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CRITICAL ASSESSMENT OF THERMODYNAMIC DATA FOR THE Ag–Ge SYSTEM

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ABSTRACT

Available experimental information concerning thermodynamic properties as well as phase equilibria data has been compiled for assessment of new self consistent parameters of thermodynamic models for liquid and solid phases in the Ag–Ge system. These coefficients have been optimized by using a program developed by Lukas et al., Calphad, 1 (1977) 225.

A phase diagram has been drawn and characteristic thermodynamic functions have been calculated and compared with the existing experimental values using the THERMODATA software.

Very satisfactory agreement was obtained by using six parameters for the liquid phase (L), three parameters for the silver based terminal solid solution (fcc) and one parameter for the germanium based solid solution (dia) with a classical substitutional model for the three phases.

INTRODUCTION

The main advantages of the CALPHAD method have recently been extensively developed [2]. This evaluation is one of a list of systems which have been critically assessed in the framework of a S.G.T.E. (Scientific Group Thermodata Europ) project in order to produce data for selected systems and to supply specialized data banks. These data can be used for calculation of phase equilibria or thermodynamic properties in multicomponent systems containing both silver and germanium.

EXPERIMENTAL DATA

Phase diagram

A review of the literature concerning the Ag–Ge system has been published in ref. 3.

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The system is a simple eutectic, with the following phases: the liquid phase (L); the fcc terminal solid solution, with the Al structure isotypic with Cu, (fcc); the diamond-type terminal solid solution, with the A4 structure, (dia). There is no compound in the system.

The liquidus curve has been investigated by thermal analysis by Briggs et al. [4], Maucher [5], Predel and Bankstahl [6]. The eutectic has been given as $x^{L}_{Ge} = 0.26$, $T = 923$ K [4], $x^{L}_{Ge} = 0.241$, $T = 922$ K [5], and $x^{L}_{Ge} = 0.24$, $T = 923$ K [6].

The solid solubility of Ge in Ag has been investigated by thermal and microscopic analysis [4,5,8] and by lattice spacing studies of well-annealed alloys by Owen and Rowlands [7]. The eutectic temperature was accurately determined as $T = 924 \pm 0.5$ K.

The results of microscopic work of Hume-Rothery et al. [9] on alloys with $x_{Ge} = 0.10$–0.20 are in agreement with the results of Owen and Rowlands [7]. The maximum solubility of Ge in Ag is $x_{Ge} = 0.096$ at the eutectic temperature [7].

The solid solubility of Ag in Ge is very small. According to Bugai et al. [10], the solid solubility measured by radioactive tracer techniques shows a maximum $x_{Ag} = 2.3 \times 10^{-8}$ at $T = 1148$ K; the solubility then decreased to about $x_{Ag} = 4.6 \times 10^{-9}$ just below the melting point, and to $x_{Ag} = 2.3 \times 10^{-9}$ at $T = 973$ K.

Thermodynamic data

Liquid alloys

Castanet and coworkers [11,12] have determined the enthalpy of formation of liquid alloys in the silver–germanium system at $T = 1280$ K with a high temperature calorimeter.

The same function was measured by calorimetry at $T = 1248$ K by Wittig [13] (data have been reported in refs. 11 and 12). Batalin et al. [14] have calculated the enthalpies of mixing at $T = 1430$ K from measurements of the e.m.f. of Ag(liq) | AgI concentration cells in a NaI | (Ag–Ge)(liq) melt containing 0.07–0.87 atomic fraction of germanium.

Batalin et al. [14] have calculated the activity of Ag from e.m.f. measurements at $T = 1430$ K and the partial Gibbs energy of Ag has been deduced. Martin-Garin et al. [15] have measured the activities of Ag and Ge at $T = 1250$ K by multiple Knudsen cell mass spectrometry. Predel and Stein [16] used the e.m.f. method to measure the partial Gibbs energy of germanium of two liquid alloys at $T = 1000$ K.

Solid alloys

The chemical potential of germanium in the fcc solid solution has been calculated at $T = 1000$ K and for $x_{Ge} = 0.0085$–0.0585 from gas–solid equilibrium experiments by Jacob et al. [17].

THERMODYNAMIC MODELS

Liquid phase

The thermodynamic descriptions of pure Ag and Ge were taken from the evaluations of the S.G.T.E. group [18]

$$
\begin{aligned}
{}^{0}G^{\mathrm{L}}_{\mathrm{Ag}} - {}^{0}G^{\mathrm{fcc}}_{\mathrm{Ag}} &= 11025.293 - 8.890146T - (103219.98 \times 10^{-25})T^{7} \\
&\qquad 298.15 < T < 1235.08 \\
&= 11507.972 - 9.300494T - (1412186.248\mathrm{x}10^{23})T^{-9} \\
&\qquad 1235.08 < T < 3000.00 \\
{}^{0}G^{\mathrm{L}}_{\mathrm{Ge}} + {}^{0}G^{\mathrm{dia}}_{\mathrm{Ge}} &= 37141.633 - 30.684649T + (85676.079\mathrm{x}10^{-25})T^{7} \\
&\qquad 298.15 < T < 1211.5 \\
&= 36791.565 - 30.381247T + (861075.152\mathrm{x}10^{23})T^{-9} \\
&\qquad 1211.5 < T < 3200.00
\end{aligned}
$$

The liquid phase was treated by means of a classical substitutional model, and the Gibbs energy is represented by the expression

$$G^{\mathrm{L}}_{\mathrm{m}} = x_{\mathrm{Ag}}{}^{0}G^{\mathrm{L}}_{\mathrm{Ag}} + x_{\mathrm{Ge}}{}^{0}G^{\mathrm{L}}_{\mathrm{Ge}} + RT\left(x_{\mathrm{Ag}} \ln x_{\mathrm{Ag}} + x_{\mathrm{Ge}} \ln x_{\mathrm{Ge}}\right) + {}^{\mathrm{E}}G^{\mathrm{L}}_{\mathrm{m}} \qquad (1)$$

where x_{Ag} and x_{Ge} are the mole fractions of Ag and Ge respectively, and ${}^{0}G^{\mathrm{L}}_{\mathrm{Ag}}$ and ${}^{0}G^{\mathrm{L}}_{\mathrm{Ge}}$ are the Gibbs energies of pure liquid Ag and Ge.

In the present study, the excess Gibbs energy ${}^{\mathrm{E}}G^{\mathrm{L}}_{\mathrm{m}}$ was expressed by means of a second order Redlich-Kister expression

$${}^{\mathrm{E}}G^{\mathrm{L}}_{\mathrm{m}} = x_{\mathrm{Ag}}x_{\mathrm{Ge}}\left[{}^{0}L_{\mathrm{Ag,Ge}} + {}^{1}L_{\mathrm{Ag,Ge}}\left(x_{\mathrm{Ag}} - x_{\mathrm{Ge}}\right) + {}^{2}L_{\mathrm{Ag,Ge}}\left(x_{\mathrm{Ag}} - x_{\mathrm{Ge}}\right)^{2}\right] \qquad (2)$$

The ${}^{\nu}L_{\mathrm{Ag,Ge}}$ are interaction parameters and may vary with temperature. A linear dependency has been assumed, which means that enthalpy and excess entropy of mixing are temperature independent.

Solid solutions

Silver rich terminal solution

The fcc phase was also analysed by applying the substitutional model. The excess Gibbs energy was expressed by means of a first-order Redlich-Kister expression. ${}^{0}G^{\mathrm{fcc}}_{\mathrm{Ag}}$ and ${}^{0}G^{\mathrm{fcc}}_{\mathrm{Ge}}$ are the Gibbs energy of pure fcc Ag and Ge. Because the fcc Ge is not stable under usual conditions of temperature and pressure, we have used the following expression for the difference ${}^{0}G^{\mathrm{fcc}}_{\mathrm{Ge}} - {}^{0}G^{\mathrm{dia}}_{\mathrm{Ge}}$, usually known as a "lattice-stability": ${}^{0}G^{\mathrm{fcc}}_{\mathrm{Ge}} - {}^{0}G^{\mathrm{dia}}_{\mathrm{Ge}} = 36000.0 - 22.3T$, assessed by Saunders [19] and ${}^{0}G^{\mathrm{fcc}}_{\mathrm{Ag}} - {}^{0}G^{\mathrm{fcc}}_{\mathrm{Ag}} = 0$.

Diamond rich terminal solution

Because the solid solubility of Ag in Ge is very small, the excess Gibbs energy was expressed by means of a zero-order Redlich-Kister expression:

${}^0G_{\mathrm{Ag}}^{\mathrm{dia}}$ and ${}^0G_{\mathrm{Ge}}^{\mathrm{dia}}$ are the Gibbs energy of pure dia Ag and Ge. The following lattice-stability has been used for dia silver: ${}^0G_{\mathrm{Ag}}^{\mathrm{dia}} - {}^0G_{\mathrm{Ag}}^{\mathrm{fcc}} = 11296.8 + 20.853386T$ and ${}^0G_{\mathrm{Ge}}^{\mathrm{dia}} - {}^0G_{\mathrm{Ge}}^{\mathrm{dia}} = 0$.

The value of dia Ag has been obtained by combining a linear approximation for ${}^0G_{\mathrm{Ag}}^{\mathrm{L}} - {}^0G_{\mathrm{Ag}}^{\mathrm{fcc}} = 11296.8 - 9.146614T$ which yields a melting point for silver equal to $T^{\mathrm{f}} = 1235.08$ K |18|, and an assumption for the quantity [20] ${}^0G_{\mathrm{Ag}}^{\mathrm{L}} - {}^0G_{\mathrm{Ag}}^{\mathrm{dia}} = -30.0T$ which has been made and which takes the same value as that proposed by Kaufman [20] for C, Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo and W. This assumption is justified by non-existing values for this "lattice-stability".

RESULTS AND DISCUSSION

All the experimental information which has been previously discussed has been used by the Lukas program [1] in order to provide the set of parameters that yields the best agreement in the least-square sense between experimental quantities and calculated ones. Table 1 shows the optimized parameters of the excess Gibbs energy for various solution phases referred to the pure elements having the same structure as the corresponding phase.

The parameter of the dia solid solution has been estimated in order to reproduce the experimental solid solubility of Ag in Ge at $T = 1148$ K [10]. The phase diagram has been calculated and compared with the experimental one in Fig. 1.

Table 2 shows experimental and calculated temperature and composition for the eutectic reaction. The agreement is quite satisfactory. The calculated temperature $T = 923.4$ K and composition $x_{\mathrm{Ge}}^{\mathrm{L}} = 0.249$ are very near the mean experimental values $T = 923$ K, $x_{\mathrm{Ge}}^{\mathrm{L}} = 0.247$. The maximum calculated solid solubility of Ge in fcc is $x_{\mathrm{Ge}}^{\mathrm{fcc}} = 0.096$ which is in complete agreement

TABLE 1

Excess Gibbs energy ${}^{\mathrm{E}}G$ coefficients for the solution phases of the Ag–Ge system

Phase	ν	${}^{\nu}a_{\mathrm{Ag,Ge}}$ (J)	${}^{\nu}b_{\mathrm{Ag,Ge}}$ (J K^{-1})
liquid	0	8708.55	−7.228525
	1	−14467.9	5.10544
	2	−7955.55	2.875185
fcc	0	3066.7	11.05926
	1	−16428.5	0
dia	0	119000.0	0

${}^{\mathrm{E}}G = x_{\mathrm{ag}} x_{\mathrm{Ge}} \sum_{\nu=0}^{n} (x_{\mathrm{Ag}} - x_{\mathrm{Ge}})^{\nu} L_{\mathrm{Ag,Ge}}(T)$

${}^{\nu}L_{\mathrm{Ag,Ge}} = {}^{\nu}a_{\mathrm{Ag,Ge}} + {}^{\nu}b_{\mathrm{Ag,Ge}}(T)$ ($\nu = 0,1,2$) (J).

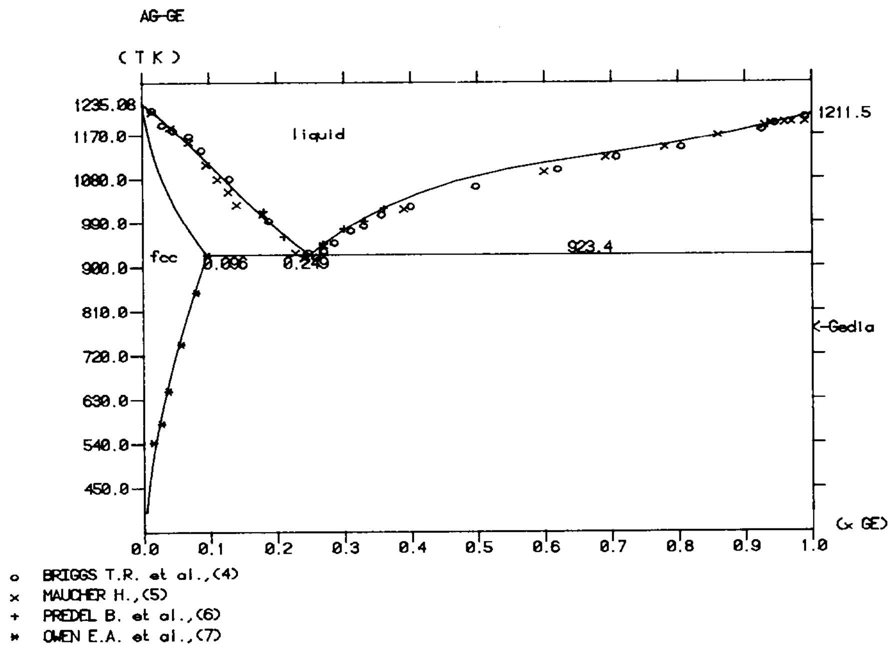

Fig. 1. Comparison between the calculated Ag–Ge phase diagram and selected experimental data.

with the experimental results of ref. 6, which can be considered as the more accurate work. The calculated solid solubility of Ag in Ge (dia) is $x_{Ag}^{dia} = 2.3 \times 10^{-8}$ at $T = 1148$ K (adjusted experimental value) and $x_{Ag}^{dia} = 7.6\ 10^{-9}$ at $T = 973$ K which must be compared with the experimental value $x_{Ag}^{dia} = 2.3 \times 10^{-9}$.

The enthalpy of mixing of the liquid phase has been calculated and compared with selected experimental data from calorimetry measurements (Fig. 2).

TABLE 2

Eutectic reaction in the Ag–Ge system

Transformation	Calculated		Experimental		Reference
	T (K)	$x = x_{Ge}$	T (K)	$x = x_{Ge}$	
L ⇆ fcc + dia	923.4	$x^L = 0.249$ $x^{fcc} = 0.096$	923	$x^L = 0.26$ $x^{fcc} \sim 0.065$	3
			922	$x^L = 0.241$ $x^{fcc} \sim 0.079$	4
			923	$x^L = 0.24$	5
			924	$x^{fcc} = 0.096$	6
			923	$x^{fcc} = 0.081$	7

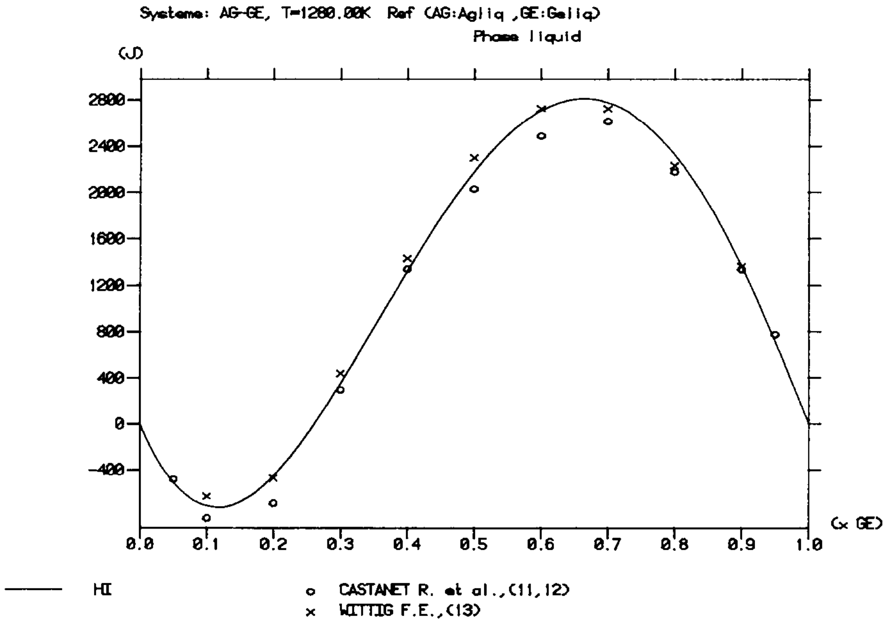

Fig. 2. Comparison between the calculated enthalpy of mixing of Ag–Ge liquid alloys (temperature-independent) and selected experimental data.

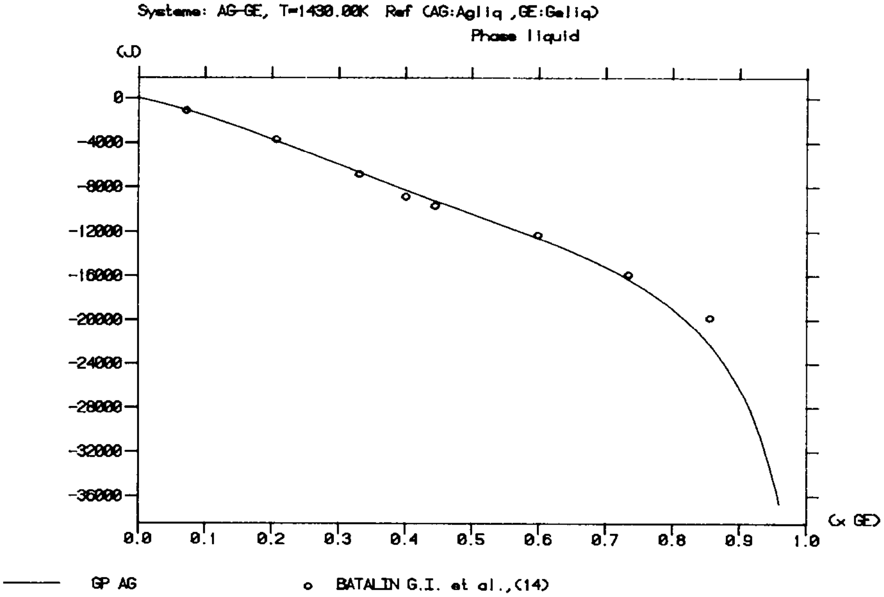

Fig. 3. Comparison between the calculated partial Gibbs energy of Ag in the liquid phase at $T = 1430$ K and the experimental data of ref. 14.

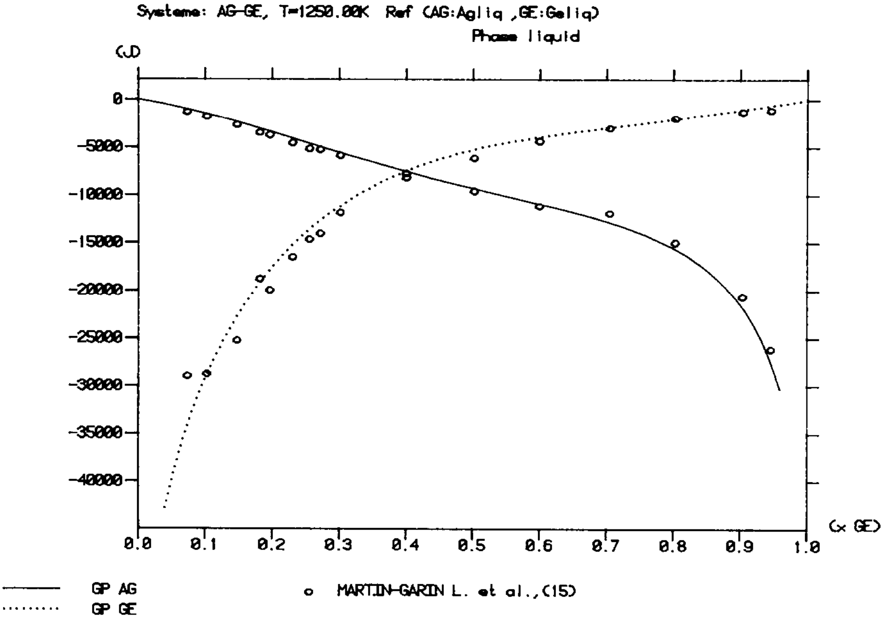

Fig. 4. Comparison between the calculated partial Gibbs energies of Ag and Ge in the liquid phase at $T = 1250$ K and the experimental data of ref. 15.

The agreement is excellent. The calculated partial Gibbs energy of silver has been compared with the experimental data of Batalin et al. [14] at $T = 1430$ K (Fig. 3), and the calculated partial Gibbs energy of silver and germanium have been calculated at $T = 1250$ K, and compared with the experimental data of Martin-Garin et al. [15] (Fig. 4). The agreement is quite satisfactory.

However, the two measurements of Predel and Stein [16] at $T = 1000$ K in the liquid do not agree very well with the phase diagram and have been discarded. The calculated partial Gibbs energy of germanium in the fcc solid solution at $T = 1000$ K is compared with the experimental data of Jacob et

TABLE 3

Comparison between the calculated partial Gibbs energy of Ge in the fcc phase at $T = 1000$ K and the experimental data of ref. 17

Composition of fcc phase x_{Ge}^{fcc}	$\Delta\bar{G}_{Ge}$ (after ref. 17)	a_{Ge} (after ref. 17)	$\Delta\bar{G}_{Ge}$ (calculated)	a_{Ge} (calculated)
0.0085	−33568	0.0176	−28214	0.033
0.0265	−23698	0.0578	−17210	0.126
0.0385	−19753	0.0929	−13310	0.202
0.0470	−17468	0.1223	−11008	0.266
0.0585	−14811	0.1684	−8635	0.354

al. [17] in Table 3. Calculated values are appreciably higher than the experimental data and it seems difficult to reconcile them.

SUMMARY

Experimental data on the Ag–Ge system have been analysed in terms of thermodynamic models for the different solution phases. A set of new coefficients has been obtained which gives good agreement between the calculated phase diagram and the experimental data, and also for thermodynamic quantities of the liquid phase. The calculated partial Gibbs energy of germanium in the fcc solid solution must be appreciably higher than the experimental one in order to be consistent with the phase diagram. These parameters can be stored in specialized data bases in order to tabulate thermodynamic functions or calculate phase equilibria in multicomponent systems containing both silver and germanium.

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