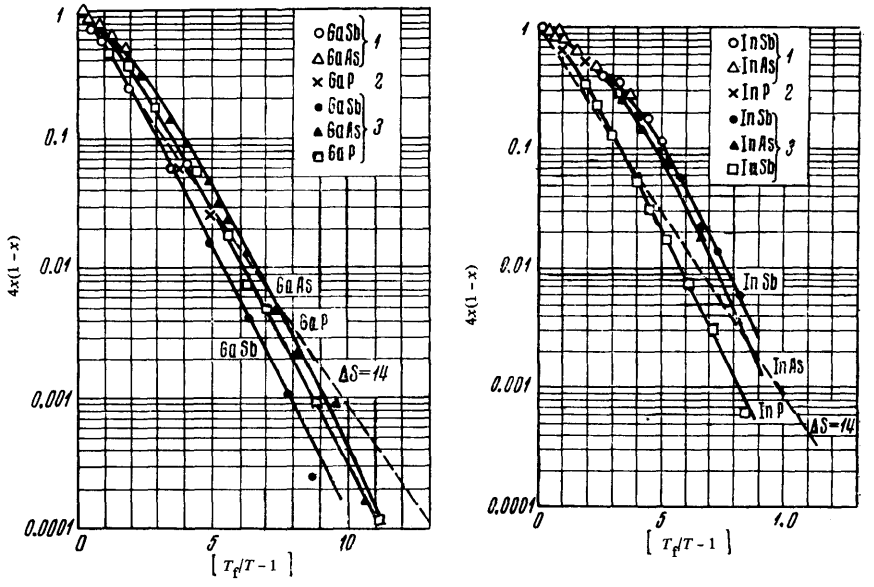


Figure 5. Dimensionless plots of the solubility of GaSb, GaAs, GaP, InSb, InAs, and InP: *1*) after Ref. 11; *2*) after Ref. 14; *3*) after Ref. 13.

Wieland[28] used regular solution theory to interpret data on the vapour pressure of III–V compounds:

$$p^{1/4} = p_0^{1/4} \cdot \exp[\omega(1-x)^2/RT] \text{ atm}, \quad (2)$$

where p is the pressure of tetra-atomic molecules of the volatile component B^V over a melt of A^{III} containing an atom fraction x of component B, and p_0 is the pressure of the same molecules over the pure liquid component B at the given temperature. In practice, Eqn. (2) is difficult to apply to the determination of the equilibrium pressure of component B over melts of approximately stoichiometric composition because of the lack of reliable vapour pressure data for the pure liquid components B (such as phosphorus, arsenic, etc.) whose vapour pressure is high at high temperatures.

According to Hall[13], $A^{III}B^V$ melts behave as ideal solutions at low temperatures. In this case $\omega = 0$, and plots of $\ln 4x(1-x)$ against $(T_f/T - 1)$ are linear for all systems, with a slope of $\Delta S_f/R$. All the plots are found to have approximately the same slope (Fig. 5), corresponding to an entropy of fusion of $\Delta S_f^* = 14$ cal mole^{-1} deg^{-1} for the ideal solution.

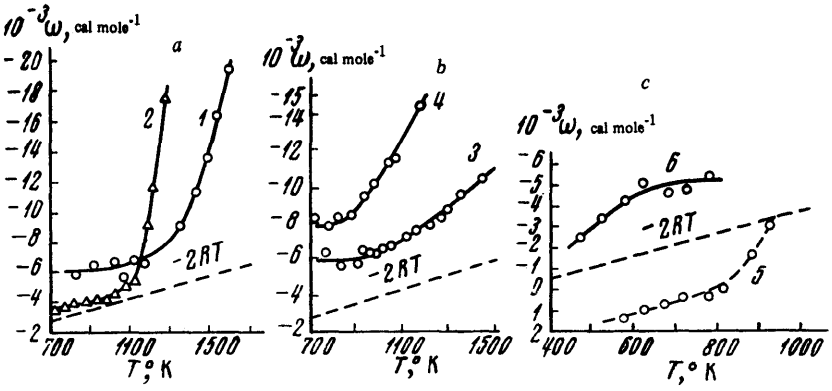


Figure 6. Variation of the energy of mixing with temperature, calculated from experimental liquidus data for A^{III}–B^{V} systems [29,30]: *1*) Ga–P, *2*) In–P, *3*) Ga–As, *4*) In–As, *5*) Ga–Sb, *6*) In–Sb.

A thermodynamic analysis of the liquidus curves for the systems formed by gallium and indium with phosphorus, arsenic, and antimony, based on Eqn. (1), has yielded the energies of mixing of those systems [29,30]. The values (Fig. 6) were found to be a function of temperature and of the concentration of the melt: hence, these systems cannot be treated as regular solutions. In all systems the energy of mixing tends towards zero as the concentration of the Group V element decreases. With the exception of the Ga–Sb system, the calculated energies of mixing are smaller than $-2RT$, pointing to a strong interaction between unlike atoms and confirming the theoretical conclusion of Pines and Kamenetskaya [31,32] that compound formation should occur in systems for which $\omega < -2RT$.

The Ga–Sb system differs from all the others [30] in having an energy of mixing more positive than $-2RT$ over the whole range of temperatures (see Fig. 6*c*), and therefore also of compositions: its value lies in the range 0–2 kcal mole^{-1}. This observation lends support to Schottky and Bever's statement [27] that gallium–antimony melts can be treated as ideal solutions. The bond in liquid gallium antimonide has a greater proportion of metallic character than in any other III–V compound [33]. This phenomenon may be responsible for the anomalous thermodynamic properties of the material.

The temperature dependence of the energy of mixing obtained in the above work [29,30] is inconsistent with the results of Thurmond [34], who found a linear dependence for the Ga—As and Ga—P systems, the quantity ω changing sign as it passes through zero. This may be due to an incorrect choice of entropies of melting by Thurmond [34]: there is serious disagreement on the entropies of melting of GaAs and GaP among different workers.

III. TEMPERATURE, HEAT, AND ENTROPY OF MELTING

The melting points of most of the antimonides and arsenides are quite accurately known; conflicting data have been published for some of the phosphides, and the values for most of the nitrides are purely tentative.

The melting points of the III–V semiconductor compounds, listed in Table 1, show a correlation with the position of the components in the Periodic Table. The melting points of the compounds decrease as the molecular weight increases. Vigdorovich and coworkers [47] have pointed out that the rule [48,49], according to which the melting points of elements with a covalent type of bond increases as the shortest interatomic distance in the crystal lattice decreases, applies also to III–V compounds (see Fig. 7). Only aluminium and gallium antimonides fall outside the linear relationship.

Table 1. Melting points (°C) of III–V compounds.

A^{III}	B^{V} N	Ref.	P	Ref.	As	Ref.	Sb	Ref.
B	~3000*	35	~2500	35	~2000	35	—	
Al	~2200***	36	>1800	37	>1700	38	1065	39
							1080	36
Ga	~1300***	40	>1350	41	1237**	6	703	11
			1522**	42				
			1500—1550	43			712	46
			1467**	14				
In	~1200		1062**	10	943**	4		
			1045	11			536	3
			1058**	44			525	11
			1055**	45				

*Cubic modification; **under equilibrium vapour pressure of the volatile component; ***under 4 atm nitrogen pressure.

In most cases, the thermodynamic characteristics of the melting of III–V compounds have been obtained by indirect calculations. Experimental and calculated values of the heat and entropy of melting of semiconductor compounds are given in Tables 2 and 4.

Glazov and Krestovnikov [50] measured the heat of melting of a number of III–V compounds, and showed that this parameter decreases when the cation or the anion are replaced by a heavier atom, in the following sequence: AlSb → GaSb → InSb and GaAs → InAs.

Melekh and Semenkovich [51] proposed an approximate method of calculating the entropies and heats of melting of compound semiconductors, based on the formula [36]

$$\Delta S_f = \sum S_{f,el.} + S_{mix}, \qquad (3)$$

where ΔS_f is the entropy of fusion of the alloy, $S_{f,el}$ is the entropy of fusion of the constituent elements, and S_{mix}

is the entropy of mixing of the alloy, calculated from the formula

$$S_{mix} = R(N_1 \cdot \ln N_1 + N_2 \cdot \ln N_2)$$

where R is the gas constant and N_1 and N_2 are the atom fractions of the elements in the binary alloy.

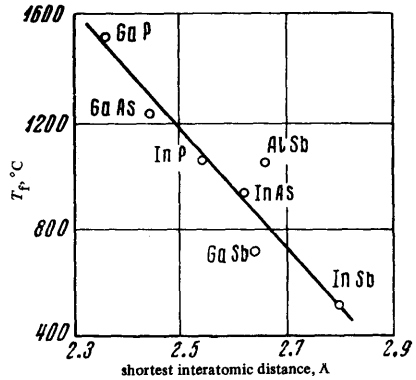


Figure 7. Melting point of some III–V compounds as a function of the shortest A^{III}–B^{V} distance in the crystal lattice [49].

Table 2. Experimental and calculated heats of fusion (kcal mole^{-1}) of some III–V compounds.

A^{III}	B^{V} P	Ref.	As	Ref.	Sb	Ref.
Al	—	—	—	—	14.2	52
					14.7	36
					14.5	51*
Ga	29.2	13	21.0	54		
	28.6	53	23.2	55	12.0	27.51
	30.7	12	20.6	51*		
In	11.0	10	12.6	56	9.0	54
	15.2	11	14.4	28	7.6	4
	12.0	54	12.9	51*	7.9	51*

*Calculated.

The same workers [51] have shown that the approximate calculation of ΔS_f by formula (3) is justified if the behaviour of the compound semiconductor at the melting point is of the semiconductor–metal type (III–V compounds, germanium, silicon, etc.). If, on the other hand, the behaviour is of the semiconductor–semiconductor type (tellurides, selenides, etc.), the term for the entropy of mixing should be omitted in formula (3). Conversely, a good agreement between the experimentally determined value of ΔS_f for a compound semiconductor and the value given by formula (3) is a convincing argument for assigning the compound to the semiconductor–metal melting type (in which a completely disordered solution is formed in the liquid state, with considerable weakening of the chemical bond). An experimental value much lower than the value given by formula (3) indicates melting of the semiconductor–semiconductor type.

It was pointed out above, in the discussion of the phase diagrams of A^{III}–B^{V} systems, that the interaction between the constituent elements of the compound depends on the atomic weight of the elements. III–V compounds and Group IV elemental semiconductors are isoelectronic analogues: they belong to the same crystal-chemical group of diamond-like semiconductors and they have similar bond types and energy spectra. Hence, many thermochemical constants of the III–V compounds can be evaluated by summing the constants for the elemental semiconductors whose atomic weights add up approximately to the molecular weight of the compound semiconductor.

Table 3. Molecular weights of III–V compounds and corresponding sums of the atomic weights of elemental Group IV semiconductors.

III–V compounds		Elemental semiconductors	
Formula	Molecular weight	Elements	Sum of atomic weights
BN	24.8	2C	24.0
AlN	40.98	C+Si	40.1
GaN	83.72	C+Ge	84.6
InN	128.76	C+α-Sn	130.7
BP	41 82	Si+C	40.1
AlP	57.98	2Si	56.18
GaP	100.7	Si+Ge	100.7
InP	145.7	2Ge	145.2
BAs	85.3	Ge+C	84.6
AlAs	101.9	Ge+Si	100.7
GaAs	144.6	2Ge	145.2
InAs	189.7	Ge+α-Sn	191.3
BSb	132.6	α-Sn+C	130.7
AlSb	148.7	α-Sn+Si	146.8
GaSb	191.4	α-Sn+Ge	191.3
InSb	236.4	2α—Sn	237.4

The molecular weights of the III–V compound semiconductors and the sums of the atomic weights of their corresponding elemental semiconductors from Group IV of the Periodic Table are listed in Table 3.

Table 4. Experimental and calculated entropies of melting (cal mole^{-1} deg^{-1}) of III–V compounds.

A^{III}	B^{V} P	Ref.	As	Ref.	Sb	Ref.
Al	14.4*		13.78*		10.8	52
					10.5	36
					10.7**	
					12.4*	
Ga	16.8	13	14.9	55	12.2	27
	17.0	12	14.0	34	12.5**	
	15.0	34	13.6	54	11.78*	
	13.78*		13.3			
			13.16**			
In	8.2	10	10.4	56	11.2	54
	11.4	11	11.8	28	9.5	4
	13.6*		10.7**		9.8	
			11.78*		10.4*	

*Calculated by adding the entropies of melting of the elemental semiconductors.
**Calculated by the method of Melekh and Semenkovich [51].

Table 4 gives the experimental and the calculated entropies of melting of the III–V compound semiconductors. The calculated values were obtained either by adding the entropies of melting of the appropriate elemental semiconductors or by means of Eqn. (3). [51]

IV. STANDARD ENTROPY

Very few data on the entropy and other thermochemical constants of III–V compounds have been published, and most of the published values are computed.

Table 5. Absolute standard entropies of Group III and V elements of the Periodic Table (cal mole^{-1} deg^{-1}), after Kubaschewski and Evans [36].

Element	S^0_{298}	Element	S^0_{298}
$B_{(sol)}$	1.07	$As_{(sol)}$	8.40
$Al_{(sol)}$	6.77	$Sb_{(sol)}$	10.50
$Ga_{(sol)}$	9.80	$C_{(sol)}$	1.36
$In_{(sol)}$	13.98	$Si_{(sol)}$	4.53
$N_{2(g)}$	22.80	$Ge_{(sol)}$	7.43
$P_{(sol)}$	10.60	α-$S_{(sol)}$	10.46

The method of calculating standard entropies for III–V compounds is described by Kubaschewski and Evans [36], who deal particularly with AlN, AlSb, and GaN. Their calculation is based on experimental data on equilibrium constants and on heats of formation, and also on the standard entropies of the component elements (Table 5).

Table 6. Shortest distances (Å) between atoms in III–V compound semiconductor lattices of the sphalerite type [18].

A^{III}	B^V			
	N	P	As	Sb
B	1.58	1.97	2.06	—
Al	—	2.36	2.43	2.64
Ga	—	2.36	2.44	2.66
In	—	2.54	2.62	2.80

They use the equations

$$\Delta G^\circ_{298} = -298\,R\ln K_p \qquad (4)$$

$$\Delta S^\circ_{298} = {}^1/_{298}(\Delta H^\circ_{298} - \Delta G^\circ_{298}) \qquad (5)$$

$$S^\circ_{298} = \Delta S^\circ_{298}(A^{III}B^V) + S^\circ_{298}(A^{III}) + S^\circ_{298}(B^V), \qquad (6)$$

where ΔG°_{298} is the free energy of formation of the compound, ΔH°_{298} is the enthalpy of formation of the compound, ΔS°_{298} is the entropy of formation, and S°_{298}, $S^\circ_{298}(A^{III})$, $S^\circ_{298}(B^V)$ are the standard entropies of the compound and of the constituent elements. R is the gas constant and K_p is the equilibrium constant of the formation reaction at pressure p.

The standard absolute entropies of III–V compounds can be calculated also from X-ray diffraction data. Renner [40] evaluated the entropies of inorganic compounds by means of the formula [57]

$$S^\circ_{298} = 1.5\,R\ln A + R\ln V - 1.5\,R\ln T_f + 12.5 \qquad (7)$$

where S°_{298} is the mean atomic entropy (cal mole^{-1} deg^{-1}), A is the mean atomic weight of the compound, T_f is the melting point of the compound (deg K), V is the mean atomic volume, which can be equated to a^3 (where a is the lattice constant, see Table 7). In the case of III–V compounds, Renner [40] subtracts a correction of 5 cal mole^{-1} deg^{-1} from the value given by Eqn. (7).

Table 7. Lattice constants (Å) of III–V compounds crystallising in the sphalerite structure.

A^{III}	B^V							
	N	Ref.	P	Ref.	As	Ref.	Sb	Ref.
B	3.615	35	4.537	59	4.777	60	—	
Al	—		5.451		5.620		6.095	
Ga	—		5.450	60	5.653	61	6.140	62
In	—		5.869		6.058	61	6.479	

The lattice constants of III–V compound semiconductors which crystallise in the sphalerite structure can be calculated [58] by multiplying the shortest interatomic distance (Table 6) by the conversion factor [18] 2.31. The values obtained in this way (no literature reference) are compared in Table 7 with the experimentally determined lattice constants of the III–V compounds.

Table 8. Standard absolute entropies of III–V compounds (cal mole^{-1} deg^{-1}).

Compound	Experimental value	Ref.	Calc. by adding the entropies of the elemental semiconductors*		Calc. from Eqn.(7), with negative correction of 5 cal mole^{-1} deg^{-1}**	
			Value	Discrepancy from experiment	Value	Discrepancy from experiment
BN	3,67	36	2.72	—0,95		—
AlN	5.0	36	5.89	+0,89		—
GaN	8,4	63	8.79	+0,39		—
InN	10.2	64	11.82	+1,62		—
BP	—		5.89	—		—
AlP	—		9.09	—		—
GaP	12.4	66	11.96	—0,44	11,14	—1.26
InP	14.28	65	14.86	+0,58	16.04	+1.76
BAs	—		8,79	—		—
AlAs	—		11.96	—		—
GaAs	15.34	65	14.86	—0.48	15,23	—0.11
InAs	18.10	65	17.89	—0,2	18,88	+0.78
BSb	—	—	12,82	—	—	—
AlSb	15.36	65	14.99	—0.37	16,57	+1.21
GaSb	18.18	65	17.89	—0.29	19.06	+0.88
InSb	20.60	65	20.92	+0.32	23.2	+2.60

*Calculated from data of Tables 3 and 5.
**Calculated from data of Table 7.
The melting points assumed in the calculations are: GaP, 1795; InP, 1330; GaAs, 1510; InAs, 1216; AlSb, 1343; GaSb, 976; InSb, 798°K.

We have calculated the standard absolute entropies of III–V compounds by adding the standard absolute entropies of the appropriate Group IV semiconductors, and we have obtained satisfactory agreement with experimental data. As Table 8 shows, the agreement is better than can be achieved using Eqn. (7).

V. SPECIFIC HEAT

Experimental measurements of specific heat are available only for a few III–V compounds. Thus, Kochetkova and Rezukhina [67] obtained the specific heat of GaSb between 20 and 700° by calorimetric measurements.

Table 9. Specific heat equations of III–V compounds (cal mole^{-1} deg^{-1}) calculated from data obtained from Eqns. (8)–(10).

A^{III}	B^{V}			
	N	P	As	Sb
Al	—	—	$9.004+3\cdot10^{-3}T$	$10.310+4\cdot10^{-3}T$
Ga	$8.122+3\cdot10^{-3}T$	$10.180+2.47\cdot10^{-3}T$*	$10.028+3\cdot10^{-3}T$	$10.668+4\cdot10^{-3}T$
In	$9.863+3\cdot10^{-3}T$	$10.180+4\cdot10^{-3}T$	$10.530+4\cdot10^{-3}T$	$11.804+2\cdot10^{-3}T$

*A correction [73] has been applied to the equation previously accepted [42,47].

Nachtrieb and Clement [68], using a similar method, obtained the following values for the mean specific heat of InSb: 0.052, 0.056, 0.062, 0.062 cal g^{-1} deg^{-1} (or 12.3, 13.2, 14.7, 14.7 cal mole^{-1} deg^{-1}) for the temperature intervals 20–90, 90–170, 170–350, and 350–500° respectively. The low-temperature specific heats of GaP and InP have been measured [66] between 40 and 300°K. Piesbergen [69] determined the temperature dependence of the specific heat of a number of III–V compound semiconductors from data on their Debye characteristic temperature. High-temperature thermodynamic quantities are difficult to calculate, because of the lack of adequate specific heat data. Hence, approximate methods of computation of the specific heat of III–V compounds are very valuable.

Table 10. Specific heat equations for Group IV semiconductors [74].

Element	Specific heat equation	Temp. range, °K
α-Sn	$5.05+4.80\cdot10^{-3}T$	273—504
C	$2.162+3.059\cdot10^{-3}T-1.303\cdot10^{5}\cdot T^{-2}$	273—1313
Si	$5.74+0.617\cdot10^{-3}T-1.01\cdot10^{5}T^{-2}$	273—1174
Ge	$5.94+0.90\cdot10^{-3}T-0.59\cdot10^{5}\cdot T^{-2}$	273—713

Attempts to apply the additivity rule to the temperature dependence of the specific heats of the constituent elements have not been successful, because the specific heat equations for the relatively low-melting components [36,57] are not valid at the higher temperatures of interest for high-melting compounds.

If the melting point is known, an equation for the temperature dependence of the specific heat can be obtained by Kelly's method [70], which assumes a linear variation of specific heat between room temperature and the temperature of the first phase transition. In addition, the following assumptions are made:

1. The molecular specific heat of the compound at room temperature is additive in terms of the atomic specific heats, as required by the rule of Dulong and Petit, and equals 12.6 cal mole^{-1} deg^{-1}. [71]

2. The specific heat of the compound at its melting point is 14.5 cal mole^{-1} deg^{-1}, by analogy with the atomic specific heat of many inorganic compounds at their melting point [36].

Table 12. Comparison of experimental and calculated standard specific heats of III–V compound semiconductors (cal mole^{-1} deg^{-1}).

Compound	Experimental value	Ref.	Calc. from the data of Table 9		Cal. from the data of Table 11	
			Value	Discrepancy from experiment	Value	Discrepancy from experiment
BN	5.61	35	—	—	3.21	−2.40
AlN	7.79	36	—	—	6.40	−1.39
GaN	—		—	—	7.15	—
InN	—		—	—	8.08	—
BP	—		—	—	6.40	—
AlP	—		—	—	9.57	—
GaP	10.43	66	10.92	+0.49	10.32	−0.11
InP	11.30	66	11.37	+0.07	11.08	−0.22
BAs	—		—	—	7.15	—
AlAs	—		9.90	—	10.32	—
GaAs	11.05	69	10.92	+0.13	11.08	+0.03
InAs	11.42	69	11.72	+0.30	12.03	+0.61
BSb	—		—	—	8.08	—
AlSb	11.07	75	11.50	+0.43	11.26	+0.19
GaSb	11.38	67	11.88	+0.50	12.02	+0.64
InSb	12.30	68	12.40	+0.10	12.96	+0.66

The precision of Kelly's specific heat equation can be improved by using Landiya's equation

$$C_p=(C_{v,at}+\alpha_{at}T^{3/2})\cdot n, \tag{8}$$

to calculate the specific heat C_p of the compound at constant pressure, where n is the number of atoms in one molecule of the compound, $C_{v,at}$ is the atomic specific heat at constant volume, α_{at} is the atomic thermal expansion coefficient. The quantities $C_{v,at}$ and α_{at} can be calculated by the equations

$$C_{v,at.}=6.6-\frac{a}{b+k(T-b)} \tag{9}$$

and

$$\alpha_{at.}=\frac{1.24}{T_f}(C_{v,at}^{298})^2\cdot10^{-3}, \tag{10}$$

where T_f is the melting point of the compound and $C_{v,at}^{298}$ is the atomic specific heat at constant volume, obtained

Table 11. Specific heat equations for III–V compound semiconductors, obtained by adding the specific heat equations of the elemental Group IV semiconductors.

A^{III}	B^{V}			
	N	P	As	Sb
B	$4.324+6.118\cdot10^{-3}T-2.606\cdot10^{5}T^{-2}$	$7.902+3.676\cdot10^{-3}T-2.313\cdot10^{5}T^{-2}$	$8.102-2.959\cdot10^{-3}T-1.893\cdot10^{5}T^{-2}$	$7.212+7.859\cdot10^{-3}T-1.303\cdot10^{5}T^{-2}$
Al	$7.902+3.676\cdot10^{-3}T-2.313\cdot10^{5}T^{-2}$	$11.480+1.234\cdot10^{-3}T-2.020\cdot10^{5}T^{-2}$	$11.680+1.520\cdot10^{-3}T-1.60\cdot10^{5}T^{-2}$	$10.790+5.417\cdot10^{-3}T-1.010\cdot10^{5}T^{-2}$
Ga	$8.102+3.959\cdot10^{-3}T-1.893\cdot10^{5}T^{-2}$	$11.680+1.52\cdot10^{-3}T-1.60\cdot10^{5}T^{-2}$	$11.880+1.80\cdot10^{-3}T-1.18\cdot10^{5}T^{-2}$	$10.990+5.70\cdot10^{-3}T-0.590\cdot10^{5}T^{-2}$
In	$7.212+7.859\cdot10^{-3}T-1.303\cdot10^{5}T^{-2}$	$9.24+4.54\cdot10^{-3}T$	$10.990+5.70\cdot10^{-3}T-0.59\cdot10^{5}T^{-2}$	$10.10+9.60\cdot10^{-3}T$

from Eqn. (9) by putting $T = 298°K$. The coefficients a, b, and k in Eqn. (9) take the following values for a compound which dissociates with evolution of a volatile component:

$$a = \frac{4400}{S^0_{298}};\quad b = 298;\quad k = \frac{(2200 - 149 \cdot S^0_{298})}{(5070 - 149 \cdot S^0_{298})}$$

The specific heat values calculated for 298°K and T_f are then used to obtain a linear equation for the temperature dependence of the specific heat, valid between 298°K and T_f. The results are summarised in Table 9.

If the thermodynamic data needed to obtain a specific heat equation for III–V compounds as a function of temperature by the above method are not available, the equation can be produced by summing the specific heat equations for the corresponding elemental semiconductors (see Table 3).

The specific heat equations for the elemental semiconductors of Group IV are listed in Table 10: the specific heat equations for III–V compounds deduced from those data are given in Table 11.

As Table 12 shows, the specific heats of III–V compounds calculated by Landiya's method agree satisfactorily with experimental values. Results fully adequate for approximate calculations are obtained also by adding the specific heat equations of the appropriate elemental semiconductors of Group IV (see Table 12).

VI. ENTHALPY AND FREE ENERGY OF FORMATION AND HEAT OF ATOMISATION OF $A^{III}B^{V}$ COMPOUNDS

The enthalpy of formation of a compound is one of its most important parameters, and is related to many of its physicochemical characteristics. Very few experimental determinations of the enthalpy of III–V compounds have been reported, particularly for compounds which tend to dissociate.

The enthalpy of formation of InSb has been determined fairly accurately by tin calorimetry [27,76], by direct fusion [77], by the e.m.f. method, and by fusion in a bomb calorimeter [81,82]. The enthalpy of GaSb has been measured calorimetrically [27] and by the e.m.f. method [80,83].

The enthalpy of dissociating compounds is difficult to measure experimentally. For InAs the problem has been solved using colorimetric [27,80] and mass-spectrometric [84,85] techniques. Values of the enthalpy of formation of GaAs have been obtained from mass-spectrometric experiments [86], from thermochemical studies of transport reactions involving the compound [87], and by the e.m.f. method [80].

The enthalpy of formation of InP has been obtained from the temperature dependence of the dissociation pressure [88,89], mass-spectrometrically [86], and also by fusion [82] and combustion in a bomb calorimeter [90]. The enthalpy of formation of GaP was first determined [91] from the temperature dependence of the dissociation pressure of the compound. Johnston [92] obtained a different value under similar conditions. Data from combustion experiments in a bomb calorimeter have been reported [90]. More recent work on the enthalpy of formation of GaP has relied on the e.m.f. method [93,94] and on calorimetric measurements [95]. The enthalpy of formation of BP has been measured calorimetrically by the reaction between the compound and gaseous F_2 to give BF_3. [96]

Renner [40] computed the enthalpies of formation of III–V compounds from reactions of the type

$$A^{III}_{(liq)} + \frac{1}{n} B^{V}_{n(g)} \rightleftarrows A^{III}B^{V}_{(g)},$$

using published values of the latent heat of fusion, enthalpy of dissociation, and specific heat of the elements [36,57].

The free energies of formation ΔG°_{298} of the compounds can be calculated from their enthalpies ΔH°_{298} and entropies ΔS°_{298} of formation:

$$\Delta G^\circ_{298} = \Delta H^\circ_{298} - T\Delta S^\circ_{298} \text{ kcal mole}^{-1} \qquad (11)$$

Table 13. Enthalpies of formation of III–V compounds, kcal mole^{-1}.

Compound	T, °K	Reactions			
		$A_{sol} + \frac{1}{2}B_{2(g)} = AB_{(sol)}$	$A_{(liq)} + \frac{1}{2}B_{2(g)} = AB_{(sol)}$	$A_{(sol)} + \frac{1}{4}B_{4(g)} = AB_{(sol)}$	$A_{(liq)} + \frac{1}{4}B_{4(g)} = AB_{(sol)}$
BN	298	60.0[97]; 61.0[98]	—	—	—
AlN	298	63.0[97]; 76.5[99]	—	—	—
		75.6±4[100]	—	—	—
GaN	298	25±0.5[101]	—	—	—
InN	298	4.6[101]	—	—	—
$BP_{(cub)}$	298	27.6±1.1*[96]	—	—	—
		19.9[102];			
		29±2[103]	—	—	—
		59.1±0.8[106]			
AlP	298	27.8[104]	—	—	—
GaP	298	42.75[105]	44.38[73]	32.6±1.5[34]	29.1[90]; 24.4[93]
					29.0[94]; 24.9[95]
	1000	—	43.82[73]	—	—
	1500	—	42.89[73]	—	29.66[73]
InP	298	—	—	—	21.54[90]
	1000	—	30.2[85]	39.4±0.5[86]	25.8[107]; 25.4[86];
			41.5[107]	30.2[40]	26.0±3.6[89]
BAs	298	29.9[104]	—	—	—
AlAs	298	13.4[104]	—	—	—
GaAs	298	39.3[85]	44.4[87]	20.4[86]; 26.3[107]	
		44.6[107]			28.9[87]
				26.3±0.75[34]	22.5[28]
		44.4±1.5[34]	45.0[107]	—	27.0[107]; 22.1[86]
	1000	—	35.0[108]	—	—
	1000–1280	—	41.1[84]; 40.0[107]	—	26.0[84]; 22.5[107]
TnAs	1000	—	39.0±2.5[108]	—	22.0[108]
GaSb	900	—	41.0[84]	—	25.5[84]
InSb	930	—	7.78[81]	—	—

*Calculated from the reaction between BP and F_2.

For a III–V compound whose vapour phase consists almost exclusively of the component B^V, the free energy ΔG°_T at a given temperature can be calculated from the experimentally observed dissociation pressure at the room temperature:

$$\Delta G^\circ_T = -\frac{RT}{x} \ln p_{B_xV} \qquad (12)$$

where p_{B_xV} is the dissociation pressure of the compound at temperature T.

Table 13 lists the enthalpies of formation of III–V compounds, measured experimentally or calculated by Eqns. (11) and (12).

The heat of atomisation is an important parameter which reflects the strength of the chemical bond in a semiconducting compound and therefore shows good correlation with its electrical and thermochemical properties [109,110].

Table 14. Heat of atomisation (kcal mole^{-1}) of A^{III} and B^V elements and of Group IV semiconductors.

Element	ΔH°_{at}	Ref.	Element	ΔH°_{at}	Ref.
$B_{(sol)}$	107.5	119	$As_{(sol)}$	69.0	121
$Al_{(re)}$	75.0	120	$Sb_{(sol)}$	62.0	121
$Ga_{(sol)}$	66.0	120	$Si_{(sol)}$	89.0	120
$In_{(sol)}$	58.2	120	$Ge_{(sol)}$	78.4	119
$N_{(g)}$	113.7	121	$\alpha - Sn_{(sol)}$	70.0	121
$P_{(sol)}$	75.2	120	$C_{(sol)}$	138.0	63

Moser and Pearson [110] have considered three idealised bond formation schemes in III–V compounds. The atoms of elements in the IIIB subgroup have three electrons with an s^2p^1 configuration in their outer unfilled shell. The atoms of elements in the VB subgroup have five electrons with the s^2p^3 configuration. When a covalent bond is formed, the Group V atom gives up one electron to the Group III atom, producing a V^+ and a III^- ion with four valence electrons each. The electrons take up the sp^3 configuration, forming tetrahedral bonds of the diamond type. However, the atoms also experience an electrostatic attraction. In the case of a neutral (atomic) bond [111], all the atoms retain their valence electrons, and the charge on all the atoms is the same. In the case of an ionic bond, three electrons are transferred from the A^{III} to the B^V atom, and III^{3+} and V^{3-} ions with filled spherical shells are formed.

Folberth [25] has shown that the bond in III–V compounds is covalent, with a significant proportion of ionic character. Because of the additional effect of the ionic contribution to the bond, III–V compounds have a higher bond strength than the Group IV elements [10].

Various empirical and theoretical methods of evaluating the degree of ionicity and the effective charges are discussed in review articles by Madelung [113], Hilsum and Rose-Innes [18], and also in papers by Suchet [114] and Syrkin and coworkers [115]. Sirota and coworkers [116–118] have derived the effective charges and the ionic contributions to the bond energies for aluminium, gallium, and indium phosphides, arsenides, and antimonides from electron density maps.

The heat of atomisation $\Delta H^\circ_{at}{}^{AB}$ is the sum of the enthalpy of formation of the compound from its atoms ($\Delta H^\circ_{298}{}^{AB}$) and of the heats of transformation of the components to the gaseous state ($\Delta H^\circ_g{}^{,A}$ and $\Delta H^\circ_g{}^{,B}$):

$$\Delta H^{\circ,AB}_{at.} = \Delta H^{\circ,AB}_{298} + \Delta H^{\circ,A}_g + \Delta H^{\circ,B}_g \quad . \qquad (13)$$

Since the heat of atomisation is known experimentally to be an insensitive function of temperature [109] and does not need to be reduced to a standard state, it can be evaluated by the additive method used above to calculate various thermochemical constants (latent heat of fusion, entropy, and specific heat): in this case, from a summation of ΔH°_{at} values for the elemental semiconductors. The data required for the calculation are given in Table 14.

Table 15. Heat of atomisation (kcal mole^{-1}) of III–V compounds.

Compound	Experimental		Obtained by adding ΔH°_{at} values for elemental semiconductors		Difference, %
	$-\Delta H^\circ_{298}$; AB	$-\Delta H^\circ_{at}$; AB	Sum of ΔH°_{at} for C, Si, Ge, and α-Sn	$-\Delta H^\circ_{at}$; AB	
BN	60.0[97]	281.2	2C	276.0	−1.8
AlN	63.0[97]	251.7	C + Si	227.0	−9.8
GaN	25.0[101]	204.1	C + Ge	216.4	+5.4
InN	4.6[101]	176.5	C + α-Sn	208.0	+10.8
BP	27.6[96]	210.3	Si + C	228.0	+7.9
AlP	—	—	2 Si	178.0	—
GaP	24.4[94]	165.6	Si + Ge	167.4	+1.1
InP	22.3[107]	155.7	2 Ge	156.8	+0.7
BAs	—	—	Ge + C	216.4	—
AlAs	—	—	Ge + Si	167.4	—
GaAs	17.7[107]	152.7	2 Ge	156.8	+2.6
InAs	14.8[97]	151.0	Ge + α-Sn	148.4	−1.7
BSb	—	—	α-Sn + C	208.0	—
AlSb	—	—	α-Sn + Si	159.4	—
GaSb	9.9[97]	137.9	α-Sn + Ge	148.0	+7.5
InSb	8.2[79]	128.4	2 α-Sn	140.0	+9.0

Experimental and calculated values of the heat of atomisation of III–V compound semiconductors are compared in Table 15. It is evident from this Table that the difference between the experimental values and those calculated additively does not exceed 11%, with a mean deviation of 5.3%. This degree of accuracy is fully adequate for many approximate calculations.

VII. VAPOUR PRESSURE

Reliable data on the vapour pressure of the volatile components over III–V compounds tending to dissociate are essential to the design of rational methods of synthesis and crystal growth for these compounds. The measurement of vapour pressure in these systems has some unusual features.

Phase equilibria in two-component systems are more complex than the corresponding equilibria in one-component systems: hence, it becomes more difficult to measure the saturated vapour pressure p and also to estimate the reliability of the results. For a solid or a liquid sample in equilibrium with the vapour of the volatile component the number of degrees of freedom given by Gibbs' phase rule is two, i.e. $p = f(T, x)$. For solids this conclusion applies at temperatures below the solidus line, for liquids above the liquidus line of the phase diagram. As a special case, the sample can have the stoichiometric composition, and in this case the system is monovariant, i.e. $p = f(T)$.

If a solid sample is heated above the solidus line, or a liquid sample is cooled below the liquidus line, a third phase appears. In a system of this type, for which a detailed analysis was given by Vigdorovich and Nashel'skii [122], the number of degrees of freedom is one, i.e. $p = f(T)$ at $x = \text{const}$ or $p = f(x)$ at $T = \text{const}$. In the special case of a stoichiometric solid and a stoichiometric liquid an additional constraint is present and the system becomes invariant, and a unique vapour pressure of the volatile component can be measured at the melting point.

The gas-phase composition varies from point to point if the temperature of the sample is not uniform, since molecular dissociation processes (under the influence of temperature) and atomic association processes (under the influence of pressure) take place in the gas phase in opposite directions [88]. Hence, calculations by the Mendeleev–Clapeyron equation are difficult to apply, since they involve the molecular weight of the vapour phase. Furthermore, the measurement of vapour pressure for compound semiconductors which undergo dissociation presents a number of experimental difficulties, including the need to work at high temperatures and pressures and the aggressive nature of the vapours and the melts towards most commonly used container materials. Nashel'skii [123] has reviewed experimental methods of measuring the vapour pressure of dissociating semiconductor compounds, including III–V compounds.

If the experimental difficulties prove insurmountable, the vapour pressure of III–V compound semiconductors can be estimated from thermochemical data by means of Eqn. (12), Many workers have carried out calculations of this type [40,42,49,73]. The temperature dependence of the vapour pressure of the volatile component is usually reported in the form of plots of $\lg p_{B_x^V}$ against $1/T$ (Fig. 8), or in the form of an equation of the type

$$\lg p_{B_x^V} = -\frac{A}{T} + B \quad . \qquad (14)$$

Values of the A and B coefficients of Eqn. (14) for arsenides and phosphides are given in Table 16.

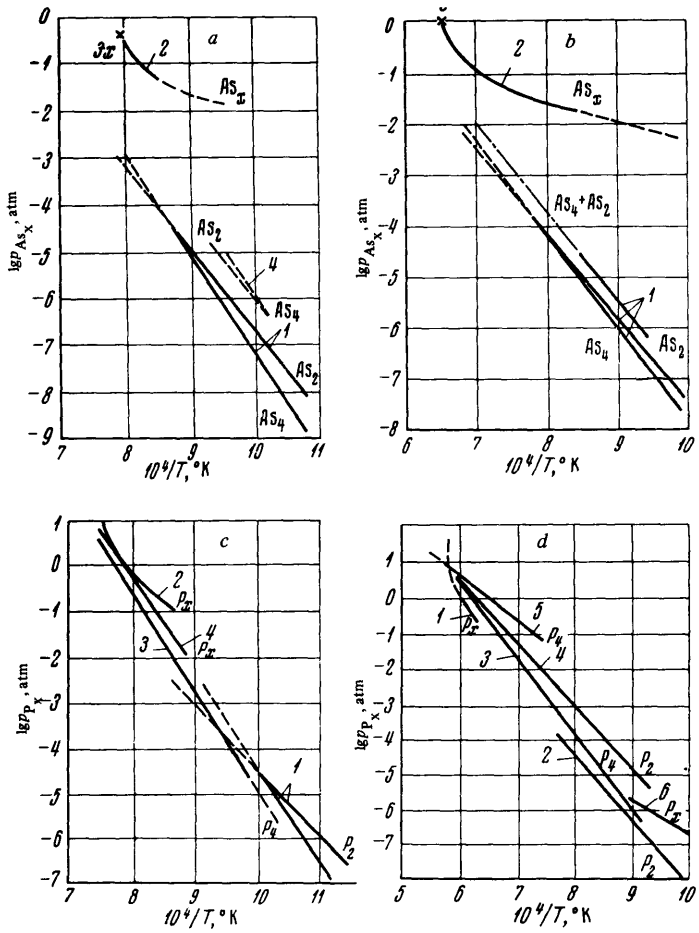


Figure 8. Dissociation pressure of some III–V compounds: (*a*) indium arsenide and (*b*) gallium arsenide [*1*) Ref. 84, 86; *2*) Ref. 44; *3*) equilibrium vapour pressure of arsenic at the melting point of the compound; *4*) Ref. 40]; (*c*) indium phosphide [*1*) Ref. 84, 86; *2*) Ref. 92; *3*) Ref. 44; *4*) Ref. 88, 89]; (*d*) gallium phosphide [*1*) Ref. 44; *2*) Ref. 92; *3*) and *4*) Ref. 73; *5*) Ref. 91; *6*) Ref. 127].

The dissociation pressure of InSb and GaSb is very low [84,86]. The vapour pressure of Sb and InSb over InSb has been measured [125] by an effusion method, with radioactive isotopes. The vapour pressure of Sb over GaSb samples of different composition has been measured [126] by the "dew-point" method.

Table 16. Experimental values of the temperature dependence of the dissociation pressure of III–V arsenides and phosphides (atm).

Compound	Molecular composition of vapour	Numerical values of constants in Eqn.(14)		Temp. range, °K		Equilibrium pressure of the B^V component at the melting point of the compound	
		A	B				
InAs	As_2	18.840	24.00	911—1195	109	0.33	11
	As_4	22.725	27.25				
GaAs	As_2	17.340	9.86	950—1200	109	0.9	11
	As_4	19.320	24.66			~1.0	44
InP	P_2	14.850	10.32	775—900	109	~21	44
		21.300	16.84				
	P_4	23.000	21.00	973—1318	89	~40	88
		19.200	13.80	1123—1243	88		
GaP	P_2	13.650	6.90	973—1073	127	~20	12
		18.870	13.60	1054—1278	92	~35	44
	P_4	12.510	8.167	1350—1678	91		

All the thermochemical data relating to III–V compound semiconductors indicate a gradual variation with the molecular weight of the compound. The lattice parameter, specific heat, and standard entropy increase with molecular weight in an isoelectronic series. Conversely, the melting point, heat of fusion, entropy of fusion, enthalpy of formation, and heat of atomisation decrease with increase of molecular weight in an isoelectronic series.

These changes are consistent with the changes in the nature and strength of the chemical bond [124,128] in III–V compounds expected from the position of their constituent elements in the Periodic Table.

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