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A THERMODYNAMIC EVALUATION OF THE Au–Ge AND Au–Si SYSTEMS

P.-Y. CHEVALIER

Thermodata, Domaine Universitaire de Grenoble, BP 66, 38402 Saint Martin d'Hères Cédex (France)

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ABSTRACT

The different phases of the Au–Ge and Au–Si systems were analysed in terms of thermodynamic models based on selected values for the pure elements.

A set of self-consistent parameters was obtained using the optimization procedure developed by H.L. Lukas, E.Th. Henig and B. Zimmermann (Calphad, 1 (1977) 225–236).

The phase diagrams and the characteristic thermodynamic functions were calculated and compared with the corresponding experimental values.

INTRODUCTION

This work is part of a project performed by the Scientific Group Thermodata Europe (SGTE) to produce optimized data for condensed multicomponent systems. A very important effort has been made to obtain self-consistent data so that they can be used for complex thermodynamic calculations. The systems Ag–Ge, Ag–Si, Ag–Sn, Au–Bi, Au–Sn, Bi–Ge and Bi–In, have already been studied [1].

THE Au–Ge SYSTEM

Short presentation of the different phases

The assessed Au–Ge phase diagram, reported by Okamoto and Massalski [2], is a simple eutectic. The different phases are listed below with the symbols used.

(1) Liquid phase (L).

(2) Terminal rich gold solid solution with a face centred cubic (A1) prototype structure; the maximum solid solubility of germanium in gold is 3 at.% at the eutectic temperature (f.c.c.).

(3) Pure germanium with the diamond (A4) structure; the equilibrium solid solubility of gold in germanium (including both substitutional and interstitial gold atoms) is not well determined (Gedia).

Experimental information

Phase diagram

The phase equilibria of the Au–Ge system have been determined experimentally using conventional techniques by Jaffee et al. [3] (liquidus, thermal analysis; solidus, solvus, lattice parameter), Predel and Bankstahl [4], Legendre and Souleau [5] (liquidus, thermal analysis), Owen and Roberts [6] (solidus, solvus, lattice parameter), Muller and Merl [7] (solvus, electrical resistivity) and Evans and Prince [8] (eutectic, thermal analysis).

The eutectic point has been located at $x_{Ge}^{(L)} = 0.24$, $T = 632$ K [9], $x_{Ge}^{(L)} = 0.27$, $T = 629$ K [3], $T = 636$ K [6], $x_{Ge}^{(L)} = 0.28$, $T = 630$ K [4], $x_{Ge}^{(L)} = 0.27$, $T = 637$ K [5] and $x_{Ge}^{(L)} = 0.28$, $T = 635$ K [8].

Thermodynamic properties

A literature survey on the thermodynamic properties of the Au–Ge and Au–Si systems was carried out using the "Thermdoc bibliographic data base" integrated in the THERMODATA system [9].

Liquid alloys. The enthalpy of mixing of the liquid phase has been measured by Predel and Stein [10] (tin solution calorimetry; $T = 1423$ K, $x_{Ge} = 0.1$–0.9), Predel and Schallner [11] (e.m.f. of a galvanic concentration cell; $T = 1000$ K, $x_{Ge} = 0.2$–0.6), Hager et al. [12] (mass spectrometry; $T = 1673$ K, $x_{Ge} = 0.10$–0.90), Itagaki and Yazawa [13] (adiabatic calorimetry; $T = 1373$ K, $x_{Ge} = 0.10$–0.90), Schluckebier and Predel [14] (calorimetry; $T = 635$ K, $x_{Ge} = 0.28$) and Hassam et al. [15] (calorimetry, $T = 1373$ K, $x_{Ge} = 0.085$–0.924).

The partial Gibbs free energies of gold and germanium in the liquid phase have been determined by Predel and Schallner [11] (e.m.f. of a galvanic concentration cell; $T = 1000$ K, $x_{Ge} = 0.20$–0.60) and Hager et al. [12] (mass spectrometry; $T = 1673$ K, $x_{Ge} = 0.1$–0.9).

f.c.c. solid solutions. The partial Gibbs free energy of germanium in the f.c.c. solid solution has been measured by Jacob et al. [16] (X-ray fluorescence technique; $T = 1000$ K, $x_{Ge} = 0.0068$–0.0142) and the partial Gibbs free energies of both gold and germanium have been measured by Predel and Schallner [11] (e.m.f.; $T = 1000$ K, $x_{Ge} = 0.01$–0.02).

Evaluation method

The Gibbs energies of the different solution phases were described using a simple substitutional model. The excess Gibbs energy was determined using a Redlich–Kister polynomial equation of the form

$$\Delta^{E}G = x_{Au}x_{Ge}\sum_{\nu=0}^{n}(x_{Au}-x_{Ge})L^{(\nu)}_{Au,Ge}(T) \qquad (1)$$

where

$$L^{(\nu)}_{Au,Ge}(T) = a^{(\nu)}_{Au,Ge} + b^{(\nu)}_{Au,Ge}T \qquad (2)$$

The coefficients $L^{(\nu)}_{Au,Ge}$ are linear functions of the temperature, i.e. $a^{(\nu)}_{Au,Ge}$ and $b^{(\nu)}_{Au,Ge}$ correspond to the temperature-independent values of the enthalpy and the excess entropy of mixing. This assumption is justified because no sensible variation of the enthalpy of mixing has been determined experimentally.

The values used for the lattice stabilities of the pure elements were taken from the SGTE assessment [17] for the stable solid and liquid phases and from the assessment of Saunders [18] for the metastable phases (required to express the excess properties of mixing of the f.c.c. solid solution phase).

The following values were used from refs. 17 and 18

$$\begin{aligned}
{}^{0}G^{L}_{Au} - {}^{0}G^{f.c.c.}_{Au} &= 12\,589.413 - 9.41674T + 8.13956\times10^{-22}T^{7} \\
&\qquad 298.15 < T < 1337.58 \\
&= 12\,522.9 - 9.36453T + 3.98771\times10^{28}T^{-9} \\
&\qquad 1337.58 < T < 3200.0 \\
{}^{0}G^{L}_{Ge} - {}^{0}G^{dia}_{Ge} &= 37\,141.633 - 30.684649T + 85676.079\times10^{-25}T^{7} \\
&\qquad 298.15 < T < 1211.50 \\
&= 36\,791.565 - 30.381247T + 861075.152\times10^{23}T^{-9} \\
&\qquad 1211.50 < T < 3200.0 \\
{}^{0}G^{f.c.c.}_{Ge} - {}^{0}G^{dia}_{Ge} &= 36\,000.0 - 22.3T
\end{aligned}$$

The different parameters of the various solution phases ϕ, $a^{(\nu)}_{Au,Ge}(\phi)$ and $b^{(\nu)}_{Au,Ge}(\phi)$, were optimized using a program developed by Lukas et al. [19] which takes into account all the available experimental information and accuracy, after having discarded some values either for experimental reasons or because they have been measured too indirectly.

Results and discussion

Table 1 shows the optimized parameters of the excess Gibbs energies for the various solution phases referred to the pure elements with the same structures as the corresponding phase.

The phase diagram was calculated using the optimized coefficients and is compared with the experimental phase diagram in Fig. 1.

The eutectic reaction was calculated to be at $T = 634.13$ K and $x^{f.c.c.}_{Ge} = 0.031$, which is in excellent agreement with the experimental data of ref. 8. A

TABLE 1

Excess Gibbs energy $\Delta^{E}G$ coefficients for the liquid and f.c.c. phases ($\Delta^{E}G = x_{Au}x_{Ge}\sum_{\nu=0}^{n}(x_{Au} - x_{Ge})L^{(\nu)}_{Au,Ge}(T)$ (J (g-at)$^{-1}$); $L^{(\nu)}_{Au,Ge}(T) = a^{(\nu)}_{Au,Ge} + b^{(\nu)}_{Au,Ge}T$ ($\nu = 0, 1, 2, 3$) (J))

Phase	ν	$a_{Au,Ge}$ (J)	$b_{Au,Ge}$ (J K^{-1})
Liquid	0	−18059.75	−13.08541
	1	−6131.60	−9.10177
	2	−4733.85	−3.25908
	3	−8120.50	−5.82538
F.c.c.	0	14369.40	−28.58012

satisfactory general agreement is observed, except for the liquidus in the gold-rich region. Even experimentally, the liquidus boundaries are not well established, resulting in disagreements of as much as 50 °C.

Figure 2 shows the good agreement between the calculated enthalpy of mixing of the liquid without variation in temperature and selected experimental data of refs. 10, 11 and 15.

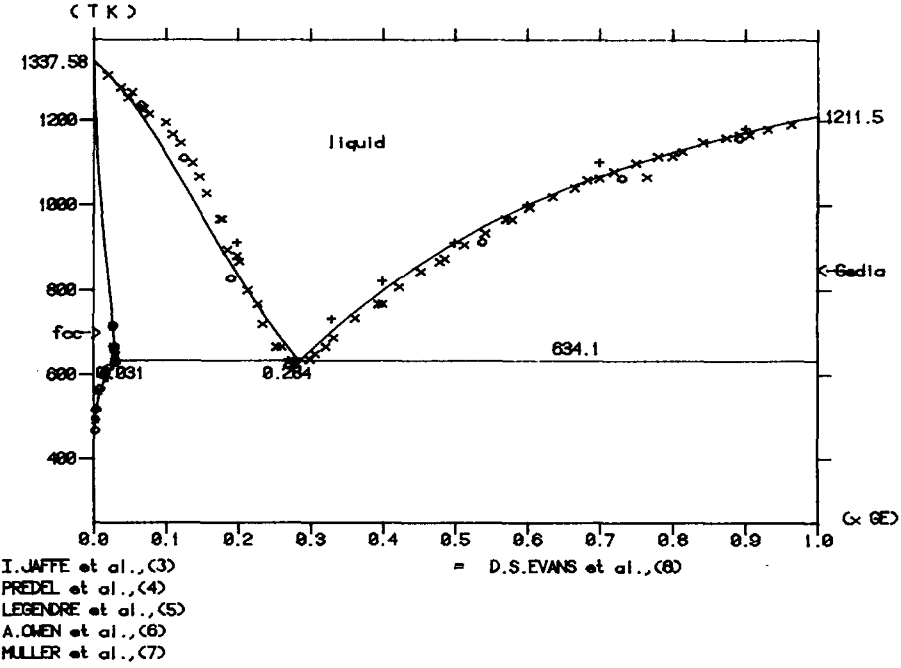

Fig. 1. Comparison between the calculated Au–Ge phase diagram and selected experimental data.

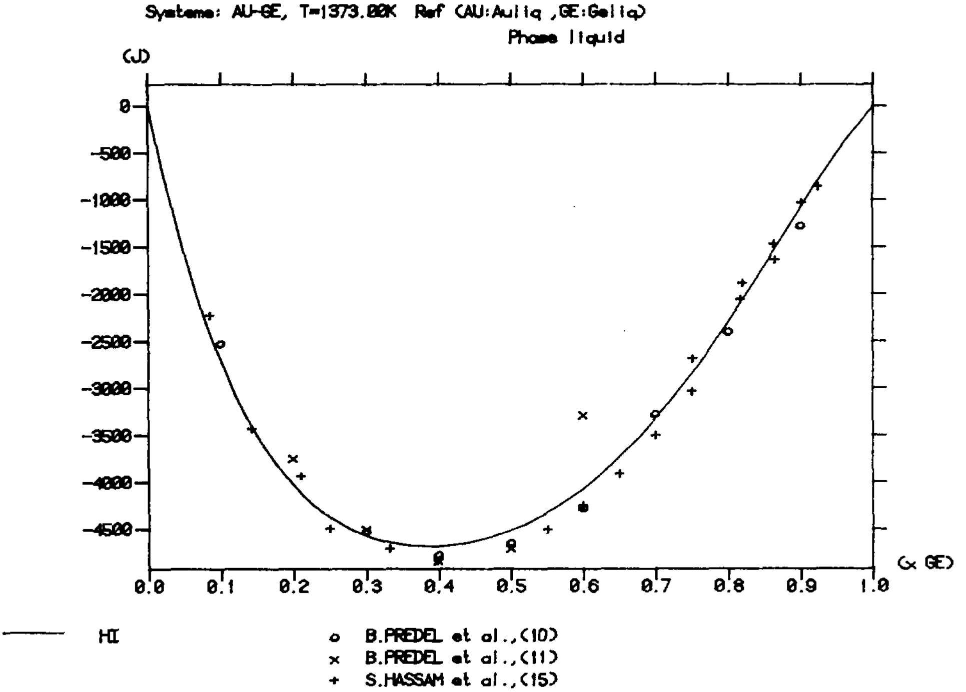

Fig. 2. Comparison between the calculated enthalpy of mixing of the liquid phase and selected data of refs. 10, 11 and 15.

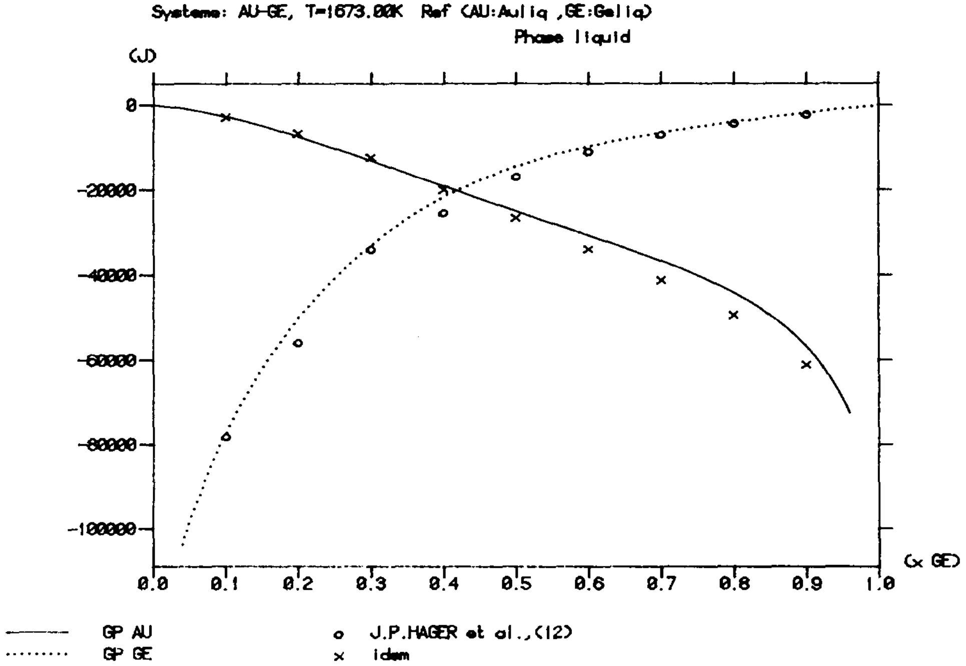

Fig. 3. Comparison between the calculated partial Gibbs free energies of the liquid phases and selected data of ref. 12.

In Fig. 3, the partial Gibbs free energies of gold and germanium in the liquid phase calculated at $T = 1673$ K are compared with selected data of Hager et al. [12]. The agreement is satisfactory.

THE Au-Si SYSTEM

Short presentation of the different phases

The assessed phase diagram, reported by Okamoto and Massalski [20], is a simple eutectic.

The different phases are listed below, with the symbols used.

(1) Liquid phase (L).

(2) Pure gold with face-centred cubic (A1) prototype structure; the solid solubility of silicon in gold is not well determined (Auf.c.c.).

(3) Terminal rich silicon solid solution with the diamond (A4) structure. The solid solubility of gold in silicon has been reported in ref. 20 as follows: $x_{Au} = 0.075 \times 10^{-6}$ at $T = 1173$K; $x_{Au} = 0.25 \times 10^{-6}$ at $T = 1273$ K; $x_{Au} = 0.625 \times 10^{-6}$ at $T = 1373$ K; $x_{Au} = 1.2 \times 10^{-6}$ at $T = 1473$ K; $x_{Au} = 1.8 \times 10^{-6}$ at $T = 1573$ K; $x_{Au} = 2 \times 10^{-6}$ at $T = 1598$ K (maximum).

Experimental information

Phase diagram

The liquidus of the Au-Si system has been determined experimentally using conventional techniques by Heath [21] (chemical analysis of gravity-segregated eutectic liquid), Gerlach and Goel [22] (thermal analysis), Predel and Bankstahl [23] (thermal analysis) and Anantatmula et al. [24] (equilibration of specimens at temperature above and below the liquidus line followed by quenching into iced brine).

The eutectic point has been located at $x_{Si}^{(L)} = 0.17$, $T = 643$ K [22], $x_{Si}^{(L)} = 0.186, T = 643$ K [21], $x_{Si}^{(L)} = 0.195$, $T = 618$ K [23], $x_{Si}^{(L)} = 0.19$, $T = 636$ K [24] and $x_{Si}^{(L)} = 0.186$, $T = 636$ K [20].

Thermodynamic properties

The enthalpy of mixing of the liquid phase has been measured by calorimetry by Hassam et al. [25] at $T = 1487$ K and $x_{Si} = 0.055$—0.718.

The activities of gold and silicon in the liquid phase have been determined by Knudsen-cell mass spectrometry at $T = 1690$ K and $x_{Si} = 0$–1 by Bergman et al. [26].

Evaluation method, results and discussion

The same method was used as for the Au–Ge system.

The following values were used for silicon from refs. 17 and 18

$$\begin{aligned} {}^0G^{\mathrm{L}}_{\mathrm{Si}} - {}^0G^{\mathrm{dia}}_{\mathrm{Si}} &= 50\,696.360 - 30.099439T + 20\,930.656 \times 10^{-25}T^{7} \\ &\qquad 298.15 < T < 1687.00 \\ &= 49\,848.165 - 29.559068T + 42\,036\,924.397 \times 10^{23}T^{-9} \\ &\qquad 1687.00 < T < 3600.00 \qquad \text{(ref. 17)} \end{aligned}$$

$${}^0G^{\mathrm{f.c.c.}}_{\mathrm{Si}} - {}^0G^{\mathrm{dia}}_{\mathrm{Si}} = 51\,000 - 21.8T \qquad \text{(ref. 18)}$$

$$\begin{aligned} {}^0G^{\mathrm{dia}}_{\mathrm{Au}} - {}^0G^{\mathrm{f.c.c.}}_{\mathrm{Au}} &= 30.0T + 12\,552.0 - 9.38411T \\ &= 12\,552.0 + 20.61589T \end{aligned}$$

The value of dia Au was obtained by combining a linear approximation of ${}^0G^{\mathrm{L}}_{\mathrm{Au}} - {}^0G^{\mathrm{f.c.c.}}_{\mathrm{Au}} = 12\,552.0 - 9.38411\ T$ (which yields a melting point of gold equal to $T^{\mathrm{f}} = 1337.58$ K [17]) and an assumption for the quantity ${}^0G^{\mathrm{L}}_{\mathrm{Au}} - {}^0G^{\mathrm{dia}}_{\mathrm{Au}} = -30.0$ T (which consists of taking the same value as Kaufman [27] for aluminium and other elements).

The optimized parameters of the excess Gibbs energies of the liquid and f.c.c. phases are reported in Table 2.

The calculated and experimental phase diagrams are compared in Fig. 4.

The eutectic reaction was calculated to be at $T = 633$ K and $x^{(\mathrm{L})}_{\mathrm{Si}} = 0.197$, which is in good agreement with the mean experimental value ($T = 632$ K, $x^{(\mathrm{L})}_{\mathrm{Si}} = 0.19$) of refs. 21, 23 and 24.

The parameter of the dia solid solution ($L^{(0)}_{\mathrm{Au,Si}}$ or λ) was adjusted to reproduce a maximum solid solubility of gold in silicon of 2×10^{-6} at $T = 1598$ K.

The solubility curve of gold in silicon was calculated as follows: $x_{\mathrm{Au}} = 2.0 \times 10^{-6}$ at $T = 1598$ K; $x_{\mathrm{Au}} = 2.7 \times 10^{-6}$ at $T = 1573$ K; $x_{\mathrm{Au}} = 4.3 \times 10^{-6}$ at $T = 1473$ K; $x_{\mathrm{Au}} = 4.0 \times 10^{-6}$ at $T = 1373$ K; $x_{\mathrm{Au}} = 3.5 \times 10^{-6}$ at $T = 1273$ K; $x_{\mathrm{Au}} = 2.6 \times 10^{-6}$ at $T = 1173$ K ($\lambda = 70\,000$) and $x_{\mathrm{Au}} = 1.0 \times 10^{-6}$ at $T = 1598$ K; $x_{\mathrm{Au}} = 1.90 \times 10^{-6}$ at $T = 1473$ K; $x_{\mathrm{Au}} = 1.67 \times 10^{-6}$ at

TABLE 2

Excess Gibbs energy $\Delta^{\mathrm{E}}G$ coefficients for the liquid phase ($\Delta^{\mathrm{E}}G = x_{\mathrm{Au}}x_{\mathrm{Si}}\Sigma^{n}_{\nu=0}(x_{\mathrm{Au}} - x_{\mathrm{Si}})L^{(\nu)}_{\mathrm{Au,Si}}(T)$ (J (g-at)$^{-1}$); $L^{(\nu)}_{\mathrm{Au,Si}}(T) = a^{(\nu)}_{\mathrm{Au,Si}} + b^{(\nu)}_{\mathrm{Au,Si}}T$ ($\nu = 0, 1, 2, 3$) (J))

Phase	ν	$a_{\mathrm{Au,Si}}$ (J)	$b_{\mathrm{Au,Si}}$ (J K^{-1})
Liquid	0	−23863.9	−16.23438
	1	−20529.55	−6.03958
	2	−8170.50	−4.27320
	3	−33138.25	26.56665
Dia	0	70000	0

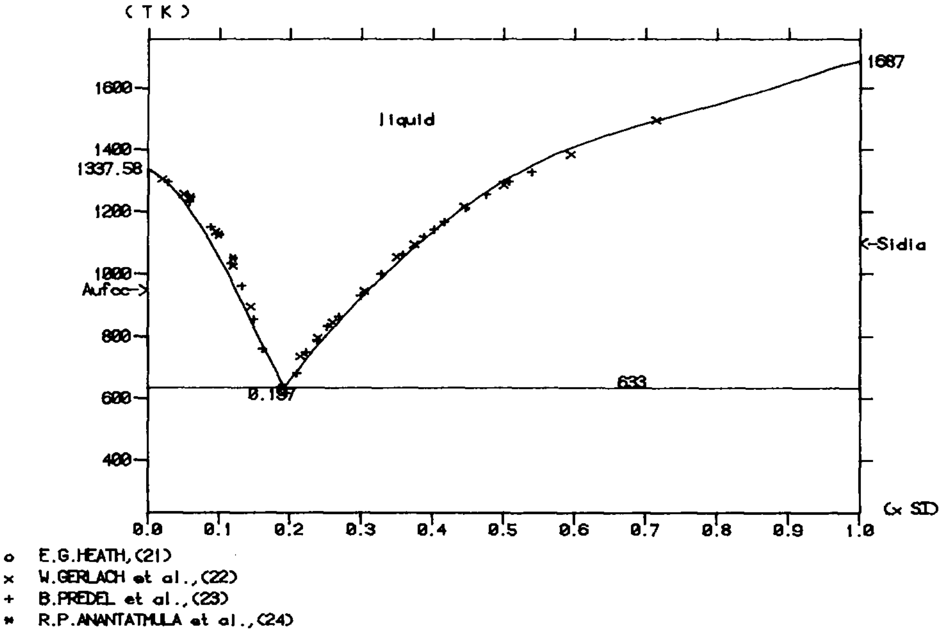

Fig. 4. Comparison between the Au–Si phase diagram and selected experimental data.

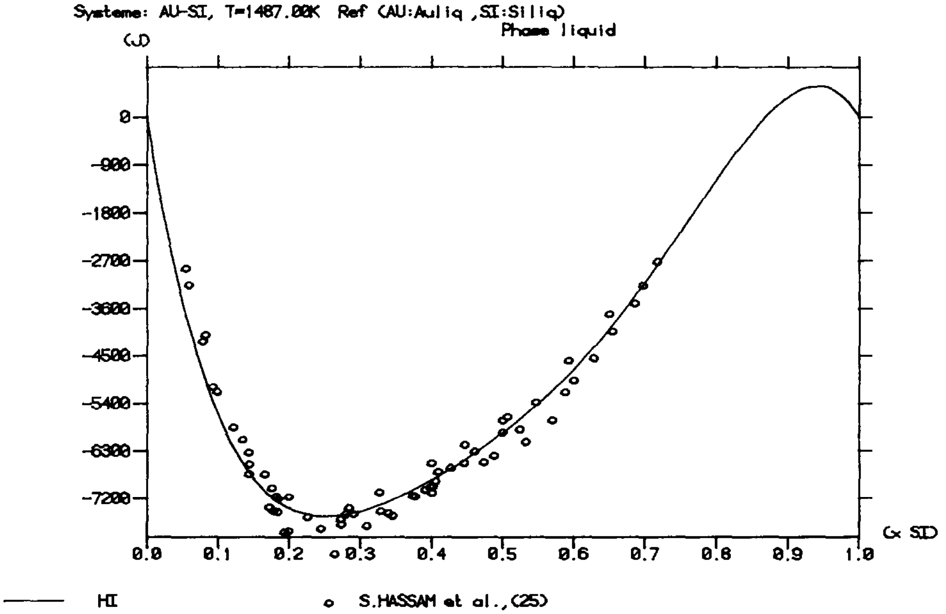

Fig. 5. Comparison between the calculated enthalpy of mixing of the liquid phase and selected data of ref. 25.

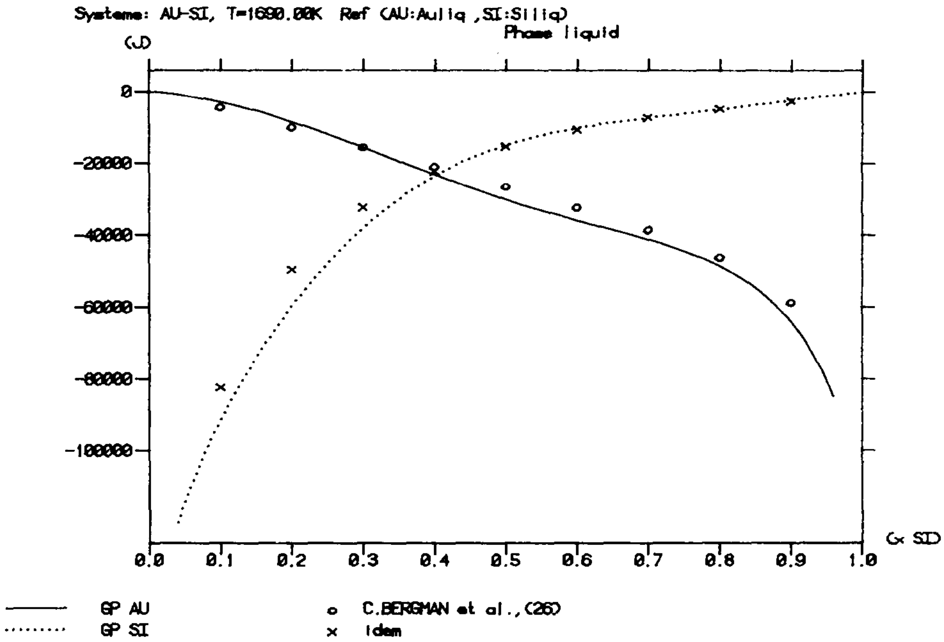

Fig. 6. Comparison between the calculated partial Gibbs free energies of the liquid phases and selected data of ref. 26.

$T = 1373$ K; $x_{\mathrm{Au}} = 1.33 \times 10^{-6}$ at $T = 1273$ K; $x_{\mathrm{Au}} = 0.96 \times 10^{-6}$ at $T = 1173$ K; $x_{\mathrm{Au}} = 1.27 \times 10^{-6}$ at $T = 1573$ K ($\lambda = 80000$).

Figure 5 shows the comparison of the calculated enthalpy of mixing of the liquid phase with selected data of ref. 25.

In Fig. 6, the partial Gibbs free energies of gold and silicon in the liquid phase calculated at $T = 1690$ K are compared with the data of ref. 26. The agreement is very good.

SUMMARY

A set of self-consistent parameters was optimized for the liquid and f.c.c. phases in the Au–Ge and Au–Si systems.

Comparison with the available experimental information is satisfactory, but the liquidus in the gold-rich region of the Au–Ge system requires more precise experimental work.

These parameters can be used for thermodynamic calculations in multicomponent systems.

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