

CHEMICAL THERMODYNAMICS  
 AND THERMOCHEMISTRY

A Thermodynamic Description of the Barium–Copper System

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Received January 31, 1995

**Abstract**—Combined treatment of experimental liquidus temperatures, nonvariant equilibrium temperatures, and the thermodynamic properties of the phases occurring in the Ba–Cu system was performed to obtain expressions for the Gibbs energies of melts and the intermetallic phases BaCu and BaCu<sub>13</sub>. These results were used to calculate the phase diagram that most closely agreed with all available measurement data on the Ba–Cu system.

The purpose of this work was to obtain a consistent thermodynamic description or, as is often put, optimize the phase diagram of the Ba–Cu system. This implies combined treatment of all available experimental data to determine the Gibbs energies for the phases occurring in the Ba–Cu system.

INITIAL EXPERIMENTAL DATA

In [1, 2] (a detailed review of these works is given in [3]), the phase diagram of the Ba–Cu system was studied with the thermal analysis method by taking measurements during cooling melts (Fig. 1). Two compounds (BaCu and BaCu<sub>13</sub>) with negligibly narrow solid solution regions were found to occur in the sys-

tem. The mutual solubility of the metals is also low. In [4], liquidus temperatures and the temperatures of nonvariant equilibria in the phase diagram of the Ba–Cu system were remeasured to obtain the results that closely agreed with those reported in [1, 2]. The most important difference was in the temperature of peritectic decomposition of BaCu<sub>13</sub>. It was shown in [4] by measuring heating curves that in the region of BaCu<sub>13</sub>, supercooled melts were easily formed, which was probably the reason why too low peritectic decomposition temperature was determined in [1, 2] by cooling melts.

The partial enthalpies of solution of the metals (Fig. 2) were determined in [5, 6]. The data of these works contradict each other: the partial enthalpies of solution of

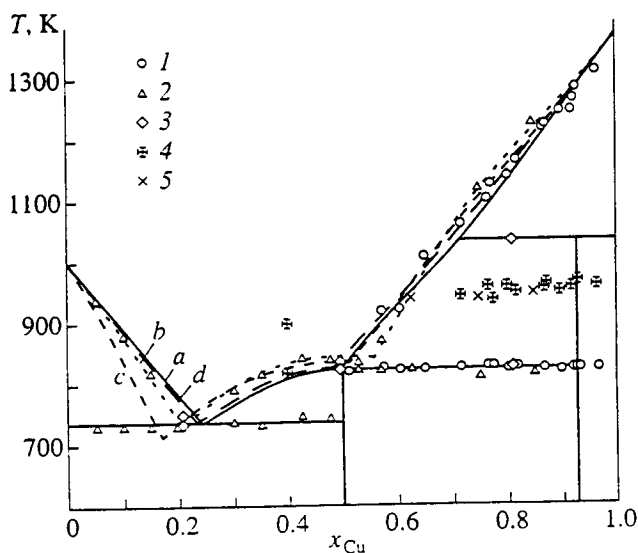


Fig. 1. Phase diagram of the Ba–Cu system. Experimental data used in treatment: (1) [1], (2) [2], and (3) [4]; data not used in treatment: (4) [1] and (5) [2]; the calculated curves: (a) this work, (b) [3], (c) [11], and (d) [4].

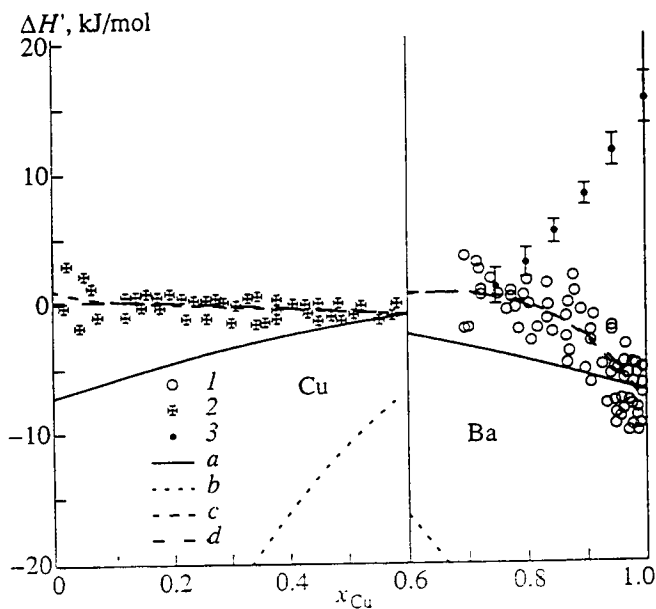
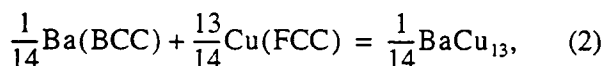


Fig. 2. Partial enthalpies of solution of the components. Experimental data: (1) and (2) [5] and (3) [6]; (a)–(d) as in Fig. 1.

barium and copper have different signs. The reasons for the discrepancies are unclear, but it appears that the thermal effects of the formation of Ba–Cu alloys are not large. As concerns the thermodynamic properties of the BaCu and BaCu<sub>13</sub> intermetallic compounds, the enthalpy of formation of BaCu only is known. This value was determined by solution calorimetry in [4].

*Thermodynamic models of phases.* Following [1, 2], the mutual solubilities of solid metals and the region of homogeneity of intermetallic compounds were considered as negligibly small. The Gibbs energies of barium and copper were taken from [7]. The Gibbs energies of the compounds and melts were calculated with the approximation of zero heat capacity changes in the formation of the phases



$\Delta C_p(1) = \Delta C_p(2) = 0$ , and the Gibbs energy of melts was described by the Reidlich–Kister equation

$$\Delta_{\text{mix}}G = x_{\text{Ba}}RT \ln x_{\text{Ba}} + x_{\text{Cu}}RT \ln x_{\text{Cu}} + \sum_i x_{\text{Ba}} x_{\text{Cu}} (A_i + B_i T) (x_{\text{Cu}} - x_{\text{Ba}})^i, \quad (3)$$

where  $x_{\text{Ba}}$  and  $x_{\text{Cu}}$  are the mole fractions of barium and copper,  $T$  is the temperature,  $R$  is the universal gas constant, and  $A_i$  and  $B_i$  are the interaction parameters. The enthalpies and entropies of reactions (1) and (2) and the unknown interaction parameters  $A_i$  and  $B_i$  in equation (3) for the Gibbs energy of melts had to be determined. The vector of the unknowns will further be denoted as  $\Theta$ .

*Statistical treatment of experimental data.* Combined treatment of the available experimental data was performed using the method called “nonlinear physico-chemical model + linear error model” [8]. All experimental values were assumed to fit the equation

$$y_{ij} = f_i(x_{ij}, \Theta) + \varepsilon_{ij}, \quad (4)$$

where index  $i$  numbered experiments, index  $j$  numbered experimental points obtained in experiment  $i$ , and the vector  $\Theta$  components were the unknown values. In various experiments,  $y$  and  $x$  corresponded to different physical values (temperature and composition, enthalpy of solution and composition, etc.) with different functional dependences  $f_i$  between them.

In the description of the phase diagram, the dependences for liquidus temperatures and the temperatures

of nonvariant equilibria were written in terms of the direct minimization method (see, e.g., [9]):

$$T_{ij,\text{mono}} = T_{ij}^{\text{calcd}} \{x_{ij}, \Theta\} + \varepsilon_{ij}, \quad (5)$$

$$T_{ij,\text{non}} = T_{ij,\text{non}}^{\text{calcd}} \{\Theta\} + \varepsilon_{ij}, \quad (6)$$

where the indices “mono” and “non” refer to liquidus curve points and nonvariant point temperatures, respectively, and  $x_{ij}$  is the mole fraction of copper in the melt. At given parameter values, the calculated temperatures of liquidus curve points and nonvariant points,  $T_{ij,\text{mono}}^{\text{calcd}}$  and  $T_{ij,\text{non}}^{\text{calcd}}$ , respectively, were found from the equations

$$G_{m,\text{Ba,BCC}}(T) = \mu_{\text{Ba},1}(T, x, A_i, B_i),$$

$$G_{m,\text{Cu,FCC}}(T) = \mu_{\text{Cu},1}(T, x, A_i, B_i),$$

$$G_{m,\text{BaCu}} \{T, \Delta H(1), \Delta S(1)\} = \mu_{\text{Ba},1}(T, x, A_i, B_i) + \mu_{\text{Cu},1}(T, x, A_i, B_i),$$

$$G_{m,\text{BaCu}_{13}} \{T, \Delta H(2), \Delta S(2)\} = \mu_{\text{Ba},1}(T, x, A_i, B_i) + 13\mu_{\text{Cu},1}(T, x, A_i, B_i).$$

These equations were solved numerically by the Newton–Rafson method.

In addition to (5) and (6), the combined treatment included the thermodynamic data on the partial enthalpies of mixing,

$$\Delta H'_{\text{Ba},ij} = \Delta H_{\text{Ba},ij}^{\text{calcd}} \{T, x_{ij}, A_i\} + \varepsilon_{ij}, \quad (7)$$

$$\Delta H'_{\text{Cu},ij} = \Delta H_{\text{Cu},ij}^{\text{calcd}} \{T, x_{ij}, A_i\} + \varepsilon_{ij} \quad (8)$$

and the enthalpies of reaction (1)

$$\Delta H(1)_{ij} = \Delta H(1)^{\text{calcd}} + \varepsilon_{ij}. \quad (9)$$

In comparison with the other works concerned with phase diagram optimizations, the special feature of this one is the error model. In conformity with the method described in [8], it was assumed that total error  $\varepsilon_{ij}$  in (5)–(9) included several components and obeyed the equation

$$\varepsilon_{ij} = \varepsilon_{r,ij} + \varepsilon_{a,i} + \varepsilon_{b,i}(x_{ij} - x_i), \quad (10)$$

where  $x$  is the mean  $x_{ij}$  value in the  $i$ th experiment,  $\varepsilon_{r,ij}$  is the reproducibility error proper, and the  $\varepsilon_{a,i}$  and  $\varepsilon_{b,i}$  values correspond to systematic shift (calibration) and rotation (trend) errors in the  $i$ th series. The typical dependence of total errors  $\varepsilon_{ij}$  for some  $i$ th series is shown in Fig. 3. Equation (10) can be given the graphic interpretation

$$FC = FE + DC + ED.$$

Because of the presence of systematic errors  $\epsilon_{a,i}$  and  $\epsilon_{b,i}$ , which are constant in the  $i$ th series of measurements and only vary from one series to another, the total errors are scattered about the dashed line in Fig. 3, which is shifted and rotated with respect to the line corresponding to the recommended functional equation for  $f_i$ .

It was assumed that the  $\epsilon_{r,ij}$ ,  $\epsilon_{a,i}$ , and  $\epsilon_{b,i}$  errors were independent random values with zero mathematical expectations and variances equal to  $\sigma_{r,i}^2$ ,  $\sigma_{a,i}^2$ , and  $\sigma_{b,i}^2$ , respectively. The unknown physicochemical model parameters (vector  $\Theta$ ) and variances were determined using the maximum likelihood method by maximizing the expression

$$L = -\ln\{\det[D(\epsilon)]\} - \epsilon'D(\epsilon)^{-1}\epsilon, \quad (11)$$

where  $\epsilon$  is the vector of the complete residuals  $\epsilon_{ij} = y_{ij} - f_i(x_{ij}; \Theta)$  with respect to the unknown physicochemical parameters and the variances of the error components. The right-hand side of (11) is written on the assumption of a normal distribution of error components  $\epsilon_{r,ij}$ ,  $\epsilon_{a,i}$ , and  $\epsilon_{b,i}$ . The algorithm of search for the maximum of  $L$  within the framework of the employed error model is described in [8].

Several calculations with different numbers of unknown parameters were performed. The recommended solution (Tables 1 and 2), the calculated non-

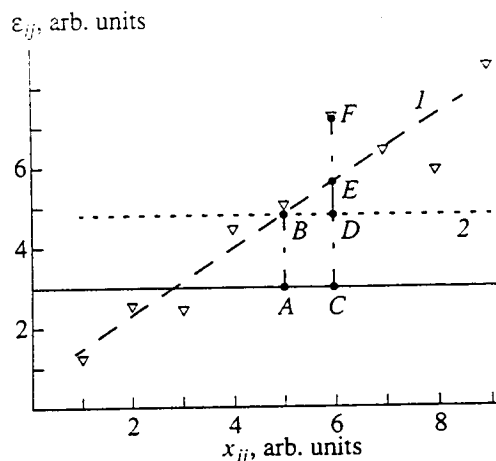


Fig. 3. Typical behavior of total errors  $\epsilon_{ij}$  for the  $i$ th series of experimental data with respect to the recommended solution; symbols are errors, (1) the best curve describing errors and (2) the best curve describing errors and parallel to the recommended solution, point A corresponds to the mean  $x_{ij}$  value in this series.

variant points of the system (Table 3) were obtained by the optimization involving four unknowns, namely, two enthalpies of reactions (1) and (2) and two melt interaction parameters  $A_0$  and  $B_0$ . The entropies of reactions (1) and (2) were set equal to zero in the model that we used from consideration of the known patterns for solid-state

Table 1. Enthalpies (J/mol) and entropies [J/(mol K)] of reactions (1) and (2)

Method	$-\Delta H^\circ (1)$	$-\Delta S^\circ (1)$	$-\Delta H^\circ (2)$	$-\Delta S^\circ (2)$
Calculations [13]	19829	18.758	4265.0	3.801
Calculations [11]	22208	19.705	2885	1.856
Calculations [4]	2679.41	0.25394	1016.90	0.0*
Experiment [4]	$2597 \pm 3915$			
Calculations (this work)	2594	0.0*	924.6	0.0*

\* The parameter was fixed in calculations.

Table 2. The thermodynamic properties of Ba-Cu melts [coefficients in (3)] according to this work and the data of [3, 4, 11]

Data	$-A_0$	$A_1$	$-A_2$	$-A_3$	$B_0$	$B_1$	$B_2$	$B_3$
	J/mol				J/(mol K)			
[3]	45121.5	1143	0*	0*	42.86	0*	0*	0*
[11]	764.8	-2595.8	2879.6	1970.9	-18.96614	16.93798	0*	0*
[4]	713.94	-2798.20	2905.60	990.44	-5.79964	5.29005	3.47621	0*
I	7191	0*	0*	0*	3.363	0*	0*	0*

\* The parameter was fixed in calculations.

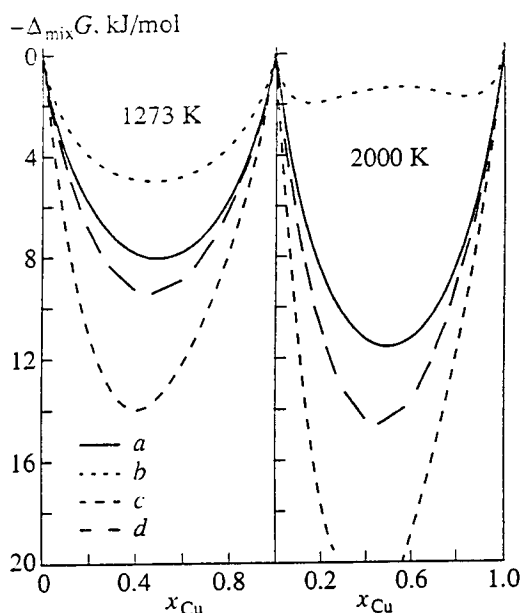


Fig. 4. Gibbs energies of mixing of liquid Ba-Cu alloys, (a)-(d) as in Fig. 1.

reactions [10]. The procedure for selecting the optimal number and the details of statistical treatment will be described in a separate communication.

## RESULTS AND DISCUSSION

Thermodynamic descriptions of the Ba-Cu phase diagram were given in [3, 4, 11]. The primary experimental data and the results of their treatment are shown in Figs. 1 and 2. The thermodynamic properties of the intermetallic compounds are summarized in Tables 1 and 2, and the nonvariant points are listed in Table 3. The Gibbs energies of mixing Ba-Cu melts are shown in Fig. 4.

The existing descriptions of the phase diagram of the Ba-Cu system on the whole correctly reproduce experimental liquidus temperatures and the temperatures of nonvariant equilibria and are close to each other (see Fig. 1 and Table 3). The principal difference between the results reported in [3, 11] and those of [4]

and the present work is in the peritectic decomposition temperature of  $\text{BaCu}_{13}$ . The descriptions given in [3, 11] are based on the experimental results obtained in [1, 2], whereas the description suggested in [4] and this work uses the data of [4], which we believe to be more reliable. In the other phase diagram regions, the least accurate results are those reported in [11]. For instance, the eutectic temperature Ba-L-BaCu calculated in [11] equals 710 K, which is noticeably lower than the experimental value of 731 K [2]. The description of the barium branch of the liquidus curve is also unsatisfactory.

The differences in the partial enthalpies of solution (Fig. 2), the thermodynamic properties of intermetallic compounds (Table 1), and the Gibbs energies of mixing of melts (Fig. 4) are far more pronounced. At the time of work [3], there were no experimental data on the enthalpies of solution, and their values were determined exclusively from the phase diagram. There is, therefore, nothing surprising in that the predicted enthalpies were noticeably different from the experimental ones. The enthalpies reported in [4, 11] are based on the experimental data given in [5] and reproduce them well. In this work, newly obtained data [6] differing from [5] are taken into account. Additional experiments are needed to give preference to either [5] or [6], and the thermal effects of the formation of liquid alloys were therefore set equal to zero.

The authors of work [3] did not pay necessary attention to the obtained thermodynamic description of melts: they did not check the behavior of the suggested dependence of the Gibbs energy of the melt on the composition at high temperatures and failed to notice that the suggested set of parameters predicts melt stratification with a  $\sim 1900$  K lower critical temperature (see Fig. 4). This type of stratification is very uncharacteristic of metallic alloys [12].

## ACKNOWLEDGMENTS

The author is thankful to G.F. Voronin, V.A. Lysenko, and I.A. Zaitsev for fruitful discussions and to the International Science Foundation for financial support (Grant MRL000).

Table 3. Nonvariant equilibria in the Ba-Cu system according to this work (I) and the data of [3, 4, 11]

Data	Ba-L-BaCu		BaCu-L-BaCu <sub>13</sub>		BaCu		BaCu <sub>13</sub> -L-Cu	
	T, K	x <sub>Cu</sub>	T, K	x <sub>Cu</sub>	T, K	x <sub>Cu</sub>	T, K	x <sub>Cu</sub>
[3]	731	0.206	823	0.550	843	0.5	943	0.632
[11]	710	0.170	832	0.520	833	0.5	934	0.612
[4]	731	0.239	823	0.494	829	0.5	1031	0.704
I	734	0.248	821	0.502	821	0.5	1031	0.717

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