

A THERMODYNAMIC EVALUATION OF THE Ge–In, Ge–Pb, Ge–Sb, Ge–Tl AND Ge–Zn SYSTEMS

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ABSTRACT

Five germanium-based binary systems have been thermodynamically assessed as a part of a long-term programme to provide thermodynamic data bases in order to perform calculations in multi-component systems. For each system, Ge–In, Ge–Pb, Ge–Sb, Ge–Tl and Ge–Zn, a set of self-consistent parameters has been obtained by using the optimization procedure developed by Lukas et al. (*Calphad*, 6 (1977) 225). Characteristic thermodynamic functions have been calculated and compared with the corresponding experimental values using the THERMODATA software.

INTRODUCTION

This work continues the series of publications by the author on the Au–Sn [1], Au–Bi [2], Ag–Ge [3], Ag–Si [4], Bi–Ge [5], Ag–Sn [6], Au–Si and Au–Ge [7], and Bi–In [8] systems. The aims of this work have been extensively discussed in the previous articles: to allow scientists to perform thermodynamic calculations in multi-component systems in order to predict phase equilibria and to minimize the number of necessary experiments.

For each of the five systems, Ge–In, Ge–Pb, Ge–Sb, Ge–Tl and Ge–Zn, the available experimental information has been compiled using the bibliographic data base THERMDOC integrated in the THERMODATA SYSTEM [9] and presented, for both phase diagram and thermodynamic properties. This information is needed to use the optimization procedure of Lukas et al. [10] to obtain a set of self-consistent parameters for each of the systems.

EVALUATION METHOD

The Gibbs free energy of different solution phases (liquid, dia) has been described using a simple substitution model. An expression for the excess

TABLE 1

Lattice stabilities for M = Ge, In, Pb, Sb, Tl and Zn, after ref. 11 for all structures

M	Transformation	$\Delta^\circ G$ (J)	Temperature range (K)
Ge	dia \rightarrow liquid	$37141.633 - 30.684649T + 85676.079 \times 10^{-25}T^7$	298.15–1211.5
		$36791.565 - 30.381247T + 861075.152 \times 10^{+23}T^{-9}$	1211.5–3200.0
In	b.c.t. \rightarrow liquid	$3282.152 - 7.636490T - 521918.380 \times 10^{-25}T^7$	298.15–429.78
	b.c.t. \rightarrow dia	$3283.660 - 7.640173T - 0.330 \times 10^{+23}T^{-9}$	429.78–3800.0
		4184.0 (estimated)	298.15–3800.0
Pb	f.c.c. \rightarrow liquid	$4672.157 - 7.750257T - 6014405.024 \times 10^{-25}T^7$	298.15–600.65
	f.c.c. \rightarrow dia	$4853.112 - 8.066587T - 805.644 \times 10^{+23}T^{-9}$	600.65–2100.0
		4184.0 (estimated)	298.15–2100.0
Sb	rho \rightarrow liquid	$19822.595 - 21.920597T - 173784.951 \times 10^{-25}T^7$	298.15–903.90
	rho \rightarrow dia	$19913.982 - 22.026755T - 16104.421 \times 10^{+23}T^{-9}$	903.90–2000.0
		4184.0 (estimated)	298.15–2000.0
Tl	h.c.p. \rightarrow liquid	$4654.235 - 8.157775T - 5946859.963 \times 10^{-25}T^7$	298.15–577.00
		$4789.301 - 8.403563T - 418.897 \times 10^{+23}T^{-9}$	577.00–3000.0
	h.c.p. \rightarrow b.c.c.	$137.793 - 9.055306T - 4.42 \times 10^{-3}T^2 + 1.77T \ln T$	298.15–577.00
		$801.583 - 1.465674T - 1513.730 \times 10^{+23}T^{-9}$	577.00–3000.0
	h.c.p. \rightarrow dia	4184.0 (estimated)	298.15–3000.0
Zn	h.c.p. \rightarrow liquid	$7157.27 - 10.292343T - 3586522.860 \times 10^{-25}T^7$	298.15–692.73
		$7450.123 - 10.736234T - 4706.568 \times 10^{+23}T^{-9}$	692.73–1700.0
	h.c.p. \rightarrow dia	4184.0 (estimated)	298.15–1700.0

Gibbs free energy has been developed by a Redlich–Kister polynomial equation of the form

$$\Delta G^E = x_{\text{Ge}}x_{\text{M}} \sum_{\nu=0}^n (x_{\text{Ge}} - x_{\text{M}})^{(\nu)} L_{\text{Ge,M}}^{(\nu)}(T) \quad (1)$$

where M = In, Pb, Sb, Tl or Zn.

The interaction terms $L_{\text{Ge,M}}^{(\nu)}$ are linear functions of temperature

$$L_{\text{Ge,M}}^{(\nu)}(T) = a_{\text{Ge,M}}^{(\nu)} + b_{\text{Ge,M}}^{(\nu)}T \quad (2)$$

where $a_{\text{Ge,M}}^{(\nu)}$ and $b_{\text{Ge,M}}^{(\nu)}$ correspond to the temperature-independent values of the enthalpy and the excess entropy of mixing. There is no compound in these systems.

The values used for the lattice stabilities of the pure components come from the S.G.T.E. assessment [11] for the stable solid and liquid phases, and those of the metastable structures (In dia, Pb dia, Sb dia, Tl dia and Zn dia) have been fixed to a positive value, 4184 J, because no data have been found in the literature. They are reported in Table 1.

EXPERIMENTAL INFORMATION

The Ge–In system

Phase diagram

The liquidus of the Ge–In system has been experimentally determined using conventional techniques by Klemm and Klemm [12] and by Keck and Broder [13]. The unpublished work of Hassion has been reported by Thurmond and Kowalchik [14].

The solubility of In in solid germanium was measured by Zhurkin et al. [15]: $x_{\text{In}} = 6.16 \times 10^{-6}$ at $T = 1205$ K, 2.48×10^{-5} at 1204 K, 4.66×10^{-5} at 1198 K, 1.06×10^{-5} at 1152 K, 1.38×10^{-4} at 1070 K, 6.6×10^{-4} at 893 K; by Thurmond et al. [16]: 8×10^{-5} at $T = 1173$ K, 3×10^{-4} at 1073 K, 4.5×10^{-4} at 973 K, 5.8×10^{-4} at 873 K, 6.5×10^{-4} at 773 K, 7×10^{-4} at 673 K; and by Trumbore [17]: 9.1×10^{-5} at $T = 1073$ K, $4.5\text{--}8.6 \times 10^{-5}$ at 973 K, $6.1\text{--}12.2 \times 10^{-4}$ at 893 K, 6.8×10^{-5} at 783 K (these results have been reported by Elliott [18].)

The solid solubility of Ge in pure indium is negligible. According to a number of authors, the phase diagram is a simple eutectic located on the indium side ($T = 429$ K).

The different phases are the liquid phase (L), the terminal germanium-based solid solution, with a diamond-type structure (dia) and pure In, with the b.c. tetragonal (A6) prototype structure (In b.c.t.).

Thermodynamic properties

The enthalpies of mixing of liquid Ge–In alloys have been measured by direct high temperature calorimetry by Predel and Stein [19]: $T = 1273$ K, $x_{\text{In}} = 0.19\text{--}0.89$; and also by Batalin et al. [20]: $T = 1500$ K, $x_{\text{In}} = 0.28\text{--}0.90$, these results are much more positive than those in ref. 19. Batalin et al. [20] were in good agreement with ref. 19, but they refer to a paper concerning the Ge–Tl, Ge–Pb and Ge–Bi systems [21]. For that reason, these data have been discarded.

The thermodynamic properties of liquid Ge–In alloys have been determined using the EMF method by Batalin et al. [22]: $T = 1230$ K, $x_{\text{In}} = 0.136\text{--}0.922$. These authors have calculated the activities of the components, the partial and integral Gibbs free energy of mixing, and have also given the confidence limits of the thermodynamic functions.

The Ge–Pb system

Phase diagram

The equilibrium phase diagram of the Ge–Pb system has been assessed by Olesinski and Abbaschian [23]. It takes into account the experimental studies of Briggs and Benedict [24], thermal analysis and metallography, of

Ruttewit and Masing [25], thermal analysis, and the unpublished work of Hassion quoted by Thurmond and Kowalchik [14], solubility measurements. The three liquidus points of ref. 25 have been discarded by Olesinski and Abbaschian [23]. The solid solubility of Pb in pure germanium has been measured using the thermal gradient method by Thurmond and Kowalchik [14]: $x_{\text{Pb}} = 8.9 \times 10^{-6}$ at $T = 1123$ K. The maximum solid solubility of Pb in germanium has been estimated to be equal to 10^{-5} at around 1123 K by Trumbore [17]. The solid solubility of Ge in lead is negligible. The different phases of the system are the liquid phase (L), the terminal germanium-based solid solution (dia) and pure lead with the f.c.c. (A1) structure, isotypic with Cu (Pb f.c.c.). The assessed eutectic point was located at $T = 600.22$ K, $x_{\text{Pb}} = 0.9993$.

Thermodynamic properties

The enthalpies of mixing of liquid Ge–Pb alloys have been measured calorimetrically by Predel and Stein [21]: $T = 1273$ K, $x_{\text{Pb}} = 0.2$ – 0.896 ; and by Mechkovskij et al. [26]: $T = 1300$ K, $x_{\text{Pb}} = 0.22$ – 0.95 . Their results are in good agreement.

The Ge–Sb system

Phase diagram

The liquidus of the Ge–Sb system has been experimentally determined by Ruttewit and Masing [25], by Stohr and Klemm [27], using thermal analysis, metallographic and R.X. studies. Liquidus points have also been reported by Zhurkin et al. [15]. The eutectic point was located at $x_{\text{Sb}} = 0.83$, $T = 861$ K by Ruttewit and Masing [25] and at $x_{\text{Sb}} = 0.87$, $T = 865$ K by Stohr and Klemm [27]. The solid solubility of Sb in pure germanium has been measured by Zhurkin et al. [15]: $x_{\text{Sb}} = 1.34 \times 10^{-6}$ at $T = 1202$ K, 1.82×10^{-5} at 1196 K, 1.05×10^{-4} at 1179 K, 2.93×10^{-4} at 1152 K, 3.26×10^{-4} at 1086 K, 7.15×10^{-4} at 966 K; by Thurmond et al. [16]: 2×10^{-4} at 1173 K, 3×10^{-4} at 1073 K, 2.2×10^{-4} at 973 K, 1.9×10^{-4} at 873 K; by Trumbore et al. [28]: 1.8×10^{-4} at 1173 K, 2.7×10^{-4} at 1073 K, 2×10^{-4} at 973 K, 1.2×10^{-4} at 873 K; by Glazov et al. [29]: 10^{-4} at 1173 K, 8×10^{-4} at 858 K, 5.2×10^{-4} at 733 K; and by Thurmond and Struthers [30]: 2×10^{-4} at 1153 K, 3×10^{-5} at 1003 K, 9×10^{-7} at 853 K. The solid solubility of Ge in pure antimony is negligible. The different phases of the system are the liquid phase (L), the terminal germanium-based solid solution (dia) and pure antimony with a rhombohedral (A7) structure isotypic with As (Sb rho).

Thermodynamic properties

The enthalpy of mixing of Ge–Sb liquid alloys has been measured calorimetrically by Predel and Stein [19]: $T = 1273$ K, $x_{\text{Sb}} = 0.202$ – 0.893 .

Enthalpy is positive over all the composition range and shows a maximum equal to $753 \text{ J (g at.)}^{-1}$

The Ge-Tl system

Phase diagram

The liquidus of the Ge-Tl system has been determined by Klemm and Klemm [12] and Savitskii et al. [31] using thermal analysis, and by Thurmond and Kowalchik [14] by calculation of the composition points based on losses of massive Ge samples held in contact with molten Tl in sealed containers. Thurmond and Kowalchik calculated the eutectic composition as $x_{\text{Ge}} = 4 \times 10^{-4}$ at 0.3 K lower than the melting point of Tl. The solid solubility of Tl in pure germanium was measured using radioactive isotope techniques by Tagirov and Kuliev [32]: $x_{\text{Tl}} = 1.8 \times 10^{-4}$ at $T = 1203 \text{ K}$, 2.2×10^{-4} at 1183 K , 1.5×10^{-4} at 1169 K , 7×10^{-5} at 1141 K , 2.1×10^{-5} at 1111 K , 3.9×10^{-6} at 1073 K . The different phases are the liquid phase (L), the terminal germanium-based solid solution (dia). Pure Tl has an h.c.p. (A3) structure isotypic with Mg (Tl h.c.p.) and transforms at 507 K to a b.c.c. (A2) structure isotypic with W (Tl b.c.c.). The solubility of Ge in pure thallium is negligible.

Thermodynamic properties

The enthalpy of mixing of Ge-Tl liquid alloys has been measured calorimetrically by Predel and Stein [21]: $T = 1273 \text{ K}$, $x_{\text{Tl}} = 0.202\text{--}0.896$. Enthalpies are positive and show a maximum of 3443 J .

The Ge-Zn system

Phase diagram

The equilibrium phase diagram of the Ge-Zn system has been determined by Gebhardt [33] using thermal and microscopic analyses, and more recently by Thurmond and Kowalchik [14]. The liquidus was measured using the EMF method by Kleppa and Thalmayer [34]. The solubility of Zn in germanium has been determined by Trumbore [17]: $x_{\text{Zn}} = (7.2 \pm 0.3) \times 10^{-5}$ at $T = 1032 \pm 10 \text{ K}$, $(4.6 \pm 2.3) \times 10^{-5}$ at $998 \pm 10 \text{ K}$, $(4.7 \pm 0.6) \times 10^{-5}$ at $987 \pm 10 \text{ K}$, $(1.37 \pm 0.7) \times 10^{-5}$ at $693 \pm 10 \text{ K}$. The solubility of Ge in pure zinc is negligible. The different phases are the liquid phase (L), the terminal germanium-based solid solution (dia). Pure zinc has an h.c.p. (A3) structure isotypic with Mg (Zn h.c.p.).

Thermodynamic properties

The thermodynamic properties of liquid Ge-Zn alloys have been measured using the EMF method by Batalin et al. [35]: $T = 950\text{--}1230 \text{ K}$, $x_{\text{Ge}} = 0.092\text{--}0.776$; and by Predel and Schallner [36]: $T = 1000 \text{ K}$, $x_{\text{Zn}} =$

0.55–0.90. The activity of Zn was also measured using the vapour pressure method by Voronin and Evseev (37): $T = 687\text{--}739\text{ K}$, $x_{\text{Zn}} = 0.8\text{--}0.985$.

RESULTS AND DISCUSSION

The previously published experimental information was used to obtain a set of self-consistent parameters for each phase of the system by means of the optimization procedure developed by Lukas et al. [1]. Table 2 shows the optimized parameters of the excess Gibbs free energy according to expressions 1 and 2 for the various solution phases referred to the pure elements having the same structure as the corresponding phase.

The Ge–In system

The phase diagram was calculated using the optimized coefficients and is compared with the experimental data in Fig. 1. The eutectic point was calculated at $x_{\text{Ge}} = 0.00053$ and $T = 429.54\text{ K}$. The calculated solid solubil-

TABLE 2

Excess Gibbs free energy for the liquid and dia solid solution phases of the Ge–M systems (M = In, Pb, Sb, Tl and Zn)

$$\Delta G^E = x_{\text{Ge}}x_{\text{M}} \sum_{\nu=0}^n (x_{\text{Ge}} - x_{\text{M}})^{(\nu)} L_{\text{Ge,M}}^{(\nu)}(T) \quad (1)$$

$$L_{\text{Ge,M}}^{(\nu)}(T) = a_{\text{Ge,M}}^{(\nu)} + b_{\text{Ge,M}}^{(\nu)}T \quad (\nu = 0,1) \quad (2)$$

M	Phase	ν	$a_{\text{Ge,M}}^{(\nu)}$ (J)	$b_{\text{Ge,M}}^{(\nu)}$ (J K ⁻¹)	Temperature range (K)
In	liquid	0	1587.18	0.38707	298.15–3200
		1	–583.48	–1.51072	
	dia	0	45000.00	0.00000	
Pb	liquid	0	15283.10	1.99204	298.15–2100
		1	–783.50	0.00000	
	dia	0	97500.00	0.00000	
Sb	liquid	0	2861.50	0.00000	298.15–2000
		1	–2072.50	0.00000	
	dia	0	58000.00	0.00000	
Tl	liquid	0	13852.70	–0.37805	298.15–3000
		1	–1445.80	0.00000	
	dia	0	75000.00	0.00000	
Zn	liquid	0	4940.90	–6.50965	298.15–1700
		1	1119.00	0.00000	
	dia	0	70000.00	0.00000	

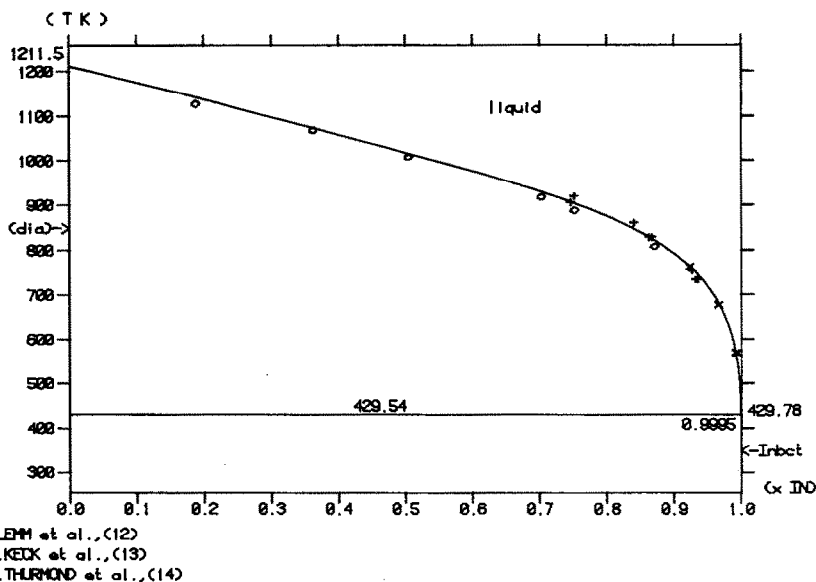


Fig. 1. Comparison between the calculated Ge-In phase diagram and selected experimental data.

ity of In in the dia solid solution is the following: $x_{\text{In}} = 10^{-4}$ at $T = 673$ K, 2.9×10^{-4} at 773 K, 5.9×10^{-4} at 873 K, 6.6×10^{-4} at 893 K, 9.4×10^{-4} at 973 K, 10^{-3} at 1073 K, 4.1×10^{-4} at 1173 K and 2.5×10^{-6} at the eutectic temperature.

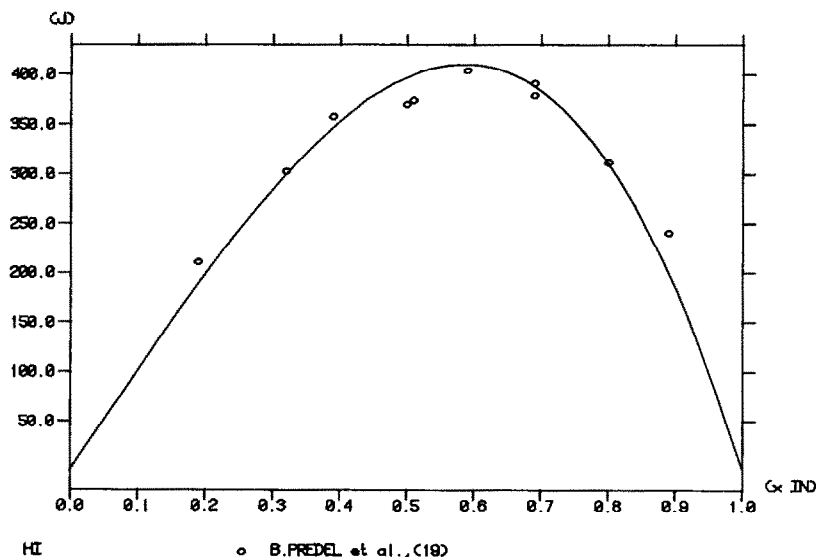


Fig. 2. Comparison between the calculated enthalpy of mixing of Ge-In liquid alloys (temperature-independent) and selected experimental data.

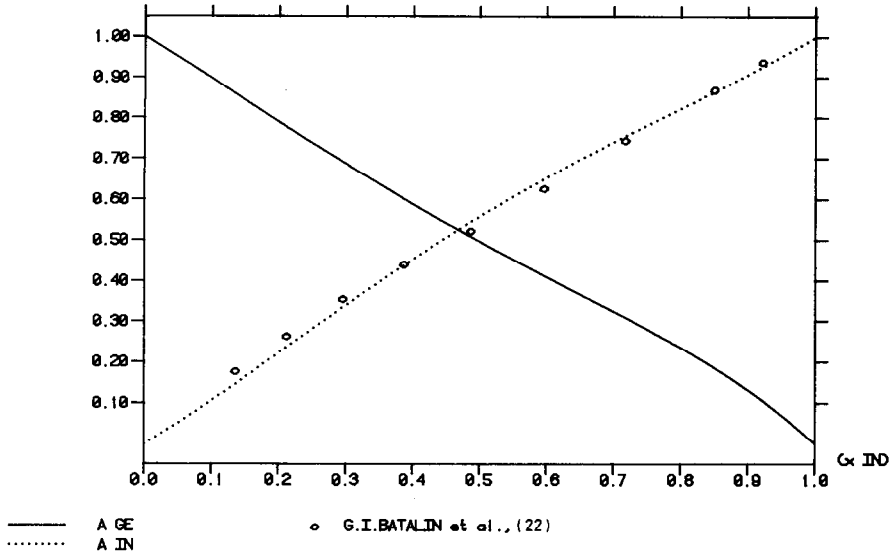
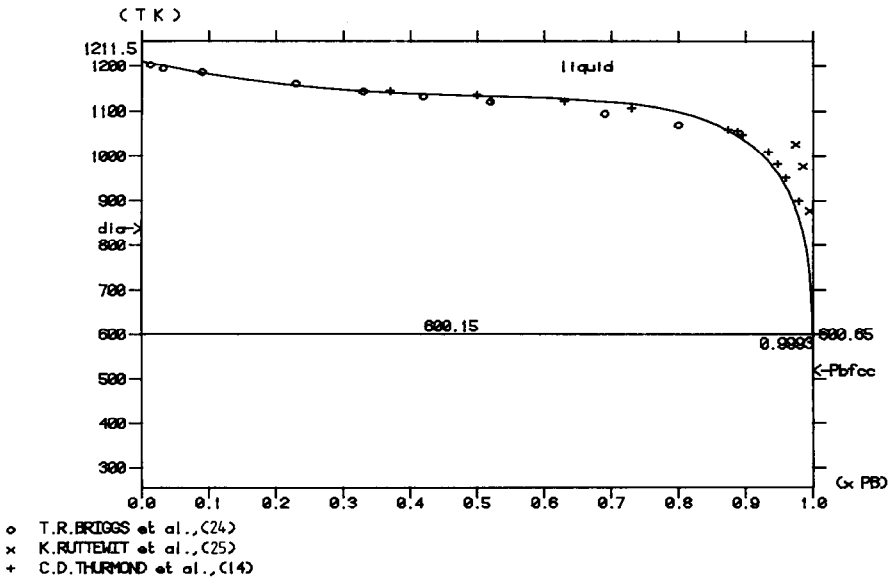


Fig. 3. Comparison between the calculated activity of Ge and In in the liquid phase at $T = 1230$ K and selected experimental data.

Figure 2 shows the comparison between the calculated enthalpy of mixing of the liquid phase and selected experimental data from ref. 19 at $T = 1273$ K. The agreement is very good. The activity of the components in the liquid



GE-PB : THERMIDATA 880816

Fig. 4. Comparison between the calculated Ge-Pb phase diagram and selected experimental data.

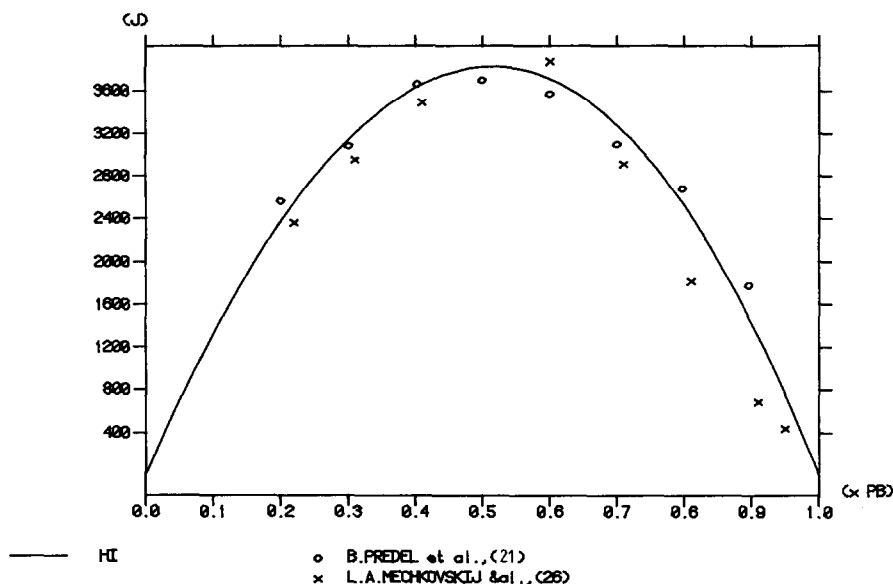


Fig. 5. Comparison between the calculated enthalpy of mixing of Ge-Pb liquid alloys (temperature-independent) and selected experimental data.

phase has been calculated at $T = 1230$ K and compared to the experimental results of ref. 22 in Fig. 3.

The Ge-Pb system

The calculated phase diagram is compared to the experimental one in Fig. 4. The eutectic point is located at $T = 600.15$ K and $x_{Ge} = 0.0007$, which is in very good agreement with the assessed values of ref. 23. The calculated solid solubility of Pb in the germanium-based solution is $x_{Pb} = 10^{-5}$ at $T = 1123$ K, and 2.2×10^{-8} at the eutectic temperature.

The calculated enthalpy of mixing (assumed to be temperature independent) has been compared to the experimental values of refs. 21 and 26 in Fig. 5.

The Ge-Sb system

The calculated phase diagram is compared to selected experimental data in Fig. 6. The eutectic point was calculated at $x_{Ge} = 0.162$ and $T = 858.5$ K, which is in good agreement with the experimental data. The solid solubility of Sb in the dia solid solution is the following: $x_{Sb} = 1.8 \times 10^{-4}$ at $T = 873$ K, 2.8×10^{-4} at 973 K, 2.8×10^{-4} at 1073 K, 1.2×10^{-4} at 1173 K, which is in sufficient agreement with the results of refs. 16 and 28. The calculated solubility of Sb in Ge is 1.56×10^{-4} at the eutectic temperature. Figure 7 shows the comparison between the enthalpy of mixing of the liquid phase and the experimental data of ref. 19 at $T = 1273$ K.

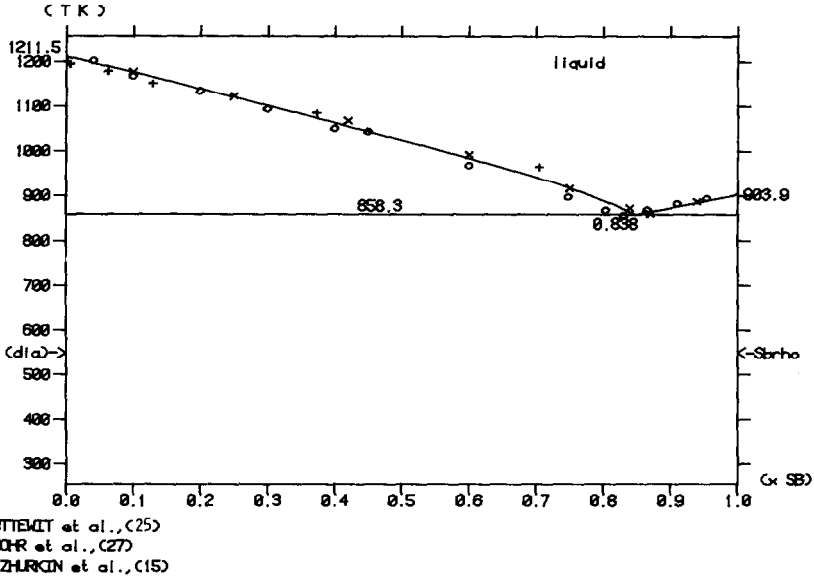


Fig. 6. Comparison between the calculated Ge-Sb phase diagram and selected experimental data.

The Ge-Tl system

Figure 8 shows the comparison between the calculated phase diagram and the experimental one. The eutectic point was calculated at $x_{Ge} = 0.0007$ and

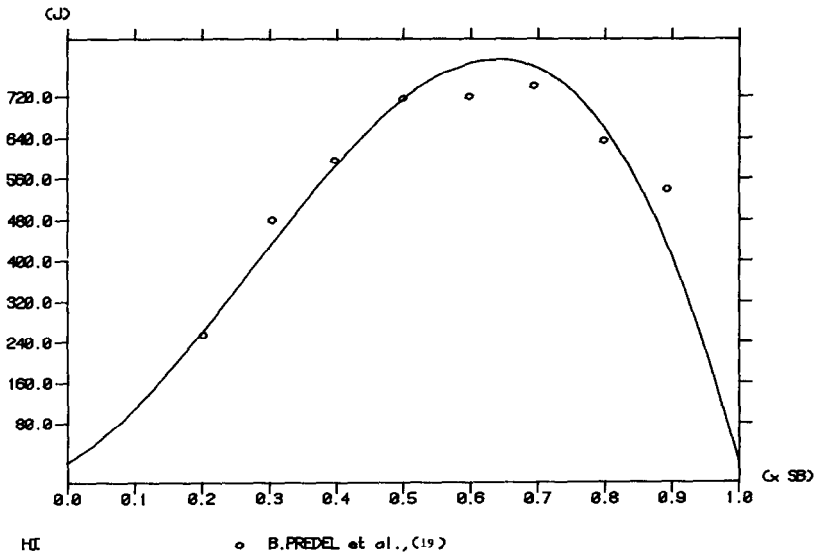
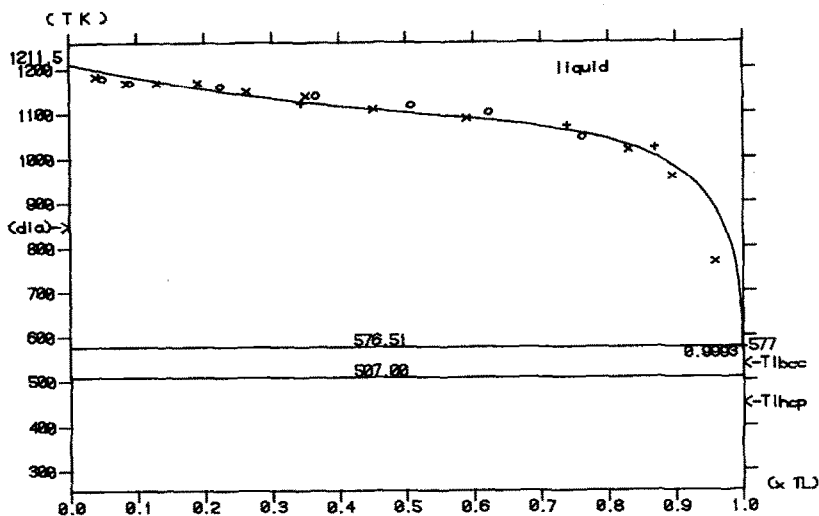


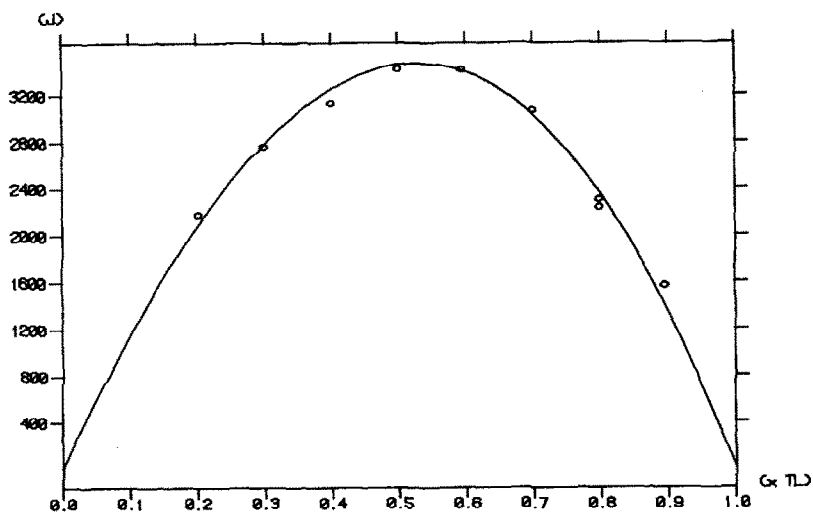
Fig. 7. Comparison between the calculated enthalpy of mixing of Ge-Sb liquid alloys (temperature-independent) and selected experimental data.



- W. KLEMM et al., (12)
 × E. M. SAVITSKII et al., (31)
 + C. D. THURMOND et al., (14)

Fig. 8. Comparison between the calculated Ge-Tl phase diagram and selected experimental data.

$T = 576.5$ K. The calculated solid solubility of Tl in the dia solid solution is the following: $x_{Tl} = 1.9 \times 10^{-5}$ at 1203 K, 5.0×10^{-5} at 1183 K, 6.6×10^{-5} at 1169 K, 8.1×10^{-5} at 1141 K, 8.3×10^{-5} at 1111 K, 7.1×10^{-5} at 1073



- HI ○ B. PREDEL et al., (21)

Fig. 9. Comparison between the calculated enthalpy of mixing of Ge-Tl liquid alloys (temperature-independent) and selected experimental data.

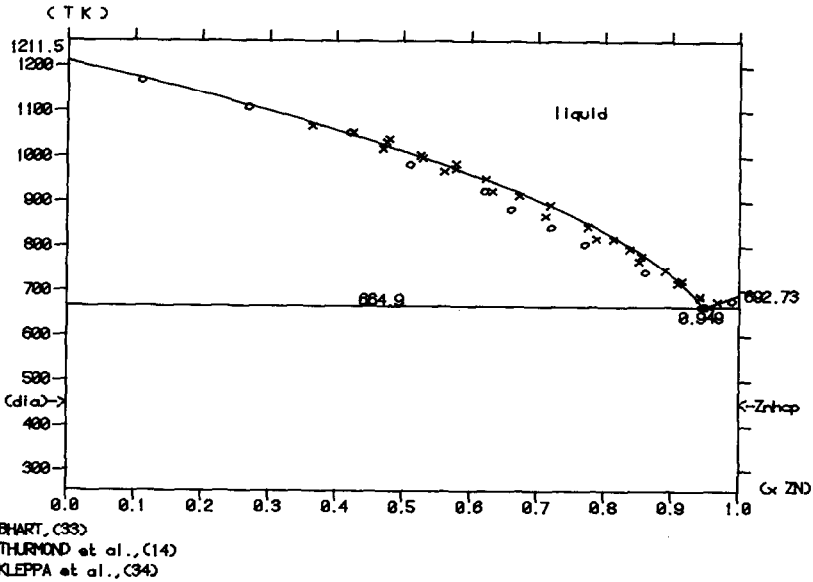


Fig. 10. Comparison between the calculated Ge-Zn phase diagram and selected experimental data.

K and 6.7×10^{-8} at the eutectic temperature. The calculated enthalpy of mixing of the liquid phase is compared to the experimental data of ref. 21 at $T = 1273$ K in Fig. 9.

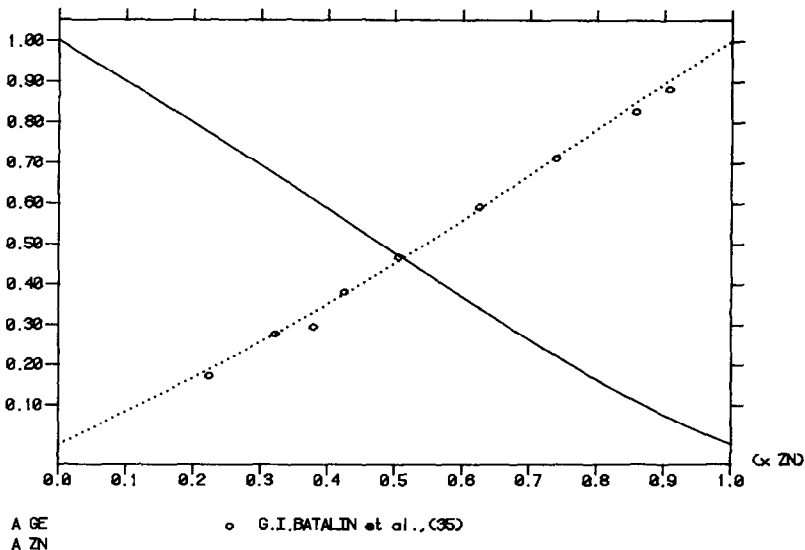


Fig. 11. Comparison between the calculated activity of Ge and Zn in the liquid phase at $T = 1230$ K and selected experimental data.

The Ge–Zn system

The calculated phase diagram is compared to selected experimental data in Fig. 10. The eutectic point was calculated at $x_{\text{Ge}} = 0.151$ and $T = 664.9$ K. The calculated solid solubility of Zn in the dia solid solution is the following: $x_{\text{Zn}} = 4.7 \times 10^{-5}$ at $T = 1032$ K, 4.1×10^{-5} at 998 K, 4.3×10^{-5} at 987 K, 2.5×10^{-6} at 693 K. Figure 11 shows the comparison between the calculated activity of the pure components in the liquid phase at $T = 1230$ K and the selected experimental data of ref. 35.

SUMMARY

A complete thermodynamic evaluation of the Ge–In, Ge–Pb, Ge–Sb, Ge–Tl and Ge–Zn systems is presented. The liquid phase (L) and the terminal germanium-based solid solution (dia) have been modelled, and a set of self-consistent parameters has been obtained for each system.

Comparison between the available experimental information and the calculated values is as satisfactory as possible despite some criticism. However, the description of the terminal germanium-based solid solution(dia) does not pretend to be very accurate for two main reasons: first, the experimental values themselves are often very scattered because the solubility of the components in pure germanium is very small and difficult to measure with great accuracy. Secondly, the lattice stabilities of the components In, Pb, Sb, Tl and Zn between the metastable germanium-type structure (dia) and their own stable solid structure are not known and were only estimated in order to reproduce metastability.

Consequently, a better description of the (dia) solid solution would need further work on these two points.

This set of parameters can be used for tabulation of standard thermodynamic functions or predicting phase equilibria in multi-component systems. It can be easily updated when new experimental information is available, after a new run with the optimization software.

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