

THERMODYNAMIC EVALUATION OF THE Au–Bi SYSTEM

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(Received 16 September 1987)

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 all phases in the Au–Bi system. These coefficients have been optimized by using a program developed by Lukas et al., *Calphad*, 1 (1977) 225.

Phase diagram and characteristic thermodynamic functions have been prepared, and compared with the experimental values from the THERMODATA software.

Very satisfactory agreement was obtained by using eleven optimized coefficients with a simple substitutional model for the liquid and fcc phases and either a linear approximation or a three terms expression for the temperature dependency of the Gibbs energy of the stoichiometric compound Au_2Bi .

INTRODUCTION

The main advantages of the thermodynamic approach have been extensively developed in a previous work [2]. This evaluation is the second 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.

SHORT PRESENTATION OF THE DIFFERENT PHASES

The assessed phase diagram, reported by Okamoto and Massalski [3] shows the existence of only one stoichiometric intermetallic compound. The various phases, with the symbols currently used are listed below.

Solution phases

- (1) liquid phase (L)
- (2) terminal Au-rich solid solution, with a face-centered cubic (Al) prototype structure (the solid solubility of Bi in gold is less than 0.06 at%) (fcc)

- (3) terminal Bi-rich solid solution, with a rhombohedral (A7) prototype structure (there is no reported mutual solid solubility of Au in Bi) (Bi(rho))

Stoichiometric compound

- (4) $\text{Au}_2\text{Bi}(\beta)$ with the fcc (C15) structure isotypic with Cu_2Mg ; stable between 389 and 644 K; this compound is reported as stoichiometric.

EXPERIMENTAL INFORMATION

Phase diagram

The phase diagram of the Au–Bi system shows two invariant reactions with the liquid phase and an intermetallic stoichiometric compound Au_2Bi , stable in a narrow temperature range.

The liquidus has been experimentally studied using conventional thermal analysis by Heycock and Neville [4,5], by Vogel [6] and by Nathans and Leider [7] for the equilibrium liquid + Bi(rho), and using a sampling method for the rest of the liquidus. For the same reasons as those described in ref. 3 (the presence of the Au_2Bi intermediate phase was not observed by Vogel [6], and the melting point of Bi was reported about 5°C lower than the accepted value by Heycock and Neville [4,5]), the accepted phase diagram comes from the work of Nathans and Leider [7] and the observed experimental temperature and composition are 644 ± 2 K, 66.9 ± 0.3 at% Bi for the peritectic reaction and 514.25 ± 0.3 K, 86.8 at% Bi for the eutectic reaction.

The data of ref. 7 were accepted instead of those of Gather and Blachnik [8], because the experimental details were not reported in ref. 8. Moreover, these authors seem to have only mentioned the results from ref. 7, except for the peritectic reaction. Other experimental temperatures and compositions for the invariant reactions (from refs. 9, 10 and 11) are reported in Table 3 and compared with those calculated.

There is no reported solubility of Au in Bi, when the solid solubility of Bi in Au shows a maximum at 1173 K equal to 0.06 at% Bi after Raub and Engel [12]: $x_{\text{Bi}} = 0.0003$ at $T = 973, 1073$ K; $x_{\text{Bi}} = 0.0004$ at $T = 1273$ K.

Thermodynamic properties

Liquid alloys

The enthalpy of mixing of liquid alloys was determined from calorimetry measurements by Kleppa [13] ($T = 623, 723$ K; $x_{\text{Bi}} = 0.68\text{--}0.99$) and by Predel and Emam [15] ($T = 1373$ K; $x_{\text{Bi}} = 0\text{--}1$).

The partial Gibbs energy of Bi was calculated from the e.m.f. measurements of Kleppa [14] ($T = 873\text{--}1073$ K; $x_{\text{Bi}} = 0.21\text{--}0.95$); the thermody-

namic activities were determined with the aid of the partial pressure comparison method by Predel and Emam [15] ($T = 1373$ K; $x_{\text{Bi}} = 0-1$).

The activity of Bi along the liquidus curve has also been measured using the e.m.f. method by Pouillard et al. [16], and with a similar method by Kameda and Azakami [17] ($T = 943-1123$ K; $x_{\text{Bi}} = 0-1$). Their graphical results at $T = 973$ K are very similar to those of ref. 14.

Stoichiometric compound

The enthalpy of formation referred to the pure solid components of the intermetallic stoichiometric compound Au_2Bi was taken from the liquid Bi solution calorimetry of Kleppa [13] and equal to 2117.1 J per gram atom (± 210), at $T = 644$ K.

The specific heat trend with temperature of Au_2Bi , as measured by Wallbrecht et al. [18], is given by $C_p = 24.54 + 6.25 \times 10^{-3}T - 30105/T^2$.

The quantity ΔC_p , i.e. the difference between the specific heat of the compound and the balanced specific heats of the pure solid elements after the S.G.T.E. values is approximatively constant and has a mean value equal to about 0.75 J per K per gram atom in the range 300–500 K.

EVALUATION METHOD

The Gibbs energy of different solution phases was described using a simple substitutional model. An expression for the excess Gibbs energy was developed by a Redlich-Kister polynomial equation of the form

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

where $L_{\text{Au,Bi}}^{(\nu)}(T) = a_{\text{Au,Bi}}^{(\nu)} + b_{\text{Au,Bi}}^{(\nu)}T$, and the interaction terms $L_{\text{Au,Bi}}^{(\nu)}(T)$ are linear functions of the temperature i.e. $a_{\text{Au,Bi}}^{(\nu)}$ and $b_{\text{Au,Bi}}^{(\nu)}$ correspond to the temperature-independent values of the enthalpy and the excess entropy of mixing.

In a first optimization, the Gibbs energy of formation of the compound Au_2Bi referred to the pure solid elements has been represented by a linear approximation

$$\Delta G = a + bT \quad (2)$$

and the first constant coefficient has been fixed to the experimental value previously described. In a second optimization, the Gibbs energy has been represented by a three term expression

$$\Delta G = A - BT + CT(1 - \ln T) \quad (3)$$

which can be written

$$\Delta G = a + bT + cT \ln T \quad (4)$$

where the term C was fixed to a constant value 0.75 J per K per gram atom

which has been calculated from the experimental work of Wallbrecht et al. [18] and from the accepted values for the pure elements ($c = -C$, $a = A$, $b = C - B$).

The values used for the lattice stabilities of the pure elements come from the S.G.T.E. assessment [19] for the stable solid and liquid phases and from the assessment of Saunders [20] for the metastable phases (required to express the excess properties of mixing of the fcc solution phase).

The following values have been used [19,20]

$$G_{\text{Au}}^{\ominus \text{L}} - G_{\text{Au}}^{\ominus \text{fcc}} = 12589.413 - 9.416744T + (8140.249 \times 10^{-25})T^7$$

for $298.15 < T < 1337.58$

$$= 12522.901 - 9.364532T + (398805.149 \times 10^{23})T^{-9}$$

for $1337.58 < T < 3200.00$

$$G_{\text{Bi}}^{\ominus \text{L}} - G_{\text{Bi}}^{\ominus \text{rho}} = 11245.936 - 20.637366T - (5972582.889 \times 10^{-25})T^7$$

for $298.15 < T < 544.52$

$$= 11336.361 - 20.811733T - (166.491 \times 10^{23})T^{-9}$$

for $544.52 < T < 3000.00$

$$G_{\text{Bi}}^{\ominus \text{fcc}} - G_{\text{Bi}}^{\ominus \text{rho}} = 9900 - 12.5T$$

The different parameters of the various solution phases, noted ϕ , $a_{\text{Au,Bi}}^{(\nu)}(\phi)$ and $b_{\text{Au,Bi}}^{(\nu)}(\phi)$, and of the stoichiometric compound Au_2Bi , have been 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 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 various solution phases referred to the pure elements having the same structure as the corresponding phase and of the Gibbs energy of formation of the stoichiometric compound referred to $\text{Au}(\text{fcc})$ and $\text{Bi}(\text{rho})$. The enthalpy of formation of Au_2Bi has been set as the experimental values from ref. 13 in the first optimization, with the third term fixed as $C = 0.75$ J per K per gram atom in the second optimization. In the optimization, greater importance was given to the phase diagram and the enthalpy of mixing of the liquid phase than to the values of the partial Gibbs energy of Bi, because they generally lead to higher values of the temperatures of the two invariant reactions than do the experimental values.

TABLE 1

Excess Gibbs energy $\Delta^E G$ (J) coefficients for the liquid and fcc phases of the Au-Bi system

$$\Delta^E G = x_{\text{Au}} x_{\text{Bi}} \sum_{\nu=0}^n (x_{\text{Au}} - x_{\text{Bi}}) L_{\text{Au,Bi}}^{(\nu)}(T)$$

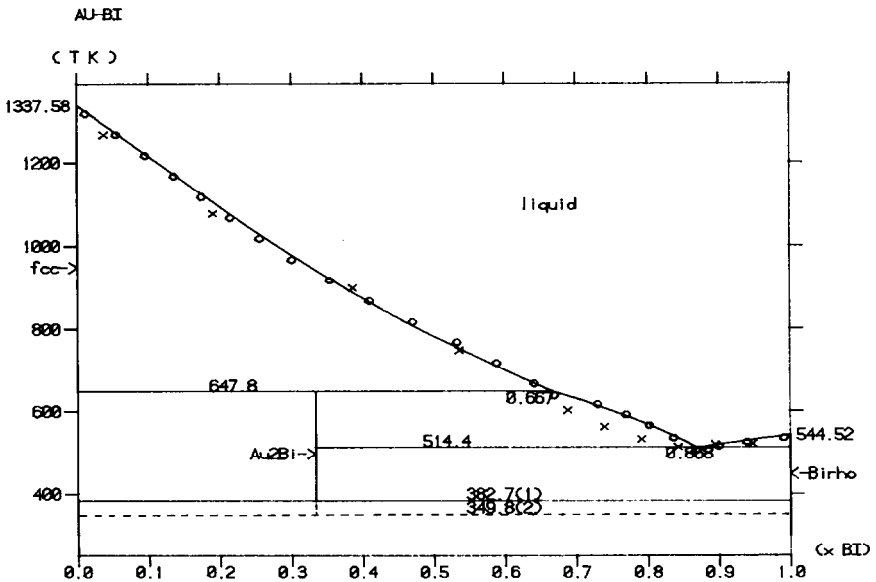
$$L_{\text{Au,Bi}}^{(\nu)}(T) = a_{\text{Au,Bi}}^{(\nu)} + b_{\text{Au,Bi}}^{(\nu)} T \quad (\nu = 0, 1, 2, 3)$$

and Gibbs energy of formation (J per gram atom) of Au_2Bi referred to as Au(fcc) and Bi(rho)

$$\Delta G = a + bT + cT \ln T$$

Phase	ν	$a_{\text{Au,Bi}}^{(\nu)}$ (J)		$b_{\text{Au,Bi}}^{(\nu)}$ (J K ⁻¹)			
		(1) ^a	(2) ^a	(1)	(2)		
Liquid	0	2778.65	2769.55	-6.22675	-6.307570		
	1	-1640.95	-1495.30	1.13053	1.133275		
	2	-3852.45	-3850.95	3.84748	3.693060		
	3	-480.25	-810.00	-0.72860	-0.344775		
fcc	0	48000.00	48000.00	0.0	0.0		
Compound	x_{Bi}	a (J)		b (J K ⁻¹)		c (J K ⁻¹)	
		(1)	(2)	(1)	(2)	(1)	(2)
Au_2Bi	0.333	2117.10 (fixed)	1385.30	-5.53243	0.43285	0	-0.75 (fixed)

^a (1) = First optimization, (2) = second optimization.



o NATHANS M.W. et al., (7)
x VOGEL R., (6)

Fig. 1. Calculated phase diagram of the Au-Bi system compared with selected experimental data.

TABLE 2
Three phase equilibria and congruent transformation in the Au-Bi system

Transformation	Calculated		Experimental		Reference
	T (K)	$x = x_{\text{Bi}}$	T (K)	$x = x_{\text{Bi}}$	
Au(fcc) \rightleftharpoons Au(liq)	1337.58	0	1337.58	0	3
Bi(rho) \rightleftharpoons Bi(liq)	544.52	1	544.52	1	3
fcc + (L) \rightleftharpoons Au ₂ Bi	647.8	$x^{\text{L}} = 0.667$ $x^{\text{fcc}} = 0.000044$ $x^{\text{fcc}} = 0.000049$	644	$x^{\text{L}} = 0.669 \pm 0.003$	7
			646	$x^{\text{L}} = 0.68$	8
			651	$x^{\text{L}} = 0.666 \pm 0.003$	9
			646	not reported	10
(L) \rightleftharpoons Au ₂ Bi + Bi(rho)	514.4	$x^{\text{L}} = 0.868$	514.15	$x^{\text{L}} \sim 0.86$	6
			513	$x^{\text{L}} = 0.8236$	11
			514.25	$x^{\text{L}} = 0.868 \pm 0.003$	7
			514	$x^{\text{L}} = 0.85$	8
			514 \pm 0.4	$x^{\text{L}} = 0.864 \pm 0.002$	9
Au ₂ Bi \rightleftharpoons fcc + Bi(rho)	382.7		\sim 389	estimated	3
	349.8				

^a (1) = first optimization, (2) = second optimization.

The parameter of the fcc solution phase has been estimated in order to reproduce the solid solubility of Bi in Au which is equal to 0.03 at% Bi in the range 973–1073 K.

The phase diagram was calculated from the first set of coefficients and compared with the experimental one in Fig. 1. Table 2 shows experimental and calculated temperature and composition for the invariant equilibria and calculated temperature of the decomposition of the stoichiometric compound resulting from the two different optimizations. There is no significant difference between the two sets of coefficients, except for the temperature of decomposition of Au_2Bi .

Excellent agreement is observed for all the invariant temperatures and compositions. For the eutectic reaction, the agreement is perfect with the experimental results of refs. 7 and 9, whereas for the peritectic reaction, the results seem to be a compromise between the temperatures of refs. 7 and 9, and are very close to those of refs. 8 and 10. The temperature of decomposition of Au_2Bi needs to be determined by future experimental work. The calculated solid solubility of Bi in Au is $x_{Bi} = 0.0003$ at $T = 973$ K, $x_{Bi} = 0.00033$ at $T = 1073$ K, $x_{Bi} = 0.0003$ at $T = 1173$ K, $x_{Bi} = 0.00015$ at $T = 1273$ K, which agrees with the experimental results of Raub and Engel [12] in the range 773–1073 K; however, the maximum at 1173 K is not observed.

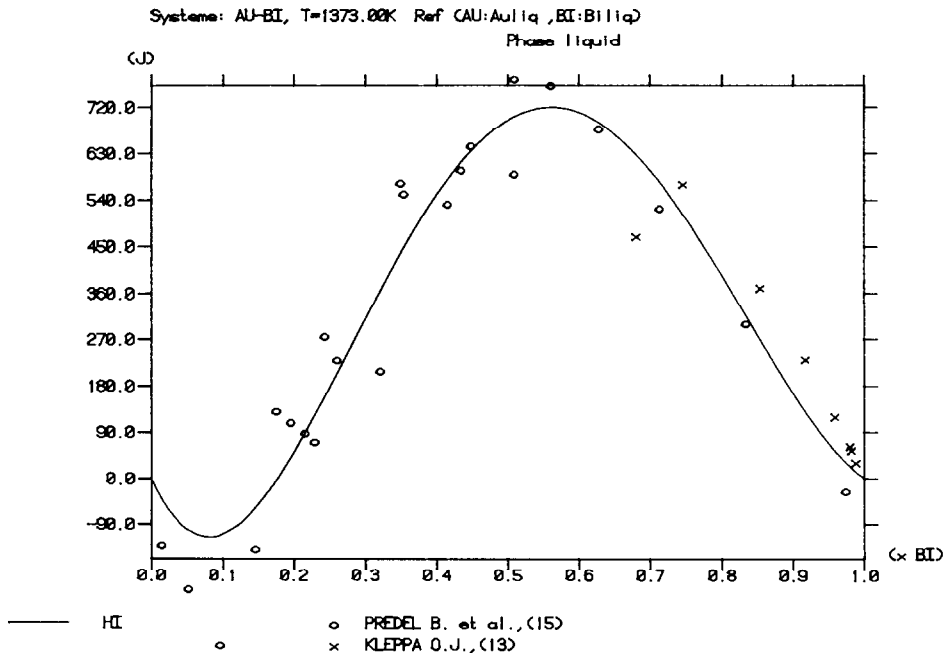


Fig. 2. Calculated enthalpy of mixing of the liquid phase (temperature-independent) compared with selected experimental data.

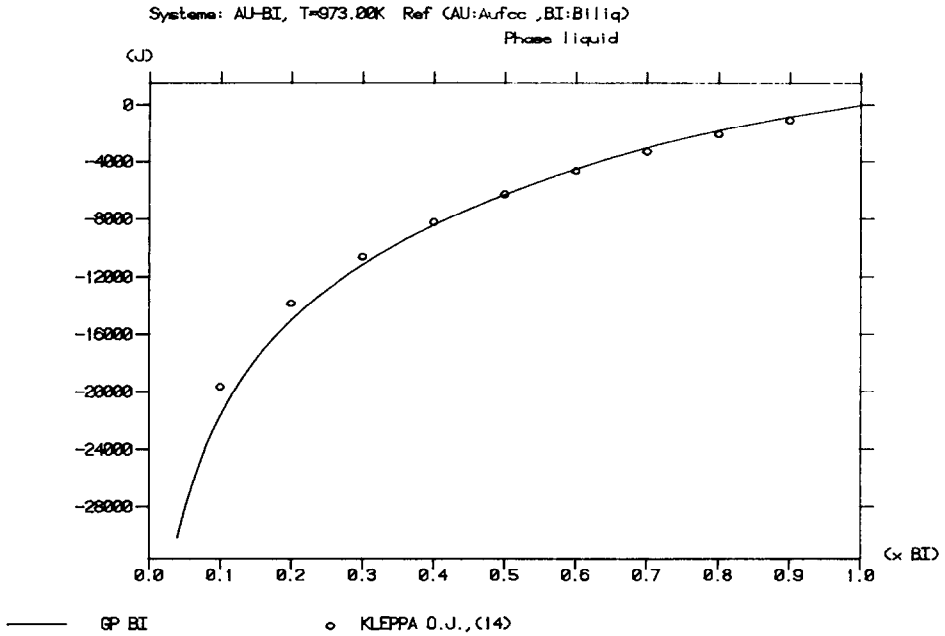


Fig. 3. Calculated partial Gibbs energy of Bi at $T=973$ K compared with selected experimental data.

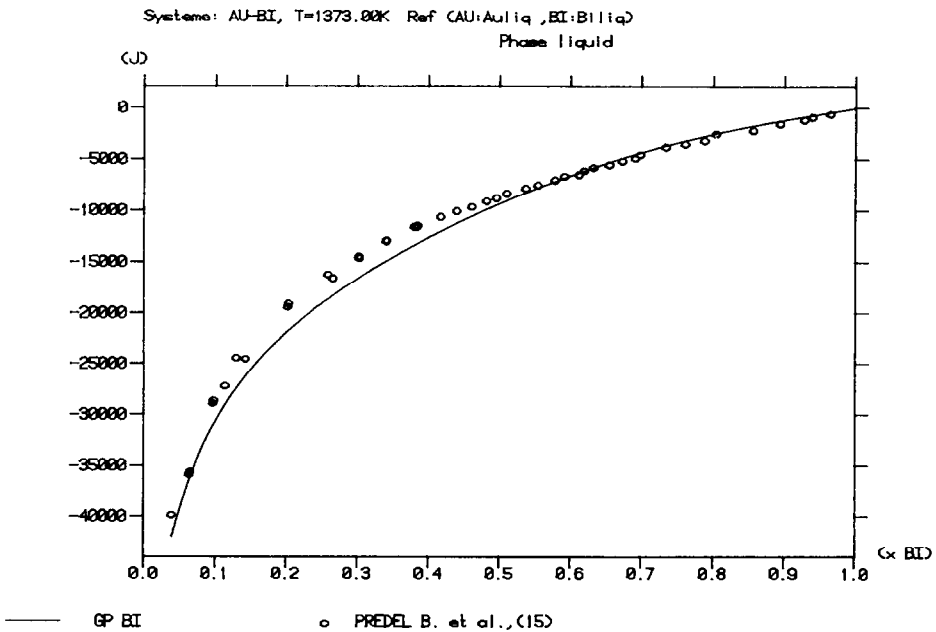


Fig. 4. Calculated partial Gibbs energy of Bi at $T=1373$ K compared with selected experimental data.

Moreover, the shape of the experimental solubility curve is not accurate enough to try a best fit with the calculated one. Another possibility is to adjust the fcc parameter to reproduce the value $x_{\text{Bi}} = 0.0006$ at $T = 1173$ K, which gives a value of 41 000 for this parameter. In this case, the calculated solid solubility of Bi in Au is $x_{\text{Bi}} = 0.00038$ at $T = 773$ K, $x_{\text{Bi}} = 0.00056$ at $T = 873$ K, $x_{\text{Bi}} = 0.00070$ at $T = 973$ K, $x_{\text{Bi}} = 0.00072$ at $T = 1073$ K, $x_{\text{Bi}} = 0.00062$ at $T = 1173$ K, $x_{\text{Bi}} = 0.00030$ at $T = 1273$ K.

The calculated enthalpy and entropy of formation of the compound Au_2Bi referred to the pure solid elements at $T = 644$ K in the second optimization is $\Delta^f H = 1868.3$ J per gram atom; $\Delta^f S = 5.167924$ J per K per gram atom.

Figure 2 shows the comparison between the enthalpy calculated using the first set of coefficients and experimental enthalpy of mixing of liquid alloys according to the methods of Kleppa [13] and Predel and Emam [15].

Figures 3 and 4 show the comparison of the calculated partial Gibbs energy of Bi using the first set of coefficients at $T = 873$ K with the values of ref. 14, and at $T = 1373$ K and compared with the values of ref. 13. The small difference between the calculated and experimental curves come from the predominant importance given to the phase diagram to reproduce the invariant temperatures, and because the activity of Bi determined by ref. 13 leads to higher invariant temperatures, which is in disagreement with the majority of authors.

All the graphical outputs were calculated using the first set of coefficients, because there is no significant change with the other.

SUMMARY

A complete thermodynamic description of the Au–Bi system is presented. Various phases of the system were modeled, and two sets of self-consistent parameters were obtained either with a linear approximation for the Gibbs energy of formation of the compound Au_2Bi , or with a constant estimated value of ΔC_p . Agreement between the available experimental information and the calculated values is satisfactory, except for the activity of Bi at high temperature which does not agree perfectly with the phase diagram.

These parameters can be stored in specialized data banks and used for the tabulation of thermodynamic functions or the calculation of phase equilibria in multicomponent systems containing gold and bismuth.

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