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On the Interaction Between Gold and Copper in Mercury

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On the base of cyclic voltammetry, chronoamperometry and potentiometry experiments with the use of the hanging mercury drop electrodes, there was found that a solid AuCu compound is formed in the complex Au—Cu amalgam. The stability of AuCu is controlled by its solubility product, which is equal $(7.1 \pm 1.5) \cdot 10^{-6} M^2$ at 298 K. The temperature dependence of the solubility product allowed to determine ΔH_{AuCu} of formation in mercury. This value is compared with ΔH_{AuCu} of the reaction in the binary system. On the basis of the *Born-Haber* cycle one may conclude that the AuCu formed in mercury phase should have the same structure as in the binary alloy. Some thermodynamic aspects of reactions in the Au—Cu—Ga amalgam are discussed. The solubility of copper in mercury was experimentally confirmed and is equal $(1.1 \pm 0.1) \cdot 10^{-2}$ at.%.

(Keywords: Au—Cu—Ga *amalgam; Electroanalysis of* Au—Cu *amalgam; Solubility of* AuCu *in mercury; Solubility of* Cu *in mercury; Thermodynamics of* AuCu *formation in mercury)*

Über die Wechselwirkung zwischen Gold und Kupfer in Quecksilber

Mit Hilfe von voltammetrischen, chronoamperometrischen und potentiometrischen Experimenten mit der hängenden Quecksilbertropfelektrode wurde eine feste AuCu-Verbindung in Au—Cu-Amalgam gefunden. Die Beständigkeit der Verbindung AuCu wird durch das Löslichkeitsprodukt bestimmt, das gleich $(7{,}1 \pm 1{,}5) \cdot 10^{-6} M^2$ bei 298 K ist. Die Temperaturabhängigkeit des Löslichkeitsproduktes erlaubt die Bestimmung der Bildungswärme ΔH_{AuCu} der Verbindung in Quecksilber. Dieser Wert wird mit der Bildungswärme ΔH_{AuCu} im binären System verglichen. Auf der Basis des *Born-Haber*-Kreisprozesses kann man schließen, daß das in Quecksilber gebildete AuCu dieselbe Struktur wie im binären System hat. Verschiedene thermodynamische Aspekte der Reaktionen in Au—Cu—Ga-Amalgam werden diskutiert. Die Löslichkeit von Kupfer in Quecksilber wurde experimentell bestätigt und beträgt $(1{,}1 \pm 0{,}1) \cdot 10^{-2}$ at.%.

Introduction

Though Au—Cu binary alloys have been very intensively studied[1–4], there is practically no systematic work concerning the Au—Cu—Hg system. Solely *Sennechales*[5], during his investigations of the rate of amalgamation, reported, that certain compositions of the Au—Cu alloys are more resistive against mercury attack. In the abstract of an unpublished work of *Kaplin* and coworkers[6] one may find an information about interactions between gold and copper in the complex amalgam. Independently, we investigated quantitatively mercury rich region of this system in our laboratory[7-9]. We were interested in stoichiometry and stability of intermetallic compounds formed in the Au—Cu—Hg system. Such information would give also a basis to discuss the thermodynamical aspects of the reaction between AuGa and Cu proceeding in mercury phase, which was investigated by *Stepanova*[10].

We used our formerly elaborated electrochemical methods[11-13]. As a tool the conventional hanging drop electrodes[14] were applied. They were filled up with mercury (*HMDE*) or gold amalgam (*HGADE*). This procedure has several advantages, especially for systems with rather low solubility of components. In this case, the solubilities of copper and gold in mercury at 298 K are equal $1.0 \cdot 10^{-2}$ at.% ($6.6 \cdot 10^{-3} M$) and 0.145 at.% ($9.8 \cdot 10^{-2} M$)[15], respectively. However, for experiments lasting up to 200 s one may work with $3 \cdot 10^{-2} M$ copper amalgam which is still homogenous.

Experimental

All reagents, water, mercury and gold were of the same degree of purity, as in the preceeding papers[12, 13]. $Cu(ClO_4)_2$ and $Ca(ClO_4)_2$ were prepared by dissolution of $CuCO_3 \cdot Cu(OH)_2 \cdot 7\,H_2O$ and $CaCO_3$ (respectively) in $HClO_4$. $Ca(ClO_4)_2$ was then twicely recrystallized. The solutions of $Cu(ClO_4)_2$ and $CuSO_4$ were potentiostatically electrolyzed for one day at cathodic potential + 0.060 V (vs. SCE). All background electrolytes were similarly purified for one day at cathodic potential —1.00 V.

The equipment used in potentiometric measurements contained a (home made) constant current supply with stability 0.1% and a Radelkis OP-205 precision *pH*-meter. In voltammetric and chronoamperometric studies a Radelkis OH-102 polarograph was used.

Gold concentrations in the *HGADE* were changed between $6.0 \cdot 10^{-3}$ and $9.0 \cdot 10^{-2} M$. The radius of the hanging drop was equal to 0.54_5 mm.

The potentiometric experiments were carried out in the same way as previously[12, 13]. The constant current for copper amalgam generation was changed from 1.00 to 400 μA and the time of electrolysis from 25 to 100 s. So the initial concentrations of copper in electrodes could be changed from $7.7 \cdot 10^{-4}$ to $2.3 \cdot 10^{-2} M$. The potentials of the electrodes were recorded up to 1000 s and for $6.0 \cdot 10^{-3}$ and $8.0 \cdot 10^{-3} M$ gold amalgam up to 2000 s.

All experiments were performed at 298.2 ± 0.2 K, unless otherwise stated.

Results and Discussion

Changes of the potentials in time of both the *HGADE* and *HMDE*, measured after the electroreduction of Cu(II) was stopped, were similar to those for the Au—Cd—Hg system[13]. After 600 s the potential differences between the both electrodes were practically constant, even for the more diluted complex amalgams.

When the observed potentials—after the electrolysis was stopped—did not change in time, there was assumed that an equilibrium in the system was reached. The composition, equilibrium constant or solubility product and other thermodynamic functions of a compound formed between gold and copper were calculated from the equilibrium potentials of the *HGADE* and the *HMDE*. An example of the dependence of

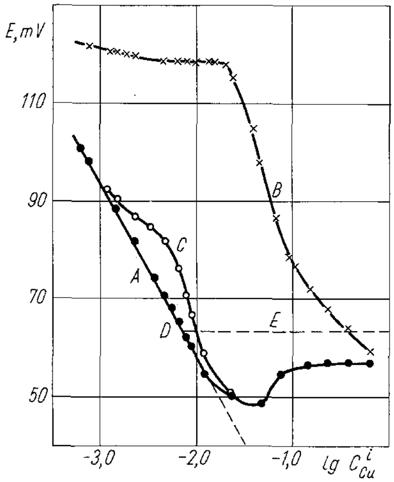

Fig. 1. Stable potentials of the *HMDE* (curve *A*) and the *HGADE* (curves *B* and *C*) vs. logarithm of initial copper concentration in the electrodes. Gold amalgam concentrations $9.0 \cdot 10^{-2} M$ (curve *B*) and $6.0 \cdot 10^{-3} M$ (curve *C*). Radius of the electrodes 0.54_5 mm. Solution $0.10 M$ $CuSO_4$, $pH = 2$

the fixed potentials on the initial concentrations of copper in the electrodes is given in Fig. 1.

As one may easy notice, the potential differences between curves A and B as well as C have typical shapes for the case of the formation of the insoluble intermetallic compound in mercury. Then the thermodynamic equilibrium is described with the solubility product

$$K_{so} = [\mathrm{Au}]\,[\mathrm{Cu}]$$

and the jump of the potential difference should correspond to concentration ratio, which is equal to stoichiometry of the compound formed.

Similar dependences were observed for $8.0 \cdot 10^{-3}$, $1.0 \cdot 10^{-2}$, $2.0 \cdot 10^{-2}$, $5.0 \cdot 10^{-2}$ and $7.0 \cdot 10^{-2} M$ gold amalgams. The jumps on the

Table 1. *Solubility products* (K_{so}) *and dissociation constants* (K_d) *of* AuCu *in mercury at 298 K;* K_{so}^{*} *was obtained with the method of Stromberg and coworkers*[17]; C_{Au}^{i} *and* C_{Cu}^{i} *are initial concentrations of gold and copper*

C_{Au}^{i}, M	C_{Cu}^{i}, M	$K_{so} \cdot 10^6$, M^2	$K_{so}^{*} \cdot 10^6$, M^2	K_d, M
$6.0 \cdot 10^{-3}$	$1.21 \cdot 10^{-3}$–$9.20 \cdot 10^{-3}$	7.3 ± 0.6	7.0	$7.3 \cdot 10^{-2}$–$1.9 \cdot 10^{-3}$
$8.0 \cdot 10^{-3}$	$1.21 \cdot 10^{-3}$–$6.10 \cdot 10^{-3}$	7.6 ± 0.8	8.0	$3.0 \cdot 10^{-2}$–$1.5 \cdot 10^{-3}$
$1.0 \cdot 10^{-2}$	$2.3 \cdot 10^{-3}$–$7.6 \cdot 10^{-3}$	11.1 ± 5.4	15.0	$2.7 \cdot 10^{-2}$–$6.0 \cdot 10^{-4}$
$2.0 \cdot 10^{-2}$	$2.3 \cdot 10^{-3}$–$1.15 \cdot 10^{-2}$	4.3 ± 1.2	4.6	$2.8 \cdot 10^{-3}$–$2.8 \cdot 10^{-4}$
$5.0 \cdot 10^{-2}$	$7.6 \cdot 10^{-4}$–$4.6 \cdot 10^{-2}$	6.9 ± 1.9	5.9	$1.8 \cdot 10^{-2}$–$1.1 \cdot 10^{-4}$
$7.0 \cdot 10^{-2}$	$1.53 \cdot 10^{-3}$–$6.1 \cdot 10^{-2}$	6.7 ± 0.8	5.4	$4.9 \cdot 10^{-2}$–$1.2 \cdot 10^{-4}$
$9.0 \cdot 10^{-2}$	$1.30 \cdot 10^{-3}$–$2.3 \cdot 10^{-2}$	8.6 ± 1.8	6.7	$8.9 \cdot 10^{-2}$–$2.4 \cdot 10^{-4}$
	mean value:	7.1 ± 1.5		

Table 2. *Solubility products and dissociation constants of* AuCu *in mercury obtained with initial gold concentration 7.0·10*$^{-2}$ *M at 298 K;* C^b_{Cu} *is concentration of bonded copper*

t, s	i, μA	C^i_{Cu}, M	ΔE, mV	C^b_{Cu}, M	$K_{so}\cdot 10^6$, M^2	K_d, M
50	4.0	$1.53\cdot 10^{-3}$	35	$1.42\cdot 10^{-3}$	6.9	$4.9\cdot 10^{-3}$
60	5.0	$2.3\cdot 10^{-3}$	40	$2.2\cdot 10^{-3}$	6.7	$3.0\cdot 10^{-3}$
50	10.0	$3.8\cdot 10^{-3}$	48	$3.7\cdot 10^{-3}$	6.3	$1.7\cdot 10^{-3}$
40	20	$6.1\cdot 10^{-3}$	54	$6.0\cdot 10^{-3}$	6.2	$1.0\cdot 10^{-3}$
60	20	$9.2\cdot 10^{-3}$	60	$9.1\cdot 10^{-3}$	5.6	$6.2\cdot 10^{-4}$
40	50	$1.53\cdot 10^{-3}$	65	$1.51\cdot 10^{-2}$	5.7	$3.8\cdot 10^{-4}$
60	50	$2.3\cdot 10^{-2}$	68	$2.3\cdot 10^{-2}$	5.9	$2.6\cdot 10^{-4}$
50	100	$3.8\cdot 10^{-2}$	64	$3.8\cdot 10^{-2}$	8.2	$2.2\cdot 10^{-4}$
40	200	$6.1\cdot 10^{-2}$	57	$6.1\cdot 10^{-2}$	7.1	$1.2\cdot 10^{-4}$
60	200	$9.2\cdot 10^{-2}$	46	$8.9\cdot 10^{-2}$	—	—
50	400	$1.53\cdot 10^{-1}$	11	$8.8\cdot 10^{-2}$	—	—
100	400	$3.1\cdot 10^{-1}$	2	$4.0\cdot 10^{-2}$	—	—
200	400	$6.1\cdot 10^{-1}$	0	0	—	—
				mean value:	6.7 ± 0.8	

corresponding curves were placed at the initial copper concentrations which are higher than the initial concentrations of gold. It suggested a formation of a compound with excess of copper. However, the dependences for the highest initial concentrations were not regular. Before we explain this effect, we assumed simple composition of the compound formed as AuCu and calculated its solubility product. The results are collected in Table 1. It is easy to observe the stability of K_{so} and variability of K_d (dissociation constant). A sample of all single data obtained with the initial concentration of gold $7.0\cdot 10^{-2}$ M is presented in Table 2. It was possible to calculate the K_{so} values only for moderately high initial concentrations of copper. For the highest concentrations the calculated amounts of copper bonded to gold are higher than amounts of gold being present in the amalgam drop. K_{so} calculated for other formula ($AuCu_2$ and $AuCu_3$) were also not constant in this range. Likewise the K_d values of corresponding formula changed systematically with initial concentration of both metals. In such situation the assumption of AuCu formation in mercury is most reliable and the effect of undeterminableness of K_{so} for AuCu, at highest copper contents as well as highest current densities during the electrolysis step is due to precipitation of some excess of copper into Cu_7Hg_6[16]. The solubility of the last compound in mercury is only a few times higher than that of AuCu.

For evaluation of our data we used also the graphical method of *Stromberg* and coworkers[17]. The results of such analysis are inserted in a separate column. These values of K_{s0} are slightly lower than those obtained by our single calculations. This analysis showed, that the points corresponding to the highest excess of copper are out of line in the dimensionless U—V plot. The stoichiometry of the compound eveluated with this method, neglecting these out-of-line points, is equal $Au_{1.1\pm0.1}Cu$, so one ought to assume the composition AuCu, as it is formed in the binary system[1–4].

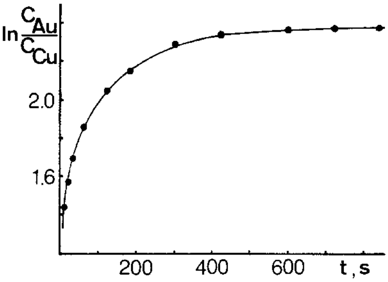

Fig. 2. Analysis of kinetic curve as a plot of $\ln C_{Au}/C_{Cu}$ vs. time. Initial concentrations of gold and copper are equal $2.0\cdot10^{-2}$ and $1.15\cdot10^{-2}\,M$, respectively. Electrolysis time 150 s with a current 10 μA from 0.1 M $Cu(ClO_4)_2$ in 5 M $NaClO_4$. Radius of the electrode 0.54_5 mm

Point D in Fig. 1, which is an intercept of the nernstian part of line A and the parallel E to the plateau part of line A (it takes into account the quasi stability of the fresh heterogenous amalgam[15]), corresponds to the solubility of copper in mercury at 298 K equal $7\cdot10^{-3}\,M$ or $(1.1\pm0.1)\cdot10^{-2}$ at.%. It is slightly higher than the selected value[15].

On basis of copper concentration changes in time one could measure the kinetics of the reaction in a similar way as we tried to do it previously[13], see Fig. 2. In this case, such analysis leads to rate constant values, which are dependent on initial concentration of the reagents. If the reaction between copper and gold fulfils a kinetic equation of the second order, one should obtain a straight-line relationship of the plot $\ln C_{Au}/C_{Cu}$ vs. time. However, the line in Fig. 2 is not linear. An approximate linearization of the points is possible for times longer than 300 s but the accuracy of the $\ln C_{Au}/C_{Cu}$ values is then poorer than at shorter times, because of the significant excess of gold in the amalgam. The dependence in Fig. 2 suggests the formation of AuCu in a sparingly soluble form in mercury, as it was found for the other systems: Au—Cd[13], Au—Sn[18], Au—Zn[8].

Our conclusion in respect to the crystallization occuring in the investigated system is supported by chronoamperometric experiments. Comparison of Cu(II) reduction curves on the *HGADE* and *HMDE* at potentials of the foot of the corresponding polarographic wave is shown in Fig. 3. Curve B in Fig. 3 recorded with the use of the *HMDE* has a typical shape. The hump observed on curve A recorded with the use of the *HGADE* may be explained by the chemical reaction which begins after a certain period of time when concentrations of the reagents reach their critical values (here of copper). In the case of homogeneous reaction no hump should be observed but systematical smooth increase of the current on the *HGADE*. Similar effects were previously reported for other systems: Au—Cd[13], Au—Zn[8] and Au—Mn[19].

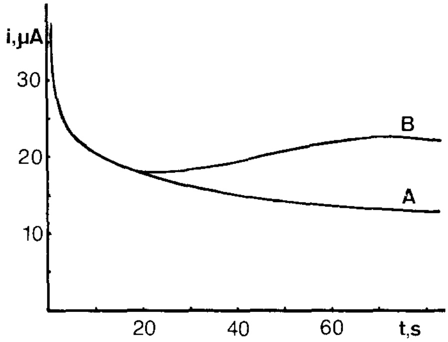

Fig. 3. Chronoamperometric reduction curves of copper(II) on $9.0 \cdot 10^{-2} M$ gold amalgam (curve *B*) and mercury (curve *A*) electrodes. Reduction potential 0.005 V (vs. SCE). Solution 0.1 *M* $CuSO_4$ in saturated K_2SO_4

We obtained an additional proof of crystallization in the investigated reaction with the use of the cyclic voltammetric method. In these studies the gold amalgam concentration was equal $9.0 \cdot 10^{-2} M$ and scan rates were changed in the range 4.16–50 mV/s. In the first set of experiments copper(II) was reduced from solution of $1.00 \cdot 10^{-3} M$ $Cu(ClO_4)_2$ in 2.5 *M* $NaClO_4$. The observed differences between the curves obtained with the use of the *HGADE* and *HMDE* were within limits of reproducibility of the technique with respect to the peak currents and potentials.

In the second set of experiments the concentration of $Cu(ClO_4)_2$ was increased to $1.00 \cdot 10^{-2} M$. Then the differences in the oxidation half cycle were observed, see Fig. 4. The smallest oxidation current was recorded for the scan rate 12.5 mV/s. The higher the scan rates the more similar were the oxidation peak currents on both electrodes. For scan rates lower than 12.5 mV/s the oxidation peak current slightly increases but the ratio of anodic peak currents on the *HGADE* and *HMDE* is further decreased in this range. No differences of peak currents and potentials were observed for the cathodic parts of the curves.

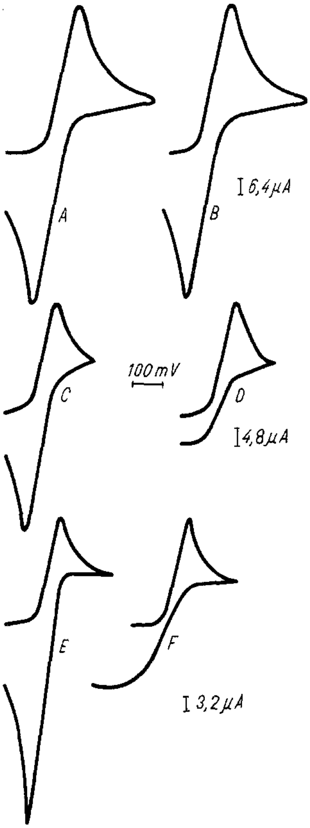

Fig. 4. Cyclic voltammetric curves of copper on mercury (curves *A*, *C*, *E*) and $9.0 \cdot 10^{-2} M$ gold amalgam electrodes (curves *B*, *D*, *F*). Scan rates for *A* and *B*, *C* and *D*, *E* and *F* curves equal 50, 12.5, 4.2 mV/s, respectively. Starting potential of polarization 0.200 V. Solution $1.0 \cdot 10^{-2} M$ $Cu(ClO_4)_2$ in 2.5 *M* $Ca(ClO_4)_2$

These results may be interpreted in terms of a moderately fast electroreduction of copper(II) followed by the almost irreversible reaction of copper with gold in mercury. The fact, that the curves recorded with the use of both electrodes from $1.00 \cdot 10^{-3} M$ Cu(II) solution are not different from each other, suggests, that the investigated process is observed, when the concentration of copper in the mixed amalgam reaches adequately high level. So the formation of the crystalline form of AuCu in mercury is strongly suggested. One cannot exclude a formation of non-remarcable amounts of soluble AuCu molecules which dissociate quite easyly during the oxidation step.

With the use of $5.0 \cdot 10^{-2} M$ gold amalgam the potentiometric experiments were performed in the temperature range 278–308 K. The following K_{so} values were obtained: $(3.0 \pm 0.6) \cdot 10^{-6}$, $(4.2 \pm 0.4) \cdot 10^{-6}$ and $(9.4 \pm 2.0) \cdot 10^{-6} M^2$ for 278, 288 and 308 K, respectively. The pK_{so} vs. $1/T$ dependence was linear. The slope of the line was calculated with the least square method of weighed polynomial. We calculated $\Delta H_{\mathrm{AuCu(Hg)}}$, $\Delta G_{\mathrm{AuCu(Hg)}}$ and $\Delta S_{\mathrm{AuCu(Hg)}}$ of the investigated reaction using the well known thermodynamic relations. $\Delta G_{\mathrm{AuCu(Hg)}}$ decreases from —53.1 (278 K) to —56.5 kJ/mol (308 K) and $\Delta S_{\mathrm{AuCu(Hg)}}$ is about 100 J/K·mol; $\Delta H_{\mathrm{AuCu(Hg)}}$ is equal -26.0 ± 3.4 kJ/mol.

The enthalpy of AuCu formation in mercury is not equal to the enthalpy of formation of this compound in the binary solid state. For the ordered structure of the solid AuCu the corresponding value of ΔH_{AuCu} is equal -18.0 ± 0.2 kJ/mol[20]. In order to complete the *Born-Haber* cycle of the whole system one needs the heats of dissolution of gold and copper in mercury. There is only one value for gold in the literature equal 8.5 ± 0.4 kJ/g-atom[21] for about 0.5 mass % at 371 K in calorimetric determination. This should not be too far from a correct value for the more diluted amalgam near room temperature (denoted $\overline{\Delta H_{\mathrm{Au}}}$), since the $\lg N_{\mathrm{Au}}$ vs. $1/T$ dependence is a straight line in this range[15] (N_{Au} is the solubility). It is not quite clear, how *Kozin* and coworkers[22] calculated $\overline{\Delta H^{\infty}_{\mathrm{Au}}}$ and $\overline{\Delta H^{\infty}_{\mathrm{Cu}}}$ equal 21.2 and 30.1 kJ/g-atom; however, we do not use them further.

There are few experimental data for the heat of dissolution of copper in mercury. So called last heats of dissolution were evaluated from $\lg N_{\mathrm{Cu}}$ vs. $1/T$ plots (N_{Cu} is the solubility) and according to different fundamental results are equal 22.2 kJ/g-atom[23] and 17.6 kJ/g-atom[24] for 370–670 K and 313–363 K temperature ranges, respectively. The result of 13.5 kJ/g-atom for 300–350 K is due to the kinetic dissolution process of amalgamated copper[25]. We may not accept these values, because in equilibrium conditions the saturated copper amalgam remains in equilibrium with a $\mathrm{Cu_7Hg_6}$ solid phase[16] but not with pure copper. So the above quoted values of $\overline{\Delta H_{\mathrm{Cu}}}$ are, more or less, due to dissolution of $\mathrm{Cu_7Hg_6}$ in the saturated amalgam but absolutely not to dissolution of metallic copper in mercury. We tried to estimate $\overline{\Delta H_{\mathrm{Cu}}}$ in the diluted solution on the basis of other thermodynamical data.

One may describe the formation of diluted (up to the saturation) copper amalgam in the similar way as it was proposed by *Bonnier* and *Desre*[26]:

$$\mathrm{Cu} + 6/7\,\mathrm{Hg} \rightarrow 1/7\,\mathrm{Cu_7Hg_6} \qquad 1/7\,\Delta H_{\mathrm{Cu_7Hg_6}} \qquad (1)$$

$$1/7\,\mathrm{Cu_7Hg_6} + \infty\,\mathrm{Hg} \rightarrow \mathrm{Cu(Hg)}_{\infty} \qquad \overline{\Delta H_{\mathrm{Cu_7Hg_6}}} \qquad (2)$$

$\Delta H_{\mathrm{Cu_7Hg_6}}$ is equal —18.9 ± 0.6 kJ/g-atom of Cu according to [16]. $\overline{\Delta H_{\mathrm{Cu_7Hg_6}}}$ is equal to heat of $\mathrm{Cu_7Hg_6}$ dissolution in great amount of mercury and is also refered to 1 g-atom of Cu. Because $\mathrm{Cu_7Hg_6}$ is decomposed above 401 ± 2 K[16], we evaluated again $\overline{\Delta H_{\mathrm{Cu_7Hg_6}}}$ using the selected solubility values[15] (mainly those of *Jangg* and *Palman*[23]) and corrected it for 6/7 of the latent heat of fusion of mercury[29]. In this way we obtained a value of 15.6 ± 0.5 kJ/g-atom, which is almost equal to the one obtained from calorimetric determinations of *Omarova* and coworkers[27]: 15.7 ± 1.2 kJ/g-atom at 298 K (after recalculation for $\mathrm{Cu_7Hg_6}$). Finally, we are able to calculate the enthalpy of dissolution of metallic copper in a great excess of mercury (for all components in their standard states at 298 K):

$$\begin{aligned}\overline{\Delta H_{\mathrm{Cu}}} &= 1/7\,\Delta H_{\mathrm{Cu_7Hg_6}} + \overline{\Delta H_{\mathrm{Cu_7Hg_6}}} = (-18.9 \pm 0.6) + (15.6 \pm 0.5) = \\ &= -\ 3.3 \pm 1.1\ \mathrm{kJ/g\text{-}atom}\end{aligned}$$

Based on the selected thermodynamical values for binary metallic systems[28, 29] we calculated in the similar way $\overline{\Delta H}$ values for the diluted amalgams of Li, Na, K, Cs, Cd and we obtained results which are equal within the systematic errors with those obtained from direct experiments.

Now we may describe the AuCu formation process in mercury in the following steps:

$$\mathrm{Cu} + \infty\,\mathrm{Hg} \rightarrow \mathrm{Cu(Hg)}_{\infty} \qquad \overline{\Delta H_{\mathrm{Cu}}} \qquad (3)$$

$$\mathrm{Au} + \infty\,\mathrm{Hg} \rightarrow \mathrm{Au(Hg)}_{\infty} \qquad \overline{\Delta H_{\mathrm{Au}}} \qquad (4)$$

$$\mathrm{Cu(Hg)}_{\infty} + \mathrm{Au(Hg)}_{\infty} \rightarrow \mathrm{AuCu(Hg}_x) + \infty\,\mathrm{Hg} \qquad \Delta H_{\mathrm{AuCu(Hg)}} \qquad (5)$$

Formation of AuCu in the binary system is described as:

$$\mathrm{Cu} + \mathrm{Au} \rightarrow \mathrm{AuCu} \qquad \Delta H_{\mathrm{AuCu}}\,. \qquad (6)$$

An interaction of solid AuCu with liquid mercury is described as:

$$\mathrm{AuCu} + \infty\,\mathrm{Hg} \rightarrow \mathrm{AuCu(Hg}_x) + \infty\,\mathrm{Hg} \qquad \Delta H_{(\mathrm{Hg})} \qquad (7)$$

It is noteworthy to add that in practice a great (but terminable) amount of mercury is used and that the $\overline{\Delta H}$ values should correspond to the concentrations of the metals when the solubility of AuCu is reached. However, no complication arises since the dissolution enthalpies are practically independent on concentrations in the low concentration range.

The overall heat balance of reactions (3)–(7) leads to the equation:

$$\Delta H_{(\mathrm{Hg})} = \overline{\Delta H_{\mathrm{Cu}}} + \overline{\Delta H_{\mathrm{Au}}} + \Delta H_{\mathrm{AuCu(Hg)}} - \Delta H_{\mathrm{AuCu}} \qquad (8)$$

If $\Delta H_{(\mathrm{Hg})}$ is equal to zero it suggests that the solid intermetallic compound precipitated in mercury has the same form as the one formed in the binary system and that the compound does not contain mercury; $x = 0$ in (5) and (7). If $\Delta H_{(\mathrm{Hg})}$ is not equal to zero one may suspect an effect of surface solvation of crystalls with mercury (insignificant), formation of a soluble form of a compound (of importance), changes of its structure and formation of an intermetallic compound of another stoichiometry or with mercury content (most important).

According to equation (8) for the ordered form of AuCu we get:

$$\Delta H_{(\mathrm{Hg})} = (-3.3 \pm 1.1) + (8.5 \pm 0.4) + (-26.0 \pm 3.4) - (-18.0 \pm 0.2) = \\ = -2.8 \pm 5.1\,\mathrm{kJ/mol\ of\ AuCu}$$

The established value of $\Delta H_{(\mathrm{Hg})}$ for the considered case suggests that the mercury phase contains an ordered form of AuCu crystalls and it is an additional proof to our conclusions of the electrochemical investigations. However, due to the accuracy of the estimation we are not able to attribute the slight effect of -2.8 kJ/mol to any other phenomenon.

Finally, we would like to comment some thermodynamical aspects of reaction in the complex Au—Cu—Ga amalgam:

$$\mathrm{AuGa}\downarrow \rightleftharpoons \mathrm{AuGa} + \mathrm{Cu} \rightarrow \mathrm{CuGa} + \mathrm{Au} \qquad (9)$$

which was investigated by *Stepanova*[10]. She observed in voltammetric experiments that introduction of copper into the Au—Ga amalgam leads to reaction (9) in the right direction. The solubility products values collected for AuCu, CuGa and AuGa are equal: $7.1 \cdot 10^{-6}\,M^2$ at 298 K, $2 \cdot 10^{-6}\,M^2$ at room temperature[30] and $2 \cdot 10^{-8}\,M^2$ at 298 K[8], respectively. Now it is quite obvious that gold interacts stronger with gallium than with copper. The interaction of copper with gold and with gallium is comparable, so the reaction (9) should go to the left side. Lack of the voltammetric oxidation currents from the Au—Cu—Ga complex amalgam may be due to formation of a more stable multicomponent compound or to a covering of the previously formed AuGa crystalls with CuGa or $\mathrm{Cu_7Hg_6}$ deposits.

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