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Thermodynamic properties of copper–arsenic liquid solutions

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Abstract

Liquid Cu–As solutions containing up to 22 at.% As were examined with the use of the cell: ($-$) Cu (s or l) $\|$KCl + NaCl, $Cu^+$$\|$Cu-As (l)($+$), within the temperature range 1223–1448 K. The isopiestic method was applied to measure the arsenic vapour pressure over the liquid alloys containing 18–40 at.% As in the temperature range 1373–1473 K. The results were combined with enthalpy of mixing to yield an analytical description of the dependence of the components' activity coefficients on temperature and composition. Thermochemical data for solid Cu_3As up to 1100 K were evaluated.

Keywords: Copper; Arsenic; Liquid; Alloys; Activity

1. Introduction

Growing interest in exploring copper ore deposits with low copper content was a reason for research on thermodynamic equilibria in metallic systems including copper and most common ore components: lead, arsenic, nickel and iron. Of these, arsenic is recognized as the most harmful, as it results in a sharp decrease in the electrical conductivity of copper and causes numerous problems with environmental pollution during each stage of processing. Experimental studies of thermodynamic activities of components in liquid Cu–As solutions are possible by means of conventional methods in the range of arsenic concentrations and temperature for which the arsenic pressure does not considerably exceed 1000 hPa. This allows one to work with closed systems, made of silica glass. The principal experimental contribution in this field was made by the Japanese workers Azakami and Yazawa [1] who used the e.m.f. technique with a liquid electrolyte to measure the copper activity over the temperature range 1073–1473 K. Hino and coworkers determined the vapour pressure of arsenic at 1273 and 1423 K over the arsenic concentration range 12–38 at.% using the isopiestic method with an all-silica glass vertical apparatus [2–4] as well as over low arsenic concentrations range (3–10 at.%) at 1423 K by means of mass spectrometry [5]. Other studies by means of transpiration technique were carried out by Bode et al. [6] at 1573 K and low arsenic concentrations not exceeding 2.5 at.% and by Jones and Philipp [7] at 1373 K over the arsenic concentration range 17.4–27.0 at.%.

Using available experimental data, Subramanian and Laughlin [8] assessed the subregular solution model expression for the excess Gibbs energy of the liquid phase. A similar assessment of the mixing thermodynamics in liquid Cu–As solutions was made by Teppo and Taskinen [9]. However, the considerable discrepancies observed between data from various experiments and the small temperature interval covered by experiments is the reason for further studies. The aim of the present work is to re-examine copper and arsenic activities using two complementary methods and to evaluate the appropriate expressions on components' activities in dependence on temperature and composition.

2. Experimental details

2.1. Electrochemical study

The concentration cell with the liquid electrolyte given by

($-$) Cu (s or l)$\|$KCl + NaCl, $Cu^+$$\|$Cu–As($+$)

was applied for copper activity determination in liquid Cu–As alloys. The overall cell reaction is

Cu(pure, s or l) $\longleftrightarrow$ Cu(in liquid solution)

which let the activity of copper be determined as

$$\ln a_{Cu} = -\frac{nFE}{RT} \tag{1}$$

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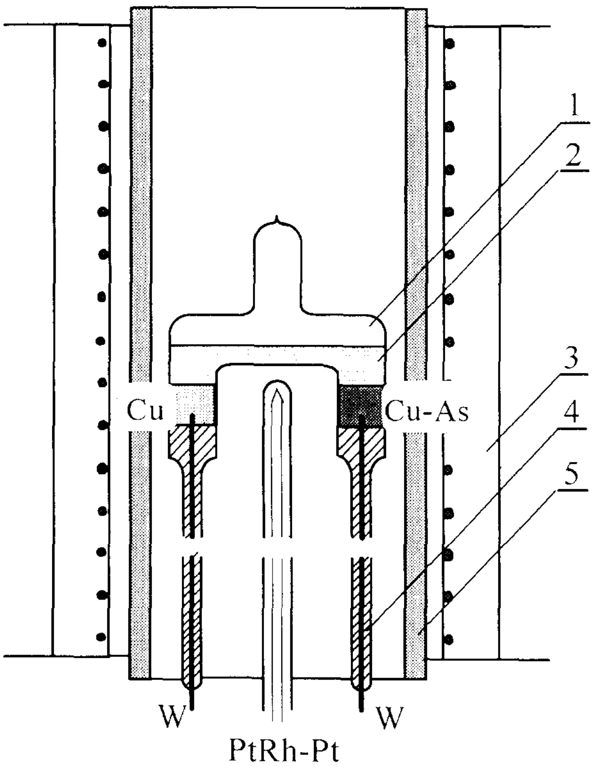

Fig. 1. Cell with liquid electrolyte for e.m.f. measurements: 1, silica glass container; 2, liquid electrolyte; 3, electric furnace; 4, tungsten leads sealed in silica glass; 5, alumina tube.

In the case of the present experiment valence $n=1$, F denotes the Faraday constant (96487.0 J V^{-1} per equivalent), E is the value of equilibrium e.m.f. of the cell, R is the gas constant (8.3143 J mol^{-1} K^{-1}) and T is the temperature. The e.m.f. method is frequently used in metallurgical research but in the case of Cu–As alloys is connected with serious difficulties. The cell has to be sealed under vacuum to prevent the oxidation of Cu^+ cations to Cu^{2+} and to reduce the evaporation of arsenic from the Cu–As electrode. The electric leads made of tungsten had to be joined with silica glass to produce vacuum-tight seals. The schematic diagram of the cell used in this study is shown in Fig. 1. The main part of the cell was made of a silica glass tube of 10 mm inner diameter. The upper tube was about 100 mm long and it served for loading the cell. Next, it was connected to the pump and the whole cell was evacuated to 10^{-2} Pa and sealed off. The cell was placed in a vertical resistance furnace in the zone of uniform temperature and was slowly heated to the desired temperature. After 1 h equilibration period the e.m.f. of the cell was recorded by means of a V-544 digital voltmeter (Meratronic, Poland). The samples of Cu–As alloys of required composition were obtained from pure copper and arsenic–copper matrix alloys produced in fused silica ampoules using an "isopiestic" procedure, which is described in Section 2.2. The salt mixture was carefully dried before experiment.

2.2. Vapour pressure measurements

The "isopiestic" method is based on the equilibration of liquid arsenic in the solution with gaseous arsenic, generated by solid–gas equilibrium in the compartment at the lower temperature. Arsenic vapour consists of four kinds of particle: As, As_2, As_3 and As_4. The equilibrium condition for isopiestic experiment, schematically demonstrated in Fig. 2, is the following:

$$P_{\mathrm{As}(T_1)}+P_{\mathrm{As}_2(T_1)}+P_{\mathrm{As}_3(T_1)}+P_{\mathrm{As}_4(T_1)}$$
$$=P_{\mathrm{As}(T_2)}+P_{\mathrm{As}_2(T_2)}+P_{\mathrm{As}_3(T_2)}+P_{\mathrm{As}_4(T_2)}=P_{\mathrm{total}} \qquad (2)$$

The equilibration was carried out in an evacuated silica capsule. Compartment 1 contained pure arsenic, and compartment 2 copper and arsenic. The capsule was placed along the axis of a horizontal furnace with a known temperature gradient. During the stationary operation of the furnace, compartment 1 remained at the temperature T_1, and compartment 2 at T_2. The total pressure of arsenic in the system was fixed by the temperature T_1 of the solid arsenic source. The partial pressures of arsenic species at temperature T_2 result from the equilibrium constants of corresponding reactions, which were evaluated in a previous publication [10] from the data of Gokcen [11]. The equilibrium constants may be calculated from the relation

$$\log K=\frac{A}{T}+B\log T+CT+D \qquad (3)$$

The appropriate parameters in Eq. (3) are collected in Table 1.

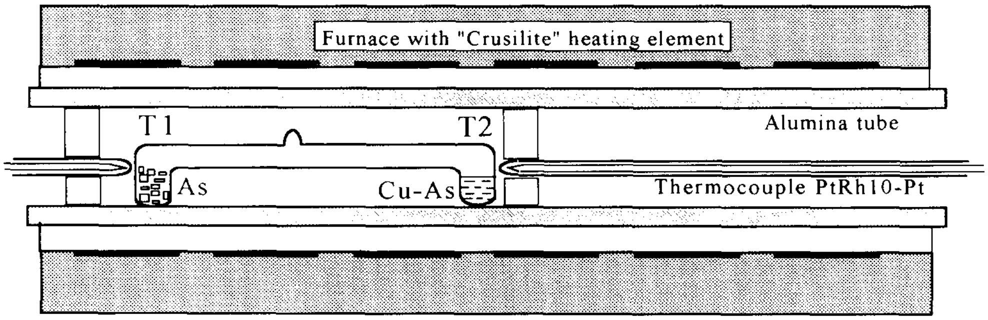

Fig. 2. Arrangement for 'isopiestic' measurements.

The capsule, schematically shown in Fig. 2, was made of silica tube, of 12 mm outer diameter. The total length of the cells was 28–36 cm. Weighed amounts of pure copper and pure arsenic were placed in appropriate compartments of the capsule. The tubes were sealed under vacuum as low as 10^{-2} Pa. The temperature in the furnace was maintained constant for 24–144 h depending on the temperature T_1 of the arsenic source and the resulting transport rate. The heating element was silicon carbide Crusilite MF, of 62 mm outer diameter. The temperature was stabilized during the required period by means of a PID controller model 3304 produced by Wilmer, Poland, operating through a transformer–thyristor power unit.

The variation in temperature during the whole run did not exceed 1 K for T_1 and 2 K for T_2. The temperatures T_1 and T_2 were measured with two Pt–(Rh–10Pt) thermocouples, placed close to the corresponding compartments of the cell. The unprotected thermocouple junctions were in touch with the walls of silica cells. Both thermocouples were calibrated. A low temperature thermocouple operating at the arsenic source was checked against the melting points of high purity (99.999%) tin and zinc, while a high temperature thermocouple was checked against the melting point of copper.

After the necessary exposure period the samples were rapidly removed from the furnace and cooled in liquid nitrogen. The mass of alloy samples obtained was 2–3 g. The concentration of arsenic in the sample was calculated from the mass balance. The chemical analysis of the chosen samples was carried out in Outokumpu Oy Laboratory in Pori (Finland) with the use of the atomic absorption technique. The results presented in Table 3 later proved that the mass balance yields accurate values of arsenic equilibrium concentration in the sample.

Table 1
Data on the equilibrium between arsenic species in gaseous and condensed phases

Reaction		*A*	*B*	$C \times 10^4$	*D*
(I)	$As_4(g) = 4\ As(g)$	−51760.8	0.48971	−0.9007	17.9297
(II)	$As_3(g) = 3\ As(g)$	−32239.5	0.30134	−0.5737	10.2499
(III)	$As_2(g) = 2\ As(g)$	−19892.6	0.68869	−0.3346	3.6403
(IV)	$As(s) = As(g)$	−15045.4	−0.31047	−0.9582	8.1968
(V)	$As(s) = As(l)$	−13888.3	−0.57404	−0.6622	7.903

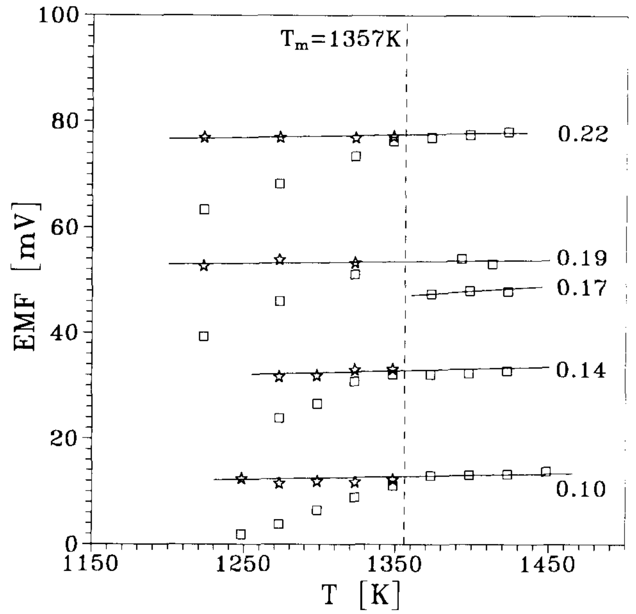

Fig. 3. Results of e.m.f. measurements: ☆, data obtained with a solid copper reference electrode and recalculated to a liquid reference; □, data obtained directly from experiments with a liquid reference.

2.3. Materials

The arsenic was of 99.999% purity from Asarco, USA and additionally distilled under vacuum; the copper was MOOB grade of 99.99% purity from Hutmen, Wrocław, Poland; the sodium chloride (NaCl) was reagent grade (purity, 99.5%) from POCh-Gliwice, Poland; the potassium chloride (KCl) was reagent grade (purity, 99.5%) from POCh-Gliwice, Poland; the cuprous chloride (CuCl) was reagent grade (purity, 99.5%) from Reachim, Russia.

3. Results

3.1. Copper activity from e.m.f. measurements

The experiments were carried out for five alloy compositions, as indicated in Table 2. The results of the e.m.f. measurements are shown in Fig. 3. Below the melting point of copper the cell worked with a solid copper reference electrode. The e.m.f. values obtained for this region were con-

Table 2
Results of e.m.f. measurements: $E = \alpha + \beta T$

Experiment	X_{As}	α	$\beta \times 10^2$	$E_{1373\ K}$ (mV)	$a_{Cu,1373\ K}$	$\ln \gamma_{Cu,1373\ K}$
1	0.10	−0.22	0.9353	12.62	0.8988	−0.00133
2	0.14	+27.54	0.3737	32.67	0.7586	−0.12546
3	0.17	+30.06	1.2727	47.53	0.6691	−0.21549
4	0.19	+50.08	0.2758	53.87	0.6342	−0.24467
5	0.22	+77.05	0.4559	83.31	0.4944	−0.45595

Table 3
Results of isopiestic experiments; where ${X_{As}}^{(a)}$ are obtained from chemical analysis, while ${X_{As}}^{(b)}$ are calculated from mass balance

Experiment	T_1 (K)	T_2 (K)	τ (h)	${X_{As}}^{(a)}$	${X_{As}}^{(b)}$	a_{As}	$\ln \gamma_{As}$
1	549	1373	144	0.254	0.247	1.097×10^{-3}	−5.417
2	540	1373	144		0.174	8.286×10^{-4}	−5.347
3	555	1373	144		0.193	1.314×10^{-3}	−4.989
4	568	1373	120		0.197	1.918×10^{-3}	−4.632
5	567	1373	120		0.251	1.865×10^{-3}	−4.902
6	622	1373	72		0.278	7.685×10^{-3}	−3.588
7	706	1373	36	0.320	0.316	4.170×10^{-2}	−2.025
8	763	1373	24		0.366	9.709×10^{-2}	−1.297
9	804	1373	24		0.368	1.534×10^{-1}	−0.915
10	732	1423	36		0.315	5.338×10^{-2}	−1.775
11	803	1423	24		0.360	1.356×10^{-1}	−0.977
12	563	1473	96	0.227	0.224	1.129×10^{-3}	−5.290
13	613	1473	72		0.252	4.267×10^{-3}	−4.079
14	722	1473	48		0.302	3.841×10^{-2}	−2.062
15	739	1473	48		0.319	5.048×10^{-2}	−1.844
16	816	1473	24		0.357	1.383×10^{-1}	−0.948

verted to represent the reaction involving liquid copper with the use of the Gibbs energy change on melting for copper [12]:

$$\Delta G^0_{Cu(s\rightarrow l)} = 13050 - 9.62T \text{ J mol}^{-1} \qquad (4)$$

The converted e.m.f. data were used together with those obtained for a liquid copper reference electrode to yield linear e.m.f. vs. temperature dependences for various alloy compositions. The results of e.m.f. measurements and calculated activity coefficients of Cu at 1373 K are presented in Table 2.

3.3. Activity coefficient of arsenic from isopiestic measurements

The given temperature T_1 of the arsenic source and the given temperature T_2 of the liquid alloy determine the value of arsenic activity in liquid solution. The activity may be alternatively defined as

$$a_{As} = \frac{P_{As(T_2)}}{P^0_{As(T_2)}} = \left(\frac{P_{As_2(T_2)}}{P^0_{As_2(T_2)}}\right)^{1/2} = \left(\frac{P_{As_3(T_2)}}{P^0_{As_3(T_2)}}\right)^{1/3} = \left(\frac{P_{As_4(T_2)}}{P^0_{As_4(T_2)}}\right)^{1/4} \qquad (5)$$

The partial pressures of gaseous arsenic species at temperature T_1 may be calculated from the equilibrium constants given in Table 1.

$$P_{As(T_1)} = K_{IV(T_1)} \qquad (6)$$

$$P_{As_2(T_1)} = \frac{{P_{As(T_1)}}^2}{K_{III(T_1)}} \qquad (7)$$

etc. The total pressure P_{total} in the cell, which is represented by the left-hand side of Eq. (2) is determined by the arsenic source temperature T_1. The partial pressures of four gaseous arsenic species at temperature T_2 were calculated from Eq. (8):

$$P_{total} = X + \frac{X^2}{K_{III(T_2)}} + \frac{X^3}{K_{II(T_2)}} + \frac{X^4}{K_{I(T_2)}} \quad X = P_{As(T_2)} \qquad (8)$$

From four solutions of Eq. (8), only one has the physical meaning of monoatomic arsenic partial pressure. Thus the values of arsenic activities, with solid arsenic as a standard, were calculated at given T_1 and T_2 from Eq. (5). To convert to liquid arsenic as a standard state, the Gibbs free energy of melting for arsenic after Gokcen [11] was used:

$$\Delta G^0_{As(s\rightarrow l)} = R(2698.3 - 0.156T \ln T - 1.3844T) \qquad (9)$$

The arsenic activities obtained are shown in Table 3. They are combined with arsenic concentration in alloys to yield the activity coefficients. In the present work, Eq. (8) was arranged with respect to As particles. However, any other particle, e.g. As_4, may be used in Eqs. (5) and (8), which would result in the same values of calculated activities. The values of arsenic activity coefficients obtained in isopiestic experiments are shown in Fig. 4 in comparison with the experimental data of Azakami and Hino [4]. Their tabulated values of T_1, T_2 and X_{As} were recalculated using the set of equilibrium constants collected in Table 1. Such a procedure was necessary, as in [2–4] the set of equilibrium constants from Hultgren's [13] monograph were used and these were improved by later studies on arsenic vapour composition [14–17]. The results obtained in the present paper are lower and show an increased scatter for arsenic concentrations close to $X_{As} = 0.25$.

4. Data treatment and discussion

The results on the arsenic activities obtained from isopiestic technique as well as the copper activities from e.m.f.

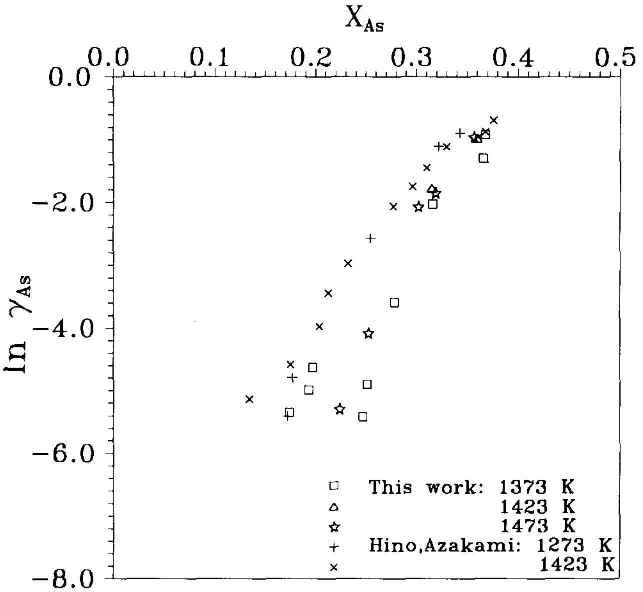

Fig. 4. Comparison of experimental results on the arsenic activity coefficient in Cu–As alloys.

measurements were combined to obtain the description of liquid Cu–As solutions, i.e. temperature- and composition-dependent relations for the activity coefficients of Cu and As. The additional information may be deduced from the only available experimental data on the heat of mixing [18], which were obtained by direct synthesis drop calorimetry.

The formalism used for description of the activity coefficients of components is that of Fitzner [19,20], who has improved the method of Krupkowski [21]:

$$\ln \gamma_{As}=\left(\frac{a}{T}+b\right)\left((1-X_{Cu})^{m}-\frac{m}{m-1}(1-X_{Cu})^{m-1}+\frac{1}{m-1}\right)+\left(\frac{c}{T}+d\right)\left((1-X_{Cu})^{m+1}-\frac{m+1}{m}(1-X_{Cu})^{m}+\frac{1}{m}\right) \quad (10)$$

$$\ln \gamma_{Cu}=\left(\frac{a}{T}+b\right)(1-X_{Cu})^{m}+\left(\frac{c}{T}+d\right)(1-X_{Cu})^{m+1} \quad (11)$$

These relations were successfully used in the case of Pb–As liquid solutions [22]. They were employed in the present work for two main reasons: the fulfilment of the Gibbs–Duhem equation and simple extension to the multicomponent systems. The parameters in Eqs. (10) and (11) were obtained by fitting them simultaneously to the experimental data from the present work, i.e. copper and arsenic activities and temperature independent heat of mixing at $X_{As}=0.25$ taken from [18]. The limiting value of ln γ_{As} at 1373 K was obtained from Darken's α function derived for both components. The following parameters of Eqs. (10) and (11) are obtained: $a=-9675.958$; $b=-11.8742$; $c=3931.611$; $d=15.0552$; $m=2.283$. The plots of Eqs. (10) and (11) together with experimental points from the present work regarding a temperature of 1373 K are presented in Fig. 5. The main features of the obtained functions are as follows: (1) a strong negative deviation from ideality for arsenic at low concentrations; (2) a positive deviation for arsenic for its concentrations above $X_{As}=0.6$; (3) a negative deviation for copper over the whole composition range; (4) a weak temperature dependence of ln γ for both components.

The experimental data obtained, together with the results of other workers, are still insufficient for setting a reliable temperature dependence, as may be seen from Figs. 4 and 5. It may be also observed that the experimental points of ln γ_{As} from the present work show a difference in comparison with the plot of Eq. (10). However, the curves of Eqs. (10) and (11) are the effect of compromise, as they also result from the copper activities from e.m.f. experiments, the heat of mixing, the limiting value of activity coefficient from Darken's method and the positive value of arsenic at its higher concentrations. The data of Hino and Azakami for 1423 K are also given for comparison in Fig. 5. They are perhaps in better agreement with the curve of Eq. (10) but the aim of the present work was to use only the present author's own data. The ln γ vs. composition dependence suggested by Teppo and Taskinen [9] shows less negative values for arsenic at 1373 K, which is due to the difference between the results from the present work and those of [2–4], demonstrated in Figs. 4 and 5. Two features of the ln γ_{As} characterization given in [9] can be hardly justified, i.e. the minimum at low arsenic concentrations and the negative values at higher arsenic concentrations.

The values of arsenic activities set by the temperatures of arsenic source and liquid alloy is strongly affected by the choice of equilibrium constants of reactions (I)–(V) (Table 1). The obtained Eqs. (10) and (11) describing activity coefficients of arsenic and copper may be used in updating the thermochemical data of the congruently melting compound Cu_3As. The standard enthalpy of formation of Cu_3As

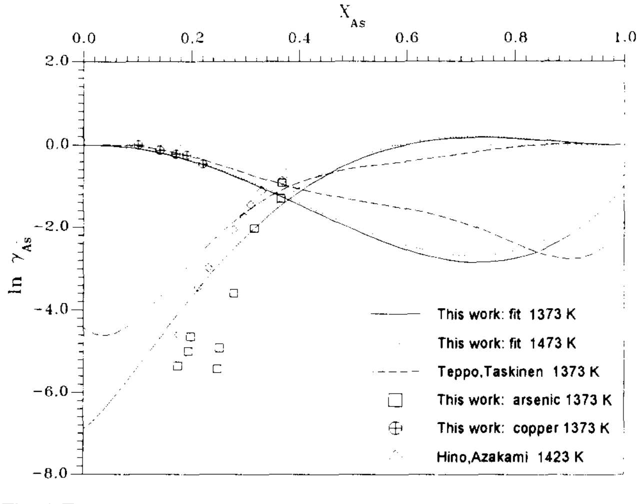

Fig. 5. Evaluated activity coefficients of components in Cu–As liquid solution.

Table 4
Recommended thermochemical data for Cu_3As where the estimated data are given in parentheses

T (K)	C_p ($J\ mol^{-1}\ K^{-1}$)	H^0 ($J\ mol^{-1}$)	S^0 ($J\ mol^{-1}\ K^{-1}$)	G^0 ($kJ\ mol^{-1}$)
298.15	93.08	−14634	(182)	(−69.0)
300	93.14	−14448	(183)	(−69.4)
400	96.15	−4984	(210)	(−89.1)
500	99.16	4782	(232)	(−111.2)
600	102.17	14849	(250)	(−135.4)
700	105.19	25217	(266)	(−161.2)
800	108.20	35886	(281)	(−188.6)
900	111.21	46856	(294)	(−217.3)
1000	114.22	58127	(305)	(−247.2)
1100	117.23	69690	(316)	(−278.3)

as given by Weibke and Kubaschewski [23] on the basis of Savelsberg's [24] work (-26.8 kJ (g-atom)$^{-1}$) differs considerably from that obtained recently by Wypartowicz et al. [18]: -14.6 kJ mol^{-1} (i.e. -3.65 kJ (g-atom)$^{-1}$). This last value together with the heat capacity data given by Barin et al. [12] were used to calculate corrected values of enthalpy $H_T{}^0$ for Cu_3As. Since the standard entropy $S_{298}{}^0$ of Cu_3As, given by Barin et al. is apparently estimated on the basis of the Latimer rule, it was also corrected. In the present work the estimation of entropy of Cu_3As formation is based on the equality of the Gibbs energy of formation of solid and liquid compounds at the point of congruent melting, 1100 K:

$$\Delta G^0_{f,Cu_3As(s)} = \Delta H^0 - T\,\Delta S^0 = \Delta G^0_{f,Cu_3As(l)} = 3RT \ln a_{Cu} + RT \ln a_{As} \qquad (12)$$

Thus the obtained value of the entropy change on formation of Cu_3As at 1100 K is -6.18 J mol^{-1} K^{-1} (estimated accuracy, ± 1 J mol^{-1} K^{-1}) and this was the starting point of the entropy calculation. This value depends on the activity coefficients of arsenic and copper resulting from Eqs. (10) and (11) obtained in the present work. The complete set of recommended thermochemical data for Cu_3As is given in Table 4. To check the compatibility of Eqs. (10) and (11) and the recommended data in Table 4, the course of the liquidus line was calculated with the simplifying assumptions that Cu_3As is the line compound, neglecting the '$Cu_{2.5}As$' compound, and assuming the α solid solution on the Cu-rich side to be ideal. The copper-rich branch of the liquidus was obtained from Eqs. (4) and (11). The part of the liquidus in the region of Cu_3As was calculated from Eq. (12). The activities of components were from Eqs. (10) and (11). The Gibbs free energy of formation for solid Cu_3As was interpolated from data in Table 4 and combined with the enthalpy and entropy for arsenic from [11] and those for copper from Barin [12]. The results of such calculations are shown as open squares in Fig. 6 in comparison with accepted phase diagram from the monograph by Massalski [25]. Since the aim of the present work was to describe the properties of the liquid phase, such agreement may be considered satisfactory. There are still not sufficient data regarding arsenic activity over the wide concentration range to reproduce the entire liquidus with Eqs. (10) and (11).

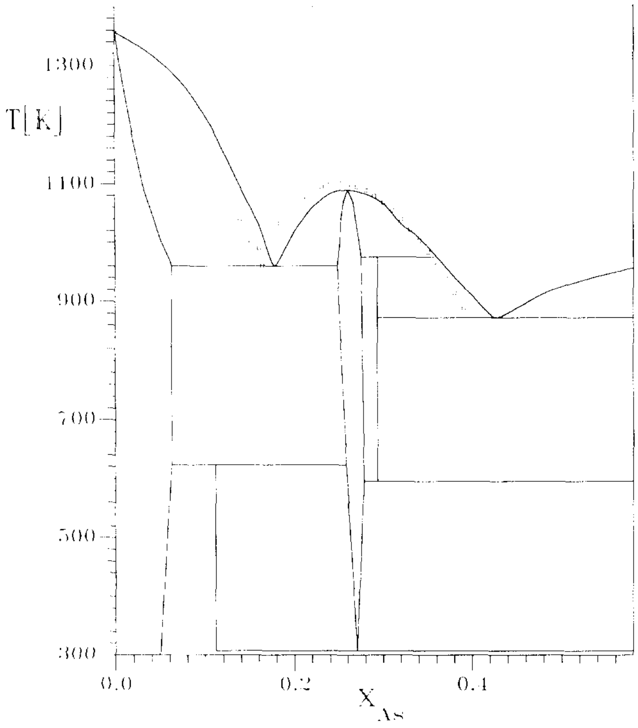

Fig. 6. Calculated parts of the liquidus in the Cu–As system (□).

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