A THERMODYNAMIC ASSESSMENT OF THE Au–In SYSTEM

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ABSTRACT

The thermodynamic properties of mixing of the various phases which exist in the Au–In system and the phase equilibria data have been analysed simultaneously using an optimization procedure. A set of thermodynamic parameters is presented, which is consistent with both types of data.

PHASE DIAGRAM

In 1938, Kubaschewski and Weibke [1] determined, by thermal analysis, the liquidus and invariant reaction temperatures of the Au–In system, which exhibits several stable solid solutions and intermetallic phases. The phase diagram was subsequently investigated mainly by Owen and Roberts [2], Hiscocks and Hume-Rothery [3] and Nikitina et al. [4] in the composition range 5–90 at% In. The following phases are known in this system.

(1) The liquid phase.

(2) The Au-rich solid solution. The maximum solubility of indium is close to 12.7 at% In at temperatures between 930 and 970 K according to Kubaschewski and Weibke [1], Owen and Roberts [2] and Hiscocks and Hume-Rothery [3]. These temperatures correspond, in certain cases, to the peritectic decomposition of the h.c.p. phase.

(3) The α_1 phase. This was identified by Wegst and Schubert [5] as Au_7In. Hiscocks and Hume-Rothery [3] provide microscopic and structural information on this phase. It is stable around 11.5 at% In with a compact hexagonal structure, intermediate between the f.c.c.-A4 and h.c.p.-A3 structures, and decomposes by peritectic reaction.

Dedicated to Professor Oswald Kubaschewski in honour of his contribution to thermochemistry.

(4) The solid solution. This has an h.c.p.-A3 structure and was studied by Kubaschewski and Weibke [1], Hiscocks and Hume-Rothery [3], Nikitina et al. [4] and Schubert et al. [6]. It decomposes peritectically. Its solubility range lies between 13 and 23 at% In.

(5) The β_1 phase identified by Schubert et al. [6]. This phase, stable at low temperature, has an average composition of 22 at% In. Its domain is very narrow and it decomposes peritectoically.

(6) The β phase, also identified by Schubert et al. [6]. This phase is stable between 548 and 610 K.

(7) The solid solution ε'. This has a composition of approximately 25 at% In and is isotypic with Cu_3Ti. It was identified by Wegst and Schubert [5]. Between 572 and 612 K it undergoes an order–disorder transformation ($\varepsilon' \rightleftarrows \varepsilon$) and decomposes peritectically.

(8) The γ phase. This decomposes non-congruently to the liquid and a γ' phase having a different structure. The equilibrium domain at low temperature is very narrow at approximately 30 at% In, but at higher temperatures, the phase region extends from 29 to 32.5 at% In (Hiscocks and Hume-Rothery [3]).

(9) The ψ phase. This is isotypic with Ni_2Al_3, and was identified by Schubert et al. [6]. This phase forms between 500 and 540 K and extends from 35.5 to 39.5 at% In at 730 K (Hiscocks and Hume-Rothery [3]) narrowing to approximately 39 at% at 497 K.
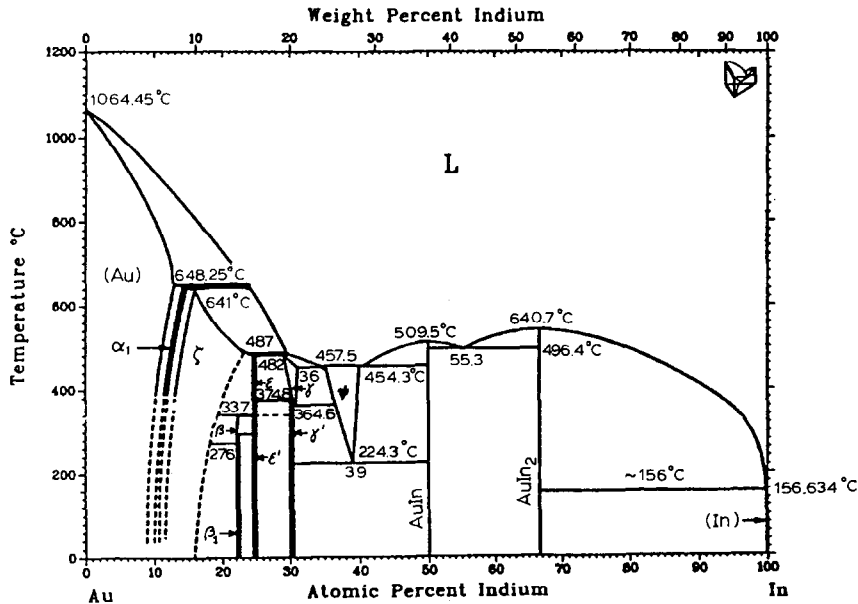

Fig. 1. Assessed phase diagram of the Au–In system [7].

TABLE 1

Assessed and calculated invariant equilibria in the Au–In system

Reaction	Composition (at% In)			T (K)	Type	Reference
(Au)+liq ⇆ α_1	12.5	24.0	14.2	922.4	Peritectic	[7]
α_1+liq ⇄ ζ	14.3	24.4	15.7	914	Peritectic	[7]
ζ+β_1 ⇄ β	21.5	22.0	17.8	548	Eutectoid	[7]
ζ+ε ⇆ β	19.3	22.2	24.5	610	Peritectoid	[7]
ζ+Au$_3$In ⇆ Au$_7$In$_2$ [a]	19.9	25.0	22.0	595	Peritectoid	Present work
ζ+liq ⇄ ε	23.0	29.2	25.0	765.5	Peritectic	[7]
ζ+liq ⇆ Au$_3$In [a]	22.5	29.6	25.0	766	Peritectic	Present work
ε+liq ⇆ γ	25.0	29.7	28.8	760	Peritectic	[7]
Au$_3$In+liq ⇄ Au$_7$In$_3$ [a]	25.0	30.4	30.0	759.5	Peritectic	Present work
γ+ψ ⇄ liq	31.4	35.3	35.0	729.5	Eutectic	[7]
Au$_7$In$_3$+Au$_{62}$In$_{38}$ ⇄ liq [a]	30.0	38.0	35.5	723.1	Eutectic	Present wrok
γ+AuIn ⇄ liq	39.5	50.0	39.8	727.3	Eutectic	[7]
Au$_{62}$In$_{38}$+AuIn ⇆ liq [a]	38.0	50.0	40.5	724.1	Eutectic	Present work
AuIn+AuIn$_2$ ⇆ liq	50.0	66.7	55.3	768.4	Eutectic	[7]
	50.0	66.7	54.8	770.5	Eutectic	Present work
AuIn$_2$+In ⇆ liq	66.7	100.0	99.9	429	Eutectic	[7]
	66.7	100.0	99.9	429.7	Eutectic	Present work
γ+AuIn ⇆ ψ	30.4	50.0	39.0	497.3	Eutectoid	[7]
Au$_7$In$_3$+AuIn ⇆ Au$_{62}$In$_{38}$ [a]	30.0	50.0	38.0	487	Eutectoid	Present work
ε ⇆ ε'	25.0	25.0		612	Congruent	[7]
AuIn$_2$ ⇄ liq	66.7	66.7		813.7	Fusion	[7]
				812	Fusion	Present work
AuIn ⇆ liq	50.0	50.0		782.6	Fusion	[7]
				783	Fusion	Present work

[a] Assumptions: β_1 and β identified as Au$_7$In$_2$, ε and ε' identified as Au$_3$In, γ and γ' identified as Au$_7$In$_3$ and ψ identified as Au$_{62}$In$_{38}$.

(10) The AuIn phase. This is stable at room temperature and melts congruently at 783 K. Its composition range is very narrow (50–50.5 at% In).

(11) The AuIn$_2$ phase. This has a non-appreciable range of stoichiometry and it melts congruently at 813 K.

(12) The In phase. Au is insoluble in this phase.

Fig. 1 shows the assessed diagram from Okamoto and Massalski [7]. The characteristics of the invariant equilibria occurring in this system are listed in Table 1.

THERMODYNAMICS

The enthalpy of mixing of the liquid alloys has been determined by several investigators. The results of Kleppa [8] and Beja [9] derived from calorimetric measurements are in good agreement. Itagaki and Yazawa [10]

also measured the enthalpy of mixing of the liquid alloys. Their values are much less negative than the determinations of Kleppa [8] and Beja [9].

The measurements of Castanet et al. [11] differ only slightly from those of Kleppa [8] and Beja [9]. They observed a temperature dependence of this property for alloys containing less than 70 at% In, which they explained by the presence of clusters in the liquid phase which disappear at higher temperatures.

Gather and Blachnik [12] also observed a temperature dependence of the enthalpy of mixing of the liquid alloys and their values lie between those of Beja [9] and Castanet et al. [11]. They also attribute this change at low temperature to the existence of a local order owing to cluster formation.

The enthalpies of formation of the solid phases determined by Kleppa [8] are very negative especially for AuIn and $AuIn_2$. Castanet et al. [11] confirmed Kleppa's determination for $AuIn_2$. Itagaki [13] measured the enthalpy of fusion of these two compounds as well as their heat capacities with an adiabatic calorimeter.

Wallbrecht et al. [14] measured the enthalpy contents and heat capacities of the γ, AuIn and $AuIn_2$ phases by differential scanning calorimetry. In addition, the enthalpy and entropy of the reaction, $\gamma \leftrightarrows \gamma'$, were also obtained from their measurements.

Indium and Au activities of the liquid alloys were derived from e.m.f. measurements of zinc activities in ternary Au–In–Zn alloys by Predel and Schallner [15]. They observed a negative deviation from ideality. The activities of indium, in the liquid phase, were also derived from e.m.f. measurements of concentration cells ($InCl_3$ in KCl–NaCl melts) by Kameda et al. [16] in the composition range 20.8–83.5 at% In between 973 and 1223 K. Castanet et al. [11] used the same technique with a different electrolyte ($InBr_3$ in KBr–LiBr) to study alloys with compositions ranging from 31.59 to 79.6 at% In and from 973 K to the liquidus temperatures. The two sets of measurements differ very slightly and the derived activities show stronger negative deviations from ideality than Predel's results. Jacob and Alcock [17] used an equilibrium technique to obtain indium activities of Au-rich solid alloys with compositions ranging from 2.94 to 12.36 at% In. The alloys, mixed with In_2O_3, were equilibrated with CO/CO_2 mixtures, the indium compositions being obtained by neutron activation analysis. Predel and Schallner [18] derived the activities of In in Au-rich solid alloys ($0.02 \ll x_{In} \ll 0.12$) from e.m.f. measurements using a solid electrolyte, again finding strong negative deviations from ideality. The agreement with Jacob's results is very satisfactory.

Brodowsky and Maaz [19] also studied Au-rich alloys by using concentration cells and a zirconia stabilized electrolyte. The partial Gibbs energies of indium at 800, 900 and 1000 K are more negative than those of the researchers previously mentioned. At 800 K, the measurements allow the phase boundary of the α_1 phase to be confirmed.

OPTIMIZATION

The thermodynamic parameters of the various phases which exist in the system were calculated by means of an optimization program developed by Lukas et al. [20], where experimental thermodynamic as well as phase diagram data are taken into account.

The Redlich–Kister equation [21] is used to represent the excess Gibbs energy of mixing G_m^{ex} of the solution phases where

$$G_m^{ex} = x_{Au}x_{In} \sum_{\nu=0}^{n} a_\nu (x_{Au} - x_{In})^\nu \tag{1}$$

and

$$a_\nu = A_\nu + B_\nu T + C_\nu T \ln T \tag{2}$$

The Gibbs energy of formation of the stoichiometric compounds is expressed by an equation similar to eqn. (2).

The Gibbs energy of fusion of Au and In has been calculated from the SGTE data-base [22]. For the metastable phases f.c.c. In, h.c.p. Au and h.c.p. In, the Gibbs energies of transformation relative to the liquid phase have been calculated together with the thermodynamic parameters of the solution phases.

The β and β_1 phases, which have a similar composition, were assumed to be Au_7In_2. Similarly, the ε and ε' phases were assumed to be the stoichiometric compound Au_3In, the γ and γ' phases were assumed to be Au_7In_3 and the ψ phase was identified as $Au_{62}In_{38}$.

In a first step, the thermodynamic parameters of the liquid, f.c.c., ζ and $AuIn_2$ phases were optimized using the experimental phase diagram data of Kubaschewski and Weibke [1], Owen and Roberts [2], Hiscocks and Hume-Rothery [3] and Nikitina et al. [4], the calorimetric measurements of Kleppa [8], Beja [9], Castanet et al. [11] and Gather and Blachnik [12], and the partial molar Gibbs energies of Castanet et al. [11], Kameda et al. [16], Jacob and Alcock [17], Predel and Schallner [18] and Brodowski and Maaz [19]. The values of Itagaki and Yazawa [10] were discarded, since they are much less negative than those of the above investigators.

The optimization converged properly when 3, 4 and 6 coefficients were used to represent the thermodynamic behaviour of these solution phases. The thermodynamic parameters of the solution phases and intermetallic compounds are listed together with those for the pure elements in their metastable states in Table 2.

The calculated values for the molar enthalpy of mixing of the liquid alloys at 823, 900 and 1300 K are shown in Fig. 2 where a very good agreement is observed. Figure 3 shows the calculated and experimental values of the partial Gibbs energy of indium at 823 K of Castanet et al. [11], where an excellent agreement is also observed. For the Au-rich phase, the calculated
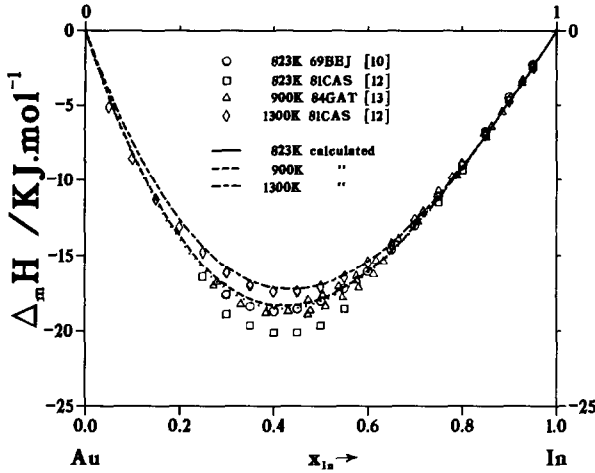
Fig. 2. Experimental and calculated molar enthalpies of mixing.

TABLE 2

Thermodynamic parameters of Au, In and the solution phases (J mol^{-1})

ΔG_{Au}^- (f.c.c. $\rightarrow$ l) = 12597.0 $-$ 9.702 T $-$ 1.162907 $\times$ 10^{-5} T^2
$\qquad$ + 0.041635 T ln T
ΔG_{Au}^- (h.c.p. $\rightarrow$ l) = 12309.0 $-$ 10.98224 T
ΔG_{In}^- (f.c.c. $\rightarrow$ l) = 2908.0 $-$ 7.113 T
ΔG_{In}^- (h.c.p. $\rightarrow$ tetragonal) = 150 $-$ 0.2 T
ΔG_{In}^- (b.c.t. $\rightarrow$ l) = 3274.3 $-$ 7.6089 T + 1.2132 $\times$ 10^{-6} T^2
$\qquad$ $-$ 1.69437 $\times$ 10^{-3} T ln T

Liquid phase
$\quad G_m^{ex} = x_{Au}x_{In}[-80027.7 + 89.717326\ T - 9.57049\ T$ ln T)
$\qquad + (x_{Au} - x_{In})(-34977.3 + 117.293782\ T - 13.0337\ T$ ln T)]

Au Phase
$\quad G_m^{ex} = x_{Au}x_{In}\ (-61378.5 + 174.988\ T - 23.185145\ T$ ln T)

ζ phase
$\quad G_m^{ex} = x_{Au}x_{In}[(-60630.0 + 16.796432\ T)$
$\qquad + (x_{Au} - x_{In})\ (7870.9 - 27.3128\ \ln T)]$

TABLE 3

Calculated and experimental enthalpy and entropy of fusion of Au–In and AuIn$_2$

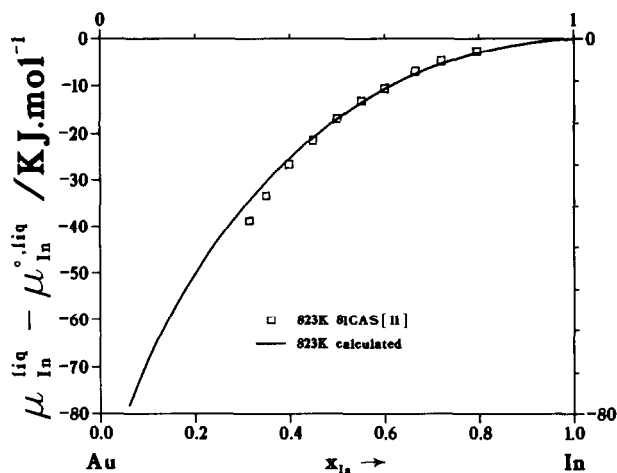| Compound	ΔH(fus) (kJ mol^{-1})	ΔS(fus) (J mol^{-1} K^{-1})	Reference
AuIn	11.5	14.7	[13]
	11.24	14.4	[14]
	9.4	12	Present work
AuIn$_2$	15.7	19.2	[13]
	14.5	17.5	[14]
	18.5	19.6	Present work

Fig. 3. Experimental and calculated partial Gibbs energies of indium in liquid alloys at 823 K.
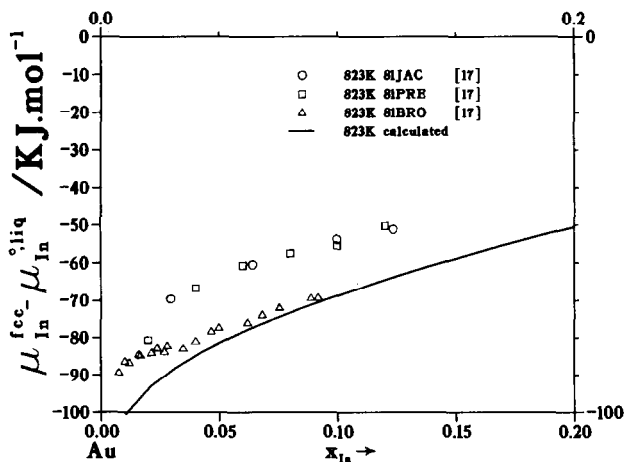

Fig. 4. Experimental and calculated partial Gibbs energies of indium in gold-rich alloys at 823 K.

TABLE 4

Calculated and experimental enthalpy and entropy of formation referred to f.c.c. Au and tetragonal In

Compound	ΔH_f (kJ mol^{-1})	ΔS_f (J mol^{-1} K^{-1})	Reference
AuIn	−21787		[8]
	−19639	1.847	Present work
AuIn$_2$	−24473		[11]
	−24783		[8]
	−26730	12.016	Present work
Au$_{62}$In$_{38}$	−14804.5	−2.0929	Present work
Au$_7$In$_3$	−12935.7	−1.937	Present work
Au$_3$In	−11055.5	−2.1659	Present work
Au$_7$In$_2$	−97620	−2.3802	Present work

Gibbs energy of In is shown in Fig. 4, and a good agreement is obtained with the values of Brodowsky and Maaz [19] but not with the results of Castanet et al. [11] and Predel and Schallner [18].

The coefficients for the Gibbs energy of formation of the compounds AuIn, $Au_{62}In_{38}$ (ψ), Au_7In_3 (γ), Au_3In (ε) and Au_7In_2 (β_1) were obtained by combining separately the calculated thermodynamic data of the solution phases and the phase diagram data relative to the equilibria involving these compounds. The calculated enthalpies and entropies of formation and fusion of the compounds are listed in Tables 3 and 4.

DISCUSSION

The calculated phase diagram is plotted in Fig. 5 where the experimental points are also shown. The agreement is satisfactory. For the phase boundaries involving equilibria between the liquid and f.c.c. phases, the maximum differences in composition are of the order of 1.5 at%. The maximum solubility of In in Au is 13.17 at% In which can be compared with 12.53 (Kubaschewski and Weibke [1]), 12.6 (Owen and Roberts [2]) and 12.7 (Hiscocks and Hume-Rothery [3]). Moreover, the α_1 phase decomposes at low temperatures and in the absence of experimental data the calculated phase boundaries have been accepted.

The calculated decomposition temperatures of Au_7In_2 and Au_3In are 600 K and 768 K, respectively compared with 610 K and 765.5 K determined by Hiscocks and Hume-Rothery [3]. In the composition range 25–35 at% In, the calculated liquidus temperatures lie between the values given by Kubaschewski and Weibke [1], Hiscocks and Hume-Rothery [3] and Nikitina
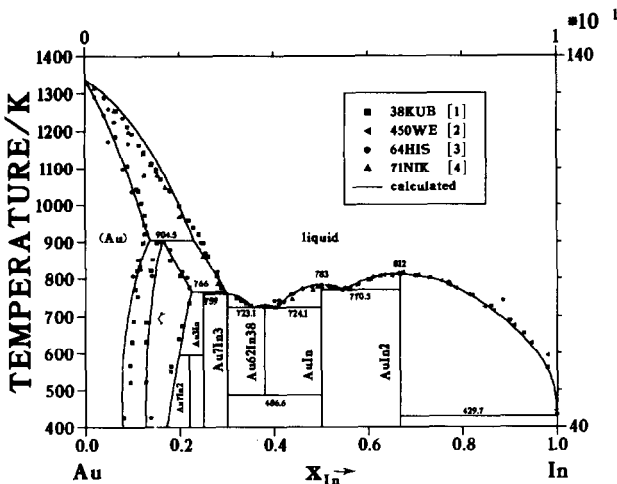

Fig. 5. Experimental and calculated phase diagram of the Au–In system.

et al. [4].

The calculated peritectic decomposition temperature of Au_7In_3 is 759 K which is in excellent agreement with Hiscocks and Hume-Rothery [3] (760 K) and differs by 9 K from that given by Nikitina et al. [4].

The calculated temperatures of the invariant reactions involving the liquid phase and $Au_{62}In_{38}$, AuIn and $AuIn_2$ differ by not more than 5 K as shown in Table 1.

CONCLUSION

A set of thermodynamic parameters for the solution phases and inter-metallic compounds of the Au–In system has been obtained by means of an optimization procedure. Certain solution phases exhibiting narrow ranges of solubility were assumed to be stoichiometric. Nevertheless, very satisfactory agreement with experiment was observed for the phase diagram calculation and for the thermodynamic properties.

REFERENCES

1 O. Kubaschewski and F. Weibke, Z. Elektrochem., 44 (1938) 870–877.
2 E.A. Owen and E.A.O. Roberts, J. Inst. Met., 71 (1945) 213–254.
3 S.E.R. Hiscocks and W. Hume-Rothery, Proc. R. Soc. London, Ser. A, 282 (1964) 318–330.
4 V.K. Nikitina, A.A. Babitsyna and Yu.K. Lobanova, Izv. Akad. Nauk. SSSR, Neorg. Mater., 7 (3) (1971) 371–376.
5 J. Wegst and K. Schubert, Z. Metallkd., 49 (10) (1958) 533–544.
6 J. Schubert, H. Breimer and R. Gohle, Z. Metallkd., 50, (3) (1959) 146–153.
7 H. Okamoto and T.B. Massalski, Binary Alloy Phase Diagrams, American Society for Metals International, 1987, pp. 269–270.
8 O.J. Kleppa, J. Phys. Chem., 60 (1956) 858–865.
9 R. Beja, Alliages binaires liquides des métaux nobles avec les métaux B, Thesis n°A.O. 3656, Univ. Aix-Marseille, France, 1969.
10 K. Itagaki and A. Yazawa, J. Jpn. Inst. Met., 35 (4) (1971) 389–394.
11 R. Castanet, W. Ditz, K.L. Komarek and E. Reiffenstein, Z. Metallkd., 72 (3) (1981) 176–180.
12 B. Gather and R. Blachnik, J. Chem. Thermodyn., 16 (1984) 487–495.
13 K. Itagaki, J. Jpn. Inst. Met., 40 (10) (1976) 1038–1046.
14 P.C. Wallbrecht, R. Blachnik and K.C. Mills, Thermochim. Acta, 48 (1–2) (1981) 69–82.
15 B. Predel and U. Schallner, Z. Metallkd., 63 (H6) (1972) 341–347.
16 K. Kameda, T. Azakami and M. Kameda, J. Jpn. Inst. Met., 38 (5) (1974) 434–439.
17 K.T. Jacob and C.B. Alcock, Acta Metall., 21 (7) (1973) 1011–1016.
18 B. Predel and U. Schallner, Thermochim. Acta, 9 (4) (1974) 433–443.
19 M. Brodowsky and J. Maaz, personal communication, 1984.
20 H.L. Lukas, J. Weiss and E.Th. Henig, Calphad, 6 (1982) 229–251.
21 O. Redlich and A.T. Kister, Ind. Eng. Chem., 40 (1948) 345–348.
22 I. Ansara and B. Sundman, Computer handling and dissemination of data, in P. Glaeser (Ed.), Proc. CODATA Conf., Ottawa, North Holland, Amsterdam, 1986, pp. 154–158.