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THERMODYNAMIC EVALUTION OF THE Ag–Si SYSTEM

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ABSTRACT

The available experimental information concerning thermodynamic properties and phase equilibria data has been compiled to assess new self-consistent parameters of thermodynamic models for all phases in the Ag–Si system. These coefficients have been optimized by using a program developed by Lukas et al., Calphad, 1 (1977) 225. Phase diagrams and characteristic thermodynamic functions have been calculated and compared to the experimental values using the THERMODATA software. A very satisfactory agreement has been obtained by using five optimized coefficients with a simple substitution model for liquid and solid solution phases.

INTRODUCTION

The main advantages of the thermodynamic approach are now well known. This evaluation is a part of an assessment of several systems which has been made under the auspices of an SGTE (Scientific Group Thermodata Europ) project in order to produce data for selected systems and to supply specialized data banks.

SHORT PRESENTATION OF THE DIFFERENT PHASES

According to the phase diagram reported by Predel and Bankstahl [2], there is no compound in the Ag–Si system. The various phases, with the symbols currently used are listed below.

Solution phases

(1) Liquid phase (L)

(2) Terminal rich silver solid solution, with a face-centered cubic (A1) prototype structure; there is no reported solid solubility of Si in Ag: (Ag f.c.c.).

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(3) Terminal rich silicon solid solution, with a f.c.c. (A4) structure isotypic with diamond. The solid solubility of Ag in Si is a maximum at $T = 1623$ K, $X_{Ag} = 0.0004$, and equal to $X_{Ag} = 0.000013$ at $T = 1473$ K after Boltaks and Shih-Yin [3], or $X_{Ag} = 0.000002$ at $T = 1473$ K after Collins and Carlson [4]: (dia).

EXPERIMENTAL INFORMATION

Phase diagram

The phase diagram of the Ag–Si system is a simple eutectic. The liquidus has been studied experimentally using thermal analysis by Arrivaut [5], Hager [6], and Predel and Bankstahl [2].

Other experimental results for the temperature and composition of the eutectic are reported in Table 2 and by Hajicek [7], Gottardi [8] from thermal and metallographic studies. Determinations of the lattice constants indicate that the mutual solid solubility is practically nil [9], when it has been more accurately determined [3,4].

Thermodynamic properties

Liquid alloys

The enthalpy of mixing of liquid alloys has been determined by calorimetry measurements at $T = 1423$ K and $T = 1550$ K over a large concentration range by Hassam et al. [10]. Their results are very different from those of Robinson and Tarby [11] who used partial presssure measurements of silver in the temperature range 1723–1873 K. However, they are in good agreement with the results of Sakao and Elliott [12], who used e.m.f. measurements in the range 1373–1598 K. Moreover, taking account the accuracy of their calorimetric experiments, Hassam et al. [10] did not observe any temperature dependence for the enthalpy of mixing.

The activity of silicon has been measured by Sakao and Elliott [12] using the e.m.f. method in the range 1373–1598 K, and for $X_{Si} = 0.0159$–0.2874. Partial molar properties of Si and Ag relative to the liquid have been calculated at $T = 1473$ K.

Robinson and Tarby [11] have used the vapor transportation method to determine the partial pressure of silver above molten Ag–Si solutions in the temperature range 1723–1873 K, and have deduced values for the activity of silver with the use of previously determined values for the partial pressure of liquid pure silver.

By equilibrating molten silver and silicon nitride at $T = 1673$ K in nitrogen + hydrogen gas mixtures and from the solubility data, Turkdogan and Grieveson [13] have determined the activity coefficient of silicon. Using this value, and that available from the silicon carbide solubility measurements, together with those derived from the phase equilibrium diagram, the activities of silver and silicon were estimated over the entire composition range.

Partial thermodynamic properties of Ag–Si alloys have been determined by Vermandé et al. [14] who used the partial pressure of silver measurements in the temperature range 1240–1700 K. The same authors have tabulated partial Gibbs energies of silver and silicon at 1460 K in the composition range $X_{\mathrm{Ag}} = 0.685-1$. These authors have observed a strong disagreement between their values and those previously determined by Tupkary [15] and O'Keefe [16]. Conversely, a very satisfactory agreement has been observed between their data and those compiled by Hultgren et al. [17].

METHOD OF EVALUATION

The Gibbs energy of the different solution phases has been described by using a simple substitutional model. The excess Gibbs energy has been determined by a Redlich–Kister polynomial equation of the form:

$$\Delta^{\mathrm{E}}G = X_{\mathrm{Ag}}X_{\mathrm{Si}} \sum_{\nu=0}^{n} (X_{\mathrm{Ag}} - X_{\mathrm{Si}}) L^{(\nu)}_{\mathrm{Ag,Si}}(T) \tag{1}$$

where

$$L^{(\nu)}_{\mathrm{Ag,Si}}(T) = a^{(\nu)}_{\mathrm{Ag,Si}} + b^{(\nu)}_{\mathrm{Ag,Si}}{*}T$$

and the coefficients $L^{(\nu)}_{\mathrm{Ag,Si}}(T)$ are linear functions of the temperature, i.e. $a^{(\nu)}_{\mathrm{Ag,Si}}$ and $b^{(\nu)}_{\mathrm{Ag,Si}}$ correspond to the independent values of the enthalpy and the excess entropy of mixing.

The values used for the lattice stabilities of the pure elements come from the SGTE assessment [18] for the stable solid and liquid phases and from the assessment of Saunders [19] for the metastable phases (required to express the excess properties of mixing of the f.c.c. and dia phases).

The following values have been used:

$$\begin{aligned}
{}^{\circ}G^{\mathrm{L}}_{\mathrm{Ag}} - {}^{\circ}G^{\mathrm{f.c.c.}}_{\mathrm{Ag}} &= 11025.293 - 8.890146T - (103219.98 \times 10^{-25})T^{7} \\
&\quad 298.15 < T < 1235.08 \\
&= 11507.972 - 9.300494T - (1412186.248 \times 10^{23})T^{-9} \qquad [18] \\
&\quad 1235.08 < T < 3000.00 \\
{}^{\circ}G^{\mathrm{L}}_{\mathrm{Si}} - {}^{\circ}G^{\mathrm{dia}}_{\mathrm{Si}} &= 50696.360 - 30.099439T + (20930.656 \times 10^{-25})T^{7} \\
&\quad 298.15 < T < 1687.00 \\
&= 49828.165 - 29.559068\mathrm{T} + (42036924.397 \times 10^{23})T^{-9} \qquad [18] \\
&\quad 1687.00 < T < 3600.00
\end{aligned}$$

$$^{\circ}G_{\mathrm{Ag}}^{\mathrm{dia}} - {}^{\circ}G_{\mathrm{Ag}}^{\mathrm{f.c.c.}} = 11296.8 - 9.1466T + 30.0T = 11296.8 + 20.8534T \qquad [18,20]$$

$$^{\circ}G_{\mathrm{Si}}^{\mathrm{f.c.c.}} - {}^{\circ}G_{\mathrm{Si}}^{\mathrm{dia}} = 51000 - 21.8T \qquad [19]$$

The value for the metastable dia silver has been approximated by taking a linear approximation for the difference of Gibbs energy between the liquid and f.c.c. phases after SGTE values [18] and a value of $-30.0\ T$ for the difference between the liquid and dia phase similar to the Kaufman's value for other elements like C, Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo and W [20]. This has been assumed because no value was available for this lattice stability.

The different parameters of the liquid and diamond phases were optimized by using a program developed by Lukas et al. [1] which takes into account all the available experimental information and accuracy, after having discarded, by a primary criticism, some values either for experimental reasons or because they were too indirectly measured.

RESULTS AND DISCUSSION

Table 1 shows the optimized parameters of the excess Gibbs energy for the liquid, diamond and f.c.c. phases referred to the pure elements having the same structure as the corresponding phase.

In the optimization, the parameters for the enthalpy of mixing of the liquid phase were fixed to the values given in Table 1, which were deduced from the equation of Hassam et al. [10]:

$$\Delta H_{\mathrm{M}}(\mathrm{Ag,Si})_{\mathrm{liq}} = X_{\mathrm{Si}}(1 - X_{\mathrm{Si}})(A + BX_{\mathrm{Si}})$$

where $A = -5014.4$ J mol^{-1} and $B = +32132.8$ J mol^{-1}. This smoothed

TABLE 1

Excess Gibbs energy for the liquid, diamond and f.c.c. phases of the Ag–Si system

$$\Delta^{\mathrm{E}}G = X_{\mathrm{Ag}}X_{\mathrm{Si}}\sum_{\nu=0}^{n}(X_{\mathrm{Ag}} - X_{\mathrm{Si}})L_{\mathrm{Ag,Si}}^{(\nu)}(T)$$

$$L_{\mathrm{Ag,Si}}^{(\nu)}(T) = a_{\mathrm{Ag,Si}}^{(\nu)} + b_{\mathrm{Ag,Si}}^{(\nu)} * T(\nu = 0, 1) \qquad (J)$$

Phase	ν	$a_{\mathrm{Ag,Si}}^{(\nu)}(T)$	$b_{\mathrm{Ag,Si}}^{(\nu)}$ (J K^{-1})
Liquid	0	11052.0 (fixed) (10)	−0.09508
	1	−16066.4 (fixed) (10)	5.31210
Diamond	0	87800	0
f.c.c.	0	100000	0

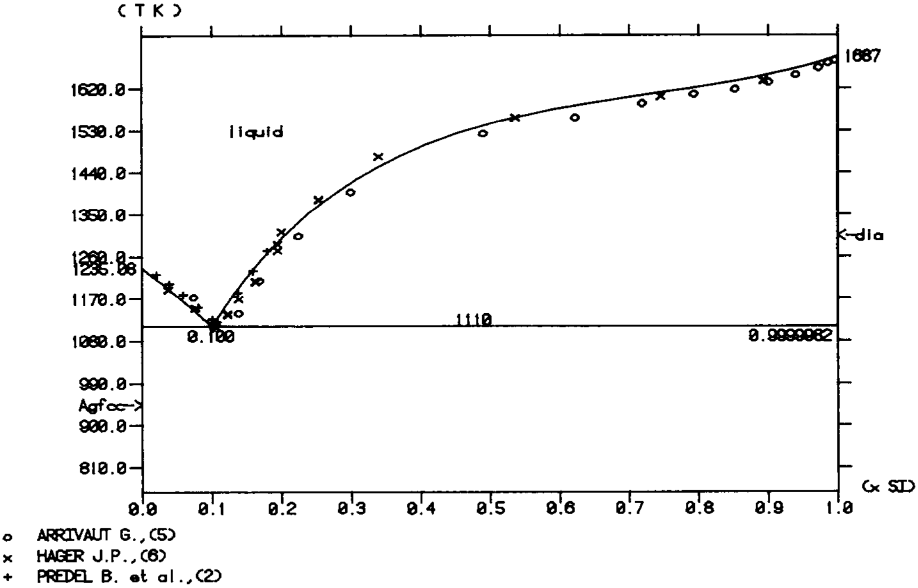

Fig. 1. Comparison between the calculated Ag–Si phase diagram and selected experimental data: (O) [5], (×) [6], (+) [2].

curve has been obtained from experimental results [10] in the temperature range 1423–1550 K.

The parameter of the diamond solid solution has been estimated in order to reproduce the solid solubility of Ag in Si as given in ref. 3. The calculated solid solubility is $X_{Ag} = 0.0004$ at $T = 1623$ K, $X_{Ag} = 0.0005$ at $T = 1473$ K, for a parameter equal to 43000; $X_{Ag} = 0.000014$ at $T = 1623$ K, $X_{Ag} = 0.000013$ at $T = 1473$ K, for a parameter equal to 87800, which has been selected in Table 1. The parameter of the f.c.c. solid solution has been arbitrarily taken to be equal to 100000 in order to reproduce a negligible solid solubility of Ge in Ag f.c.c.

TABLE 2

Three phase equilibria and congruent transformation in the Ag–Si system

Transformation	Calculated		Experimental		Ref.
	T(K)	$X = X_{Si}$	T(K)	$X = X_{Si}$	
Ag f.c.c. ↔ Ag(liq)	1235.08	0	1234	0	[17]
Si dia ↔ Si(liq)	1687.00	1	1685	1	[17]
liquid ↔ Ag(f.c.c.) + dia	1110.3	$X_{Si}^{(L)} = 0.100$	1098	$X_{Si}^{(L)} = 0.154$	[5]
		$X_{Si}^{dia} = 0.9999982$	1128	$X_{Si}^{(L)} = 0.132$	[8]
			1113 + 2.6 − 4.5	$X_{Si}^{(L)} = 0.106$	[6]
			1121	$X_{Si}^{(L)} = 0.107$	[2]

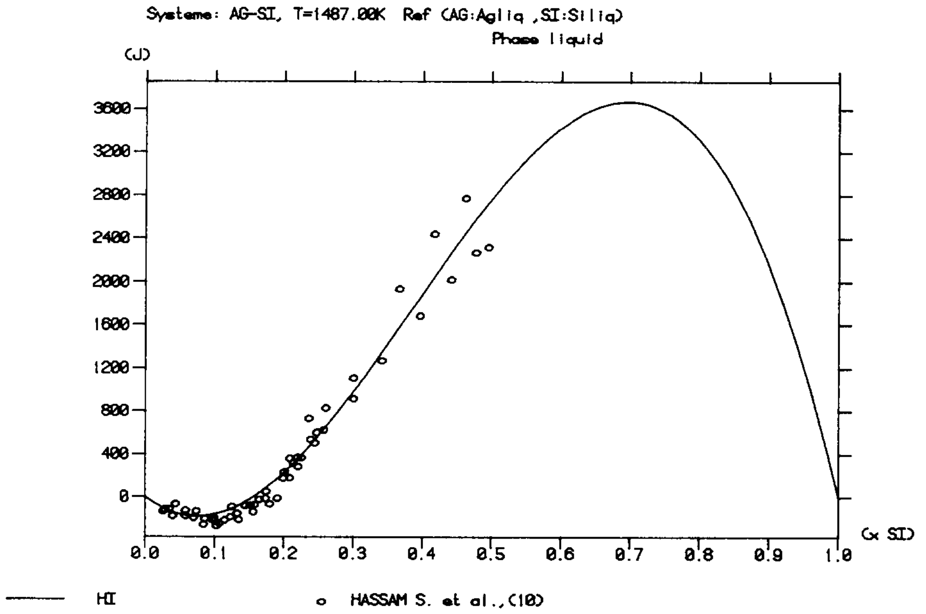

Fig. 2. Comparison between the calculated enthalpy of mixing of Ag–Si liquid alloys (temperature-independent) and selected experimental data [10] (○).

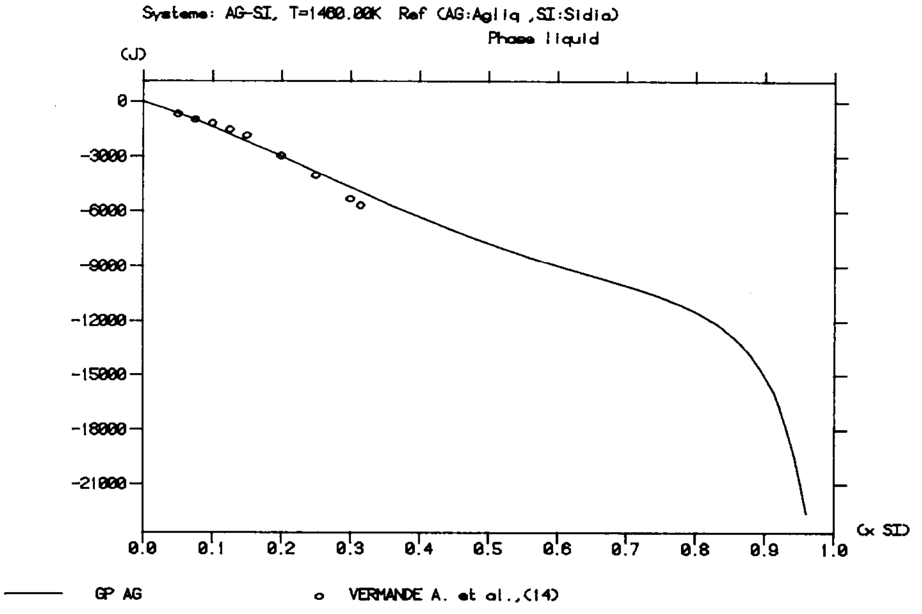

Fig. 3. Comparison between the calculated partial Gibbs energy of Ag in the liquid phase at $T = 1460$ K and the experimental data of ref. 14 (○).

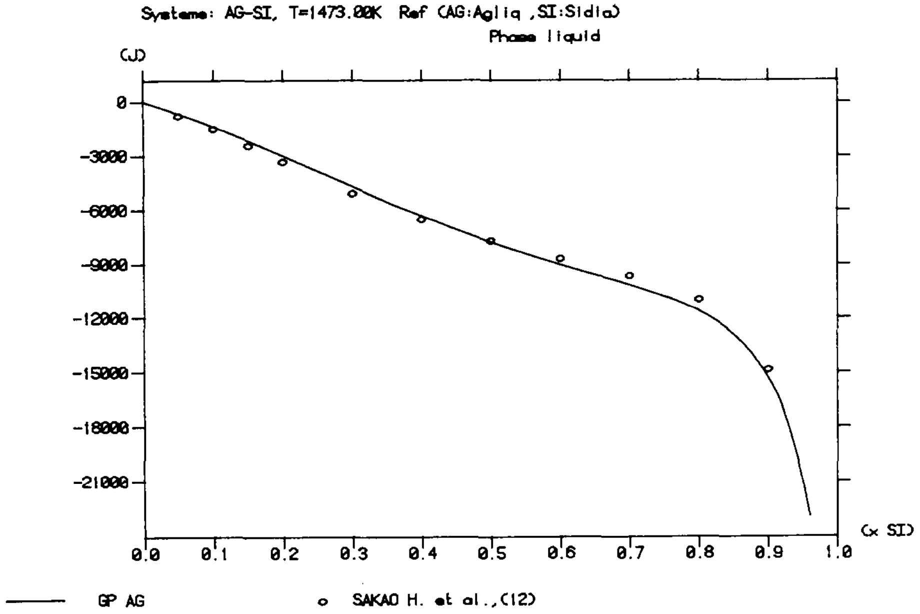

Fig. 4. Comparison between the calculated partial Gibbs energy of Ag in the liquid phase at $T = 1473$ K and the experimental data of ref. 12 (O).

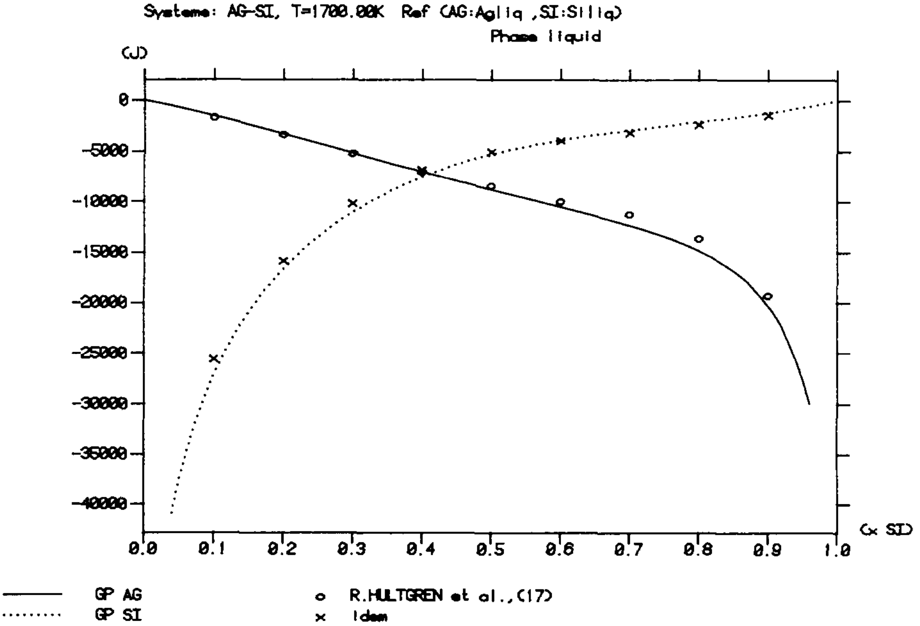

Fig. 5. Comparison between the calculated partial Gibbs energy of Ag (———) and Si (······) in the liquid phase at $T = 1700$ K and selected data of ref. 17.

The phase diagram has been calculated and compared to the experimental diagram in Fig. 1.

Table 2 shows the experimental and calculated temperature and composition for the eutectic reaction. The agreement is best with the data of refs. 2 and 6, within experimental error, which have been preferred to the previous experimental results, as well for temperature as for composition.

Figure 2 shows the comparison between the calculated enthalpy of mixing (temperature-independent) of the liquid phase and selected experimental data of [10]. The agreement is quite satisfactory.

Figures 3–5 show the comparison between the calculated partial Gibbs energies of the elements of the liquid phase and selected experimental data [12,14,17]. The agreement is quite satisfactory. Conversely, the experimental values of ref. 11 seem to be more negative than those calculated in the temperature range 1723–1823 K, and the disagreement is the same for the results in ref. 13.

SUMMARY

A complete thermodynamic description of the Ag–Si system is presented. A set of self-consistent parameters has been obtained for the various solution phases of the system. Comparison between the available information and the calculated values is as satisfactory as possible. These parameters can be used for tabulation of thermodynamic functions or calculation of phase equilibria in multicomponent systems.

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