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Invited article

Thermodynamics of the Cu–Bi system determined by vapour pressure measurements

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ABSTRACT

Application of Knudsen method for solid and liquid copper in the temperature range 1300–1725 K, liquid bismuth in temperatures 769–1129 K, and liquid Cu–Bi alloys in temperatures from 871 to 1469 K, provided experimental data which made it possible to characterize thermodynamic properties of liquid and gaseous phase of Cu–Bi system. Standard enthalpies of copper and bismuth monomers sublimation and dissociation of bismuth dimer as well as parameters of Regular Associated Solution model (RAS), describing excess Gibbs energy of liquid phase of the examined system, were determined. The obtained model takes into account also presence of disturbances in vaporization of bismuth dimer from Cu–Bi alloys by introducing into the model a parameter which describes the evaporation coefficient of that particle.

1. Introduction

Thermodynamic properties of liquid Cu–Bi alloys had been investigated in numerous research studies [1–4]. However, there are still significant discrepancies in the literature, both with respect to molar enthalpy of mixing [1,5–9] and to thermodynamic activity of components [1,6,9–18]. Also significant differences in the data of phase diagram of that system can be observed [7,9,19–25]. Additionally, characteristics of bismuth gaseous phase contains some discrepancies, mainly with respect to partial pressures of individual components of that phase [26–32]. The objective of the presented study, based on the authors' experimental data reached by Knudsen method, was to provide a description of thermodynamic properties of the two mentioned above phases of Cu–Bi system.

2. Experimental

2.1. Sample preparation

In the studies samples of solid and liquid copper, liquid bismuth, and liquid Cu–Bi alloys were investigated. The liquid alloys were obtained by melting of pure components of the system, directly prior to measurements. Copper of purity of 99.999 mass%, supplied by Institute of Electronic Materials Technology, Warsaw, and bismuth of the purity of 99.999 mass% from ABCR GmbH & Co KG, Germany, were used.

2.2. Equipment

The measurements of mass loss rate by the Knudsen method (KM) have been carried out on the „Mettler" TA1 thermobalance. Temperature was measured by Pt/Pt–10%Rh thermocouple calibrated at the melting point of bismuth, Ag–Sb eutectic alloy, aluminium, silver, copper and nickel. All the metals used for the calibration were of purity higher than 99.99 mass%.

Knudsen cells of one type were used in the experiments. Each cell was composed of alumina crucible of diameter and height of 15 mm (supplied by Frialit–Degussit) and a made of Al_2O_3 cover with a conical orifice. The latter was also supplied by Frialit–Degussit and then modified by changing the shape and area of the effusion orifice.

In the current work, because of the irregular shape of effusion orifices, the values of their effective areas ($A_e = A \cdot W$, where A is the geometrical area of the orifice and W is the transmission probability) were determined experimentally by the Knudsen method, as described in our earlier study [34]. In the current study indium of 99.999 mass% purity was used in determination of efficient surface of effusion orifices. The data on indium vapour pressure used in this determination had been experimentally produced in our earlier work [33].

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Table 1
Characteristics of the measurements and their condition.

Set	m_{Cu}, mg	m_{Bi}, mg	T/K	Knudsen cell	
				$A_e \pm \sigma$, mm^2	Symbol
1	2	3	4	5	6
Cu A	2130.19	–	1319–1355	5.94 ± 0.140	Kc 5
Cu B	–	–	1361–1443	5.94 ± 0.140	Kc 5
Cu C	2111.09	–	1445–1620	0.5436 ± 0.00994	Kc 3
Cu D	2085.84	–	1591–1744	0.0775 ± 0.00126	Kc 1
Cu E	2729.88	–	1300–1356	5.94 ± 0.140	Kc 5
Cu F	1168.07	–	1434–1490	1.813 ± 0.0231	Kc 4
Cu G	–	–	1484–1630	0.1760 ± 0.00542	Kc 2
Cu H	–	–	1638–1725	0.0661 ± 0.00092	Kc 6
Bi A	–	1108.40	954–1129	0.0661 ± 0.00092	Kc 6
Bi B	–	–	899–1008	0.1760 ± 0.00542	Kc 2
Bi C	–	2611.83	800–894	1.813 ± 0.0231	Kc 4
Bi D	–	–	768–821	5.94 ± 0.140	Kc 5
Cu 10	75.00	2333.09	945–1067	0.0661 ± 0.00092	Kc 6
Cu 10a	–	–	871–933	1.813 ± 0.0231	Kc 4
Cu 35	414.02	2461.79	1051–1108	0.0661 ± 0.00092	Kc 6
Cu 65	682.51	1178.00	1168–1183	0.0661 ± 0.00092	Kc 6
Cu 15	84.11	1671.27	1005–1084	0.0661 ± 0.00092	Kc 6
Cu 15a	–	–	929–999	0.5279 ± 0.01258	Kc 8
Cu 50	479.99	1586.02	1118–1173	0.0516 ± 0.00152	Kc 9
Cu 20	138.00	1785.36	995–1108	0.0661 ± 0.00092	Kc 6
Cu 20a	–	–	965–1023	0.5279 ± 0.01258	Kc 8
Cu 90	1630.68	651.39	1277–1292	0.0516 ± 0.00152	Kc 9
Cu 85	1563.63	929.52	1251–1275	0.0516 ± 0.00152	Kc 9
Cu 96	1714.40	234.19	1344–1381	0.0516 ± 0.00152	Kc 9
Cu 98	2519.07	185.16	1369–1469	0.0516 ± 0.00152	Kc 9
Cu 98a	–	–	1368–1422	0.1760 ± 0.00542	Kc 2

2.3. Data collection and treatment

In the experimental part of this study 26 sets of measurements of mass loss rate by the Knudsen method were performed. Table 1 shows description of the conducted tests. In the first column symbols of the measurement sets are given, and in the second and third columns masses of copper and bismuth used for the sample preparation are presented, whereas the fourth column contains the temperature ranges of the measurements. The fifth and sixth columns provide effective area of the effusion orifices together with the cell symbol, respectively. In the case of Cu B, Cu G, Cu H, Bi B, Bi D, Cu 10a, Cu 15a, Cu 20a, and Cu 98a series no data on mass is presented because they represent continuation of Cu A, Cu F, Bi A, Bi C, Cu 10, Cu 15, Cu 20, and Cu 98 series, respectively.

In the description of experimental data obtained in this study Knudsen–Herz equation was used in a form of:

$$\overline{P}_{Kn(i)} = \left(\frac{dg}{dt}\right)_i \cdot \left(\frac{2\cdot\pi\cdot R\cdot T}{M_i}\right)^{1/2} \cdot A_e^{-1} \quad (1)$$

where $\overline{P_{Kn(i)}}$ is a partial pressure of i-th component of gaseous phase measured by the Knudsen method, $(\frac{dg}{dt})_i$ represents mass loss rate of a sample due to effusion of the i-th vapour component. R and T are universal gas constant and temperature of the system, respectively. M_i represents molecular weight of the i-th component of the gaseous phase.

The results obtained during the experimental studies of pure solid and liquid copper were used directly in calculation of copper vapour pressure over both mentioned above condensed phases with application of Knudsen–Herz equation (Eq. (1)), after making an assumption that copper monomer is the only significant component of the gaseous phase [26]. It was possible to conduct these calculations separately for every measuring point. Obtained set of pairs of data describing copper vapour pressure and temperature was then used for calculation of standard enthalpy of copper sublimation by the third law method. In this case the following equations (Eq. (2)) and (Eq. (3)) were applied:

$$\Delta_r G^o_{Cu} = -R\cdot T\cdot \ln(P^o_{Cu}/101325\ \text{Pa}) \quad (2)$$

$$\Delta_r G^o_{Cu} = -\Delta_r \Phi^o_{Cu}\cdot T + \Delta_r H^o_{Cu}(298\ \text{K}) \quad (3)$$

which linked the measured pressures (P^o_{Cu}) and temperatures (T) with the standard enthalpy of copper sublimation ($\Delta_r H^o_{Cu}(298\ \text{K})$). All the data necessary in the calculations which characterise Gibbs energy functions for gaseous and condensed copper phases (Φ^o_{Cu}) were taken from the literature and compiled in Table 2. $\Delta_r G^o_{Cu}$ shows the value of Gibbs energy change in the process of copper sublimation or vaporization. The final value of standard enthalpy of copper sublimation was calculated as an arithmetic mean of all results.

For the further studies it was assumed that in the investigated gaseous phase of the Cu–Bi system such components of the phase like Cu(g), Bi(g), and Bi_2(g) particles are present in the significant amount. The presence of bismuth trimer and tetramer in the gaseous phase of the Cu–Bi system [27–29] was ommitted because of the scarce, therefore negligible, influence on the result of the studies by Knudsen method. Nevertheless it has to be noted that just as the other metals of that group of periodic system, bismuth shows the presence of four types of particles, i.e. monomer, dimer, trimer and tetramer in the gaseous phase [27–29]. In the case of

Table 2
Standard molar Gibbs free energy functions, $\Phi^o(T)$.

$\Phi^o(T) = -\frac{[G^o(T) - H^o(298\text{K})]}{T}$, J mole^{-1} K^{-1}

Component	Cu(s) [38]	Cu(l) [38]	Cu(g) [26]	Bi(l) [38]	Bi(g) [26]	Bi_2(g) [26]
T, K						
1	2	3	4	5	6	7
700		31.2566	172.0921	68.8852	192.7025	284.0183
800		35.6761	173.7615	73.1559	194.3719	286.9973
900		39.5001	175.3473	76.8696	195.9576	289.8340
1000		42.8739	176.8493	80.1491	197.4597	292.5285
1100	48.1621	45.8965	178.2677	83.0820	198.8781	295.0724
1200	49.9144	48.6380	179.6066	85.7328	200.2170	297.4740
1300	51.5851	51.1505	180.8701	88.1503	201.4805	299.7501
1358.02	52.5193	52.5193				
1400		53.4736	182.0709	90.3721	202.6813	301.9007
1500		55.6364		92.4272	203.8236	303.9509
1600		57.6597	184.2926	94.3389	204.9072	305.8922
1700		59.5603	185.3261	96.1257		