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SOLUBILITY DATA SERIES

Volume 51

INTERMETALLIC COMPOUNDS IN MERCURY

SOLUBILITY DATA SERIES

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SOLUBILITY DATA SERIES

Volume 51

INTERMETALLIC COMPOUNDS IN MERCURY

Volume Editors

JANET G. OSTERYOUNG
SUNY University at Buffalo
Buffalo, NY, USA

MARY M. SCHREINER
Niagara University
Niagara University, NY, USA

CEZARY GUMINSKI
University of Warsaw
Warsaw, Poland

ZBIGNIEW GALUS
University of Warsaw
Warsaw, Poland

Contributors (*Evaluators)

CEZARY GUMINSKI*
University of Warsaw
Warsaw, Poland

ZBIGNIEW GALUS*
University of Warsaw
Warsaw, Poland

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7 Alloys Containing Cobalt (Co) and

8 Alloys Containing Copper (Cu) and

FOREWORD

> *If the knowledge is*
> *undigested or simply wrong,*
> *more is not better.*

The Solubility Data Series is a project of Commission V.8 (Solubility Data) of the International Union of Pure and Applied Chemistry (IUPAC). The project had its origins in 1973, when the Analytical Chemistry Division of IUPAC set up a Subcommission on Solubility Data under the chairmanship of the late Prof. A. S. Kertes. When publication of the *Solubility Data Series* began in 1979, the Committee became a full commission of IUPAC, again under the chairmanship of Prof. Kertes, who also became Editor-in-Chief of the Series. The Series has as its goal the preparation of a comprehensive and critical compilation of data on solubilities in all physical systems, including gases, liquids and solids.

The motivation for the Series arose from the realization that, while solubility data are of importance in a wide range of fields in science and technology, the existing data had not been summarized in a form that was at the same time comprehensive and complete. Existing compilations of solubility data indeed existed, but they contained many errors, were in general uncritical, and were seriously out-of-date.

It was also realized that a new series of compilations of data gave educational opportunities, in that careful compilations of existing data could be used to demonstrate what constitutes data of high and lasting quality. As well, if the data were summarized in a sufficiently complete form, any individual could prepare his or her own evaluation, independently of the published evaluation. Thus, a special format was established for each volume, consisting of individual data sheets for each separate publication, and critical evaluations for each separate system, provided sufficient data from different sources were available for comparison. The compilations and, especially, the evaluation were to be prepared by active scientists who were either involved in producing new data, or were interested in using data of high quality. With minor modifications in format, this strategy has continued throughout the Series.

In the standard arrangement of each volume, the Critical Evaluation gives the following information:

(i) A text which discusses the numerical solubility information which has been abstracted from the primary sources in the form of compilation sheets. The text concerns primarily the quality of the data, after consideration of the purity of the materials and their characterization, the experimental method used, the uncertainties in the experimental values, the reproducibility, the agreement with accepted test values, and finally, the fitting of the data to suitable functions, along with statistical tests of the fitted data.

(ii) A set of recommended data, whenever possible, including weighted averages and estimated standard deviations. If applicable, one or more smoothing equations which have been computed or verified by the evaluator are also given.

(iii) A graphical plot of the recommended data, in the form of phase diagrams where appropriate.

The Compilation part consists of data sheets which summarize the experimental data from the primary literature. Here much effort is put into obtaining complete coverage; many good data have appeared in publications from the late nineteenth and early twentieth centuries, or in obscure journals. Data of demonstrably low precision are not compiled, but are mentioned in the Critical Evaluation. Similarly, graphical data, given the uncertainty of accurate conversion to numerical values, are compiled only where no better data are available. The documentation of data of low precision can serve to alert researchers to areas where more work is needed.

A typical data sheet contains the following information:

(i) list of components: names, formulas, Chemical Abstracts Registry Numbers;
(ii) primary source of the data;
(iii) experimental variables;
(iv) compiler's name;
(v) experimental values as they appear in the primary source, in modern units with explanations if appropriate;
(vi) experimental methods used;
(vii) apparatus and procedure used;
(viii) source and purity of materials used;
(ix) estimated error, either from the primary source or estimated by the compiler;
(x) references relevant to the generation of the data cited in the primary source.

Each volume also contains a general introduction to the particular type of system, such as solubility of gases, of solids in liquids, etc., which contains a discussion of the nomenclature used, the principle of accurate determination of solubilities, and related thermodynamic principles. This general introduction is followed by a specific introduction to the subject matter of the volume itself.

The Series embodies a new approach to the presentation of numerical data, and the details continue to be influenced strongly by the perceived needs of prospective users. The approach used will, it is hoped, encourage attention to the quality of new published work, as authors become more aware that their work will attain permanence only if it meets the standards set out in these volumes. If the Series succeeds in this respect, even partially, the Solubility Data Commission will have justified the labour expended by many scientists throughout the world in its production.

January, 1989

J. W. Lorimer,
London, Canada

PREFACE

The material contained in this volume complements and extends the information and experimental data contained in Volume 25 of the *Solubility Data Series, Metals in Mercury*, to include data on the solubility of intermetallic compounds in mercury. As in Volume 25, the scheme of ordering in this volume is the alphabetical ordering common in metallurgy and materials science; that is, the formulas for intermetallic compounds are written with the elements ordered according to their alphabetical order. Thus, one finds AuCd, not CdAu; Cu_3Zn, not $ZnCu_3$. Mercury, as the solvent, is always listed at the end. For a given metal, all of the alloys containing the first metal are given together, in alphabetical order of the second metal. Thus the first entries are for all of the silver-containing alloys, and so on. This ordering is preferred to a scheme based on electronegativity, because alphabetical ordering is unambiguous, whereas ordering according to electronegativity produces situations in which the difference between two elements is not large enough to specify the order. The alphabetical order is used by, among others, *Chemical Abstracts*.

In preparing the final text of this volume from the original data sheets and evaluations, the approach has been conservative. This point of view has important consequences in two areas. First, with regard to the original data, the non-standard units employed by many workers have been retained in order to avoid the inevitable introduction of errors through conversion of units. Generally the evaluators have given recommended or tentative values in standard S.I. units. However, when that has not been done, the evaluators' original text has been retained.

The symbols employed for constants characterizing equilibria involving solids are particularly troublesome. Even within individual original data sheets often the use of symbols was found to be inconsistent. In order to avoid misunderstanding all symbols such as K_{SO}, K_{SO}^*, etc. have been changed to K_S, and the units of the equilibrium constant and the context are relied upon to provide the necessary information about the nature of the equilibrium to which the constant applies. Throughout the symbol *p* has been used to stand for *-log*, as in $pK_S = -\log K_S$.

It is not possible a priori to distinguish between comments interjected by the compilers and those of the authors of the paper. Thus none of the material in any compilation has been deleted. In cases of ambiguity or self-contradiction in some aspect of a compilation, this has been noted, but the material has been retained. Only obvious errors in transcription have been changed.

In both the evaluations and compilations the original language of the contributors has been retained to the fullest extent possible. It was the feeling of the editors that retaining that style best ensures the fidelity of the volume to the initial perceptions and scientific judgments of the contributors. Errors of grammar and misspellings have been corrected, and a uniform style has been enforced on standard types of information frequently reported.

The editors are deeply grateful to Barbara Raff for her expert typing services. They also acknowledge the support of SUNY University at Buffalo.

Janet Osteryoung
Department of Chemistry
SUNY University at Buffalo
Buffalo, NY, USA

Mary M. Schreiner
Department of Chemistry
Niagara University
Niagara University, NY, USA

INTRODUCTION TO THE VOLUME

Interactions between metals which lead to the formation of intermetallic compounds occur frequently in complex liquid amalgams. Solubilities of intermetallic compounds in mercury may vary to a large extent and have been determined by a number of scientists. The real dissolution process of a solid intermetallic phase in mercury seldom has been investigated. For the most part, investigators have prepared complex amalgams by mixing two simple amalgams, by introducing a second metal to a simple amalgam, or by simultaneously introducing two metals into mercury. After some time they deduced whether an intermetallic compound had formed from changes in metal concentration or activity.

The solubility of an intermetallic compound in mercury is understood to be the concentrations of the parent metals in the saturated solution at a given temperature; in most cases the solubility products of intermetallics are determined. These solutions are mainly in equilibrium with defined solid phases. However, in several cases such phases are mixtures of crystals since solutes are partly or totally decomposed or even transformed into another solid. Unfortunately a very limited number of phase diagrams of corresponding ternary amalgam systems is known at present. Also a problem arises regarding the nature of an equilibrium solid phase. Crystals of an intermetallic in an amalgam are not always analyzed by authors and the composition of the solid is then deduced indirectly. Frequently a solid precipitated in mercury is of the same composition as one formed in the corresponding binary system. Therefore critical evaluations collect all information on the nature of the equilibrium and composition of the most stable phases in a binary alloy. Mercury is seldom the third component of a solute.

Evaluators expressed their reservation to all solubility data where the solubility of an intermetallic compound determined is higher than the solubility of one or both components. In such cases the reader is referred to the volume on solubility of metals in mercury (1).

Three methods of solubility determination are extensively used in many papers. We found it useful to describe them in greater detail here instead of repeating them in the text.

1. A resulting amalgam is oxidized under polarographic, voltammetric, chronopotentiometric or chronoamperometric conditions and currents (transition times) of the oxidation of components are recorded. Equilibrium concentrations of both components are calculated from these currents, time or charges (after integration) using a calibration curve or suitable equation of chemical electroanalysis. In this series of experiments the stoichiometry of a compound should be determined, or assumed, then using these concentrations the solubility product is calculated by simple multiplication. Almost regularly the authors report no details, as such calculations are trivial. If only one component could be oxidized then concentration of the second in M_xM_y' is calculated from the simple formula:

$$c_{M'}{}^{f} = c_{M'}{}^{i} - (y/x)(c_M{}^{i} - c_M{}^{f})$$

where i refers to initial, total, analytical, or input concentration; and where f refers to final, equilibrium, active, free, unbonded, or uncombined activity.

Stromberg and coworkers (2, 3) elaborated and applied their own method of using dimensionless parameters in the stripping analysis of complex amalgams; however, the main idea is the same.

2. A galvanic cell is formed : $M(Hg) \mid M^{n+} \mid M,M'(Hg)$ and the EMF (ΔE) is measured. Frequently $c_M{}^{i}$ in both electrodes is equal (if not, one may easily correct for this). Then practical activity, $a_M{}^{f}$, is determined from the equation : $\Delta E = (RT/nF) \ln (a_M{}^{i}/a_M{}^{f})$. For low concentrations one may assume that activity is equal to concentration. The activity coefficients of known simple amalgams are practically constant for low concentrations as typically investigated (4). No activity coefficients are known for amalgams of Ag, Au, Ba, Cu, Ga, Mg, Sb, Te, but by analogy we may assume that if concentrations of the metals are lower than 0.1 mol % the activity coefficients of these metals referred to infinitely diluted amalgams are close to unity. However, activity coefficients in binary amalgams are absolutely unknown. Now changing $c_M{}^{i}$ at fixed $c_M{}^{i}$, one obtains one of the curves in Figure 1. The position of the jump corresponds to the stoichiometry of a compound formed in the mercury medium as it is schematically shown on the plot of ΔE versus $pc_M{}^{i}$. From the character of a curve formed by experimental points authors deduce the kind of equilibrium taking place and calculate either $K_s = (c_M{}^{f})^{x} (c_M{}^{i} - (y/x)c_M{}^{i} + (y/x)c_M{}^{f})^{y}$ or $K = (1/x)(c_M{}^{i} - c_M{}^{f})/K_s$ because $c_M{}^{i}$ and $c_{M'}{}^{i}$ are known and $c_M{}^{f}$ is found from ΔE.

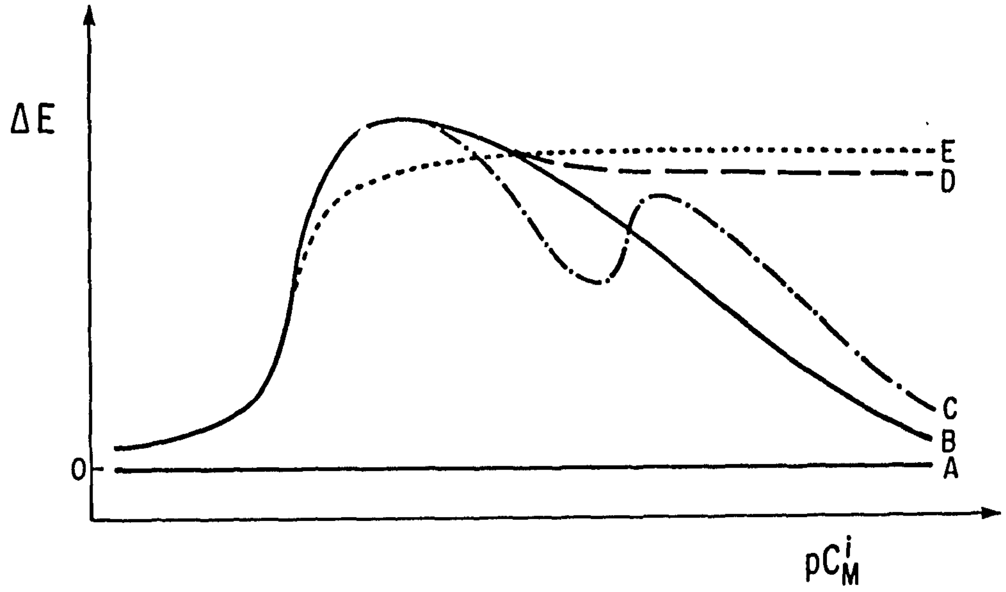

Figure 1. Schematic dependence of E on pC_M^i. A - compound between M and M′ is formed; M_xM_y' is highly soluble and fully dissociated, B - a sparingly soluble compound with $K_s = [M]^x [M']^y$; soluble part is fully dissociated, C - two sparingly soluble compounds with different stoichiometry and solubility, D - a sparingly soluble compound; soluble part is poorly dissociated; up to the solubility limit the equilibrium is described by $K = [M_xM_y']/[M]^x[M']^y$ and over this limit by K_s but a constant concentration of M_xM_y' molecules is present in the solution, E - a highly soluble compound but poorly dissociated in mercury with equilibrium constant K.

Another equivalent method of calculation using dimensionless parameters was presented by Stromberg and coworkers (5).

3. Heterogeneous and complex amalgams are titrated with mercury and heat effects for various compositions are traced. A break point on the plot relating the heat effect versus concentration of a component corresponds to the equilibrium concentration of an element. Again, K_s-values obtained by multiplication of the equilibrium concentrations are reported originally in such cases. This method was applied for significantly concentrated amalgams; therefore correction for the activity coefficients is recommended. Temperature dependences of the solubilities are given in the form of equations. They were constructed by a linear least squares fit using accepted individual data. If the accepted values of solubility at particular temperatures are given with the standard deviations then the weighted linear least squares fit method was applied:

$$(1/(N-2)) \sum_{i=1}^{N} w_{y_i} (y_i - \hat{y}_i)^2 = \min = S$$

for

$$w_y \propto 1/s_i^2 \text{ and } \hat{y}_i = (a \pm s_a) + (b \pm s_b)\, x_i$$

where $\hat{y}_i$ - adjusted value, S - variance of fit, s_i - standard deviation of y in i^{th} - measurement, w_{y_i} - weight of i^{th} - measurement, x_i - independent value, y_i - dependent value, a - intercept, b - slope, s_a and s_b - standard deviations on a and b respectively. The room temperature, which is frequently not quoted, was assumed to be 293 ± 5 K. If a work does not contain enough experimental details, then numerical results are only presented in a critical evaluation of a system. Abbreviations in the text are used according to Chemical Abstracts. The critical evaluations are marked with dates of preparation of the manuscript and they are not changed if no new material on the subject was found. Searching in the Chemical Abstracts for references on all systems was finished in April 1988. Earlier, some works collecting solubilities of intermetallic compounds in mercury were published but they were not always complete and correct. They supply no original results and have a review character. These papers are not referred to when discussing an individual system; however, we feel that these earlier efforts should be mentioned here (6-11).

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In addition to the solubilities described in further detail in the book, many other systems containing mercury were investigated semiquantitatively or qualitatively.

We found it useful to list the related references below.

List of works related to complete or partial phase relations in M-M'-Hg ternary (quaternary) systems where the solubility of intermediate phases, intermetallics or elements was not directly determined, but may be inferred sometimes from phase diagrams inserted in the original works:

Ag-Bi (48, 69)
Ag-Cu (12, 69)
Ag-Cu-Sn (12)
Ag-Pb (41, 69, 70)
Al-Ga (11)
Au-Bi (48-52)
Bi-Cd (53-55, 65, 182)
Bi-Ga (14, 224)
Bi-In (68, 206)
Bi-Pb (2, 38-40, 74, 195)
Bi-Sn (32, 33, 73, 195)
Bi-Tl (23, 24, 66)
Bi-Zn (60-63, 81)
Cd-Ga (11)
Cd-In (80, 206)
Cd-Pb (4, 42, 43, 45-47, 65, 77, 182)
Cd-Sn (35-37, 65, 182)
Cd-Tl (5, 25-27, 65, 75, 182)
Cd-Zn (56-58, 63, 65, 182)
Tl-Zn (208, 217)
Ga-Ge (11)
Ga-In (11, 13, 14)
Ga-Pb (11)
Ga-Sn (11)
Ga-Tl (11)
Ga-Zn (11, 15, 207, 209, 225)
In-Mg (71)
In-Na (67, 191)
In-Pb (79, 206)
In-Sn (17)
In-Tl (16)
Mg-Mn (10)
Na-Pb (8, 9, 59)
Na-Tl (6, 7, 191)
Pb-Sn (28-31)
Pb-Tl (3, 20-22, 78)
Pb-Zn (64, 160, 202)
Sn-Tl (18, 1   44)
Sn-Zn (1, 34, 63)

List of works referring to M_xTe_y-HgTe pseudobinary phase diagrams:

As_2Te_3-HgTe (193, 210)

Bi_2Te_3-HgTe (203, 211)

EuTe-HgTe (190)

Ga_2Te_3-HgTe (82-84, 100, 161, 194, 211)

GeTe-HgTe (92, 96-98, 211)

In_2Te_3-HgTe (83, 85-87, 95, 97, 99, 194, 220)

MgTe-HgTe (94)

MnTe-HgTe (90, 93, 189, 204, 212)

PbTe-HgTe (88, 97, 100, 187, 194, 211)

Sb_2Te_3-HgTe (96-98, 203, 211)

SnTe-HgTe (91, 96-98, 194, 211, 216)

ZnTe-HgTe (89, 98, 100, 197, 211)

List of works where an interaction of parent metals in mercury medium was found:

Ag-Cr (85)
Ag-Ga (206)
Ag-(Yb, Sm, Gd, Dy, Ho, Er) (201)
Ag-Ni-Zn (105)
Ag-Te (98, 194, 211, 223)
Al-Cu (73, 112, 188)
Al-Fe (112, 132, 149)
Al-Fe-Si (149)
Al-Mn (132)
Al-Ni (148), not confirmed in (132)
Al-Pt (108)
Al-Te (83)
As-Cu (113, 116, 169)
As-Ni (117, 169)
As-Zn (118)
Au-(Yb, Sm, Gd, Dy, Ho, Er) (201)
B-Ni-Si (186)
Ba-In (191)
Ba-Tl (191)
Bi-Cu (165), not confirmed in (112, 133)
Bi-Pt (108)
Bi-U (162)
C-Pd (129)
Cd-Ni (128), not confirmed in (144)
Cd-Pd (139)

Cd-Pt (144), not confirmed in (101)
Ce-Pb (123)
Co-Cu (114, 131)
Co-Ge (169)
Co-(Yb, Sm, Gd, Dy, Ho, Er) (201)
Co-Mo (154)
Co-Ni (113, 127, 130, 131), not confirmed in (208)
Co-Sn (103, 106, 112, 115)
Co-W (141, 157)
Cr-Fe (127)
Cr-Ga (122)
Cr-Ni (106, 113, 135, 185)
Cr-Zn (106, 126)
Cs-In (120)
Cu-Hf (138)
Cu-(Yb, Sm, Gd, Dy, Ho, Er) (201)
Cu-Ni (113, 131, 106, 214), not confirmed in (144, 158, 213)
Cu-Ni-Sn (158)
Cu-Te (96-98, 194, 211, 223)
Cu-Ti (140)
Cu-Zr (138)
Fe-Ga (122)
Fe-Ge (169)
Fe-In (150), not confirmed in (206)
Fe-(Yb, Sm, Gd, Dy, Ho, Er) (201)
Fe-Mn (113, 131)
Fe-Sn (106, 109, 111)
Fe-Te (96, 97)
Fe-Ti (155)
Fe-W (141)
Fe-Zn (107, 110, 111, 125)
Ga-Mn (206)
Ge-Ni (207)
Ga-Mn (200)
In-Mn (150), not confirmed in (206)
In-Ni (150), not confirmed in (206)
In-Pt (108)
In-Rb (121)
La-Ni (156)
(Ce, Pr, Nd, Pm, Eu, Gd, Tb, Dy, Ho, Ep, Tm, Yb, Lu)-Mn (199)
(Yb, Sm, Gd, Dy, Ho, Er)-Ni (201)
Mg-Pt (102)
Mg-Si (219)
Mg-U (162)
Mg-Zn (49)
Mn-Ni (106, 113, 131)
Mn-Sm (200)
Mn-Y (200)
Mo-Ni (154)
Na-Te (197)
Na-U (162)
Na-Zn (119), not confirmed in (8,121,137)
Ni-Te (96, 97)
Ni-Ti (147)
Pd-Sn (108)
Pt-Sb (101), not confirmed in (205)
Pt-Sn (101, 108)
Rb-Zn (121)
Te-Ti (96)
Te-Tl (211)
Th-U (180)
Ti-Zn (142)

List of works where no interaction of metals in mercury was found; when possible upper limits of component concentrations investigated are reported, at room temperature if not otherwise stated:

Ag-In (163) c_{Ag} - $5\mathrm{x}10^{-2}$ mol dm^{-3} ; c_{In} - $1\mathrm{x}10^{-2}$ mol dm^{-3}
Ag-Mg (164) c_{Ag} - $9\mathrm{x}10^{-2}$ mol dm^{-3} ; c_{Mg} - $4.4\mathrm{x}10^{-2}$ mol dm^{-3}
Ag-Ni (151) c_{Ag} - satd ; c_{Ni} - satd
Ag-Pt (108) ; c_{Pt} - satd ; T-573 K
Ag-Tl (69) c_{Ag} - $5\mathrm{x}10^{-3}$ mol dm^{-3} ; c_{Tl} - $3\mathrm{x}10^{-3}$ mol dm^{-3}

As-In (169)			
As-Sn (169)			
Au-Pb (49, 51, 52, 113, 166-168, 70)	c_{Au} - 9x10^{-2} mol dm^{-3}	; c_{Pb} - 0.12 mol dm^{-3}	
Au-Pt (108)		; c_{Pt} - satd	; T-573 K
Au-Te (98, 211)			; T-700 K
Au-Tl (51, 52, 113, 166-168)	c_{Au} - 9x10^{-2} mol dm^{-3}	; c_{Tl} - 9x10^{-2} mol dm^{-3}	
Bi-Fe (112)		; c_{Fe} - satd	
Bi-Na (8)	x_{Bi} - 0.5 mol %	; x_{Na} - 2.5 mol %	
Bi-Ni (109, 144, 214)	c_{Bi} - 3x10^{-2} mol dm^{-3}	; c_{Ni} - satd	
Bi-Pd (139)	c_{Bi} - 0.1 mol dm^{-3}	; c_{Pd} - 5x10^{-2} mol dm^{-3}	
Cd-Ce (123)			
Cd-Co (112, 128)		; c_{Co} - satd	
Cd-Cu-Pt (105)			
Cd-Fe (112, 128)			
Cd-Ir (215)			
Cd-W (214)			
Ce-Tl (123)	c_{Ce} - 0.01 mol dm^{-3}	; c_{Tl} - 0.3 mol dm^{-3}	
Co-Fe (127, 131, 196)	w_{Co} - 0.3 mass %	; w_{Fe} - 30 mass %	
Co-In (206), not confirmed in (214)	c_{Co} - satd	; c_{In} - 3.0x10^{-3} mol dm^{-3}	
Co-Mn (131)	w_{Co} - 0.05 mass %	; w_{Mn} - 0.05 mass %	
Co-Tl (214)			
Cr-Sn (103, 106)	w_{Cr} - 0.61 mass %	; w_{Sn} - 4.37 mass %	
Cs-Zn (121)			
Cu-Fe (131)	w_{Cu} - 0.3 mass %	; w_{Fe} - 0.05 mass %	
Cu-In (103, 184, 206, 214)	c_{Cu} - 0.1 mol dm^{-3}	; c_{In} - 0.1 mol dm^{-3}	
Cu-Pb (112, 134, 184, 214)	c_{Cu} - satd		
Cu-Pd (108)			; T-573 K
Cu-Tl (214)			
Cu-W (214)			
Fe-Ni (106, 131, 198)	w_{Fe} - 0.05 mass %	; w_{Ni} - 0.3 mass %	
Fe-Pb (112)	c_{Fe} - satd		
Fe-Tl (112)	c_{Fe} - satd		
In-K (145)	x_{In} - 70 mol %		
In-Li (145, 192)	x_{In} - 70 mol %		
In-Na (120, 145)	x_{In} - 68 mol %	; x_{Na} - 4 mol %	
In-Ni (103)	c_{In} - 0.1 mol dm^{-3}	; c_{Ni} - 0.1 mol dm^{-3}	
In-Zn (206)			
Ir-Pb (215)			
Ir-Zn (215)			
K-Sn (136, 143)	c_{K} - 2.0 mol dm^{-3}	; c_{Sn} - 0.85 mol dm^{-3}	
K-Tl (7)	x_{K} - 0.05 mol %	; x_{Tl} - 35 mol %	
Li-Pb (146)	c_{Li} - 0.6 mol dm^{-3}	; c_{Pb} - 1.0 mol dm^{-3}	
Li-Tl (7)	x_{Li} - 0.05 mol %	; x_{Tl} - 35 mol %	
Li-Zn (121, 146, 152)	c_{Li} - 0.8 mol dm^{-3}	; c_{Zn} - 4.1 mol dm^{-3}	

Mn-Tl (104, 124, 159)	c_{Mn} - 0.42 mol dm^{-3}	; x_{Tl} - 37.4 mol %	
Na-Zn (8, 121, 137)	x_{Na} - 4 mol %	; x_{Zn} - 6.05 mol %	
Ni-Pb (214)			
Ni-Pt (108)	c_{Ni} - satd	; c_{Pt} - satd	; T-573 K
Pb-Pt (101, 108, 144)	;	c_{Pt} - satd	
Pb-W (214)			
Pd-Pt (108)		; c_{Pt} - satd	; T-573 K
Pt-Tl (101)	c_{Pt} - satd		
Sb-Sn (103)			
Tl-W (214)			

Solubilities as well as corrosion effects of technical alloys (no defined intermetallics) in mercury are inserted in the following works:
steels - (170-173, 175-177, 181)
low-melting alloys - (174, 181, 183)
refractory alloys - (157, 171-173, 175, 178, 179, 181)

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INTRODUCTION TO THE SOLUBILITY OF SOLIDS IN LIQUIDS

Nature of the Project

The Solubility Data Project (SDP) has as its aim a comprehensive search of the literature for solubilities of gases, liquids, and solids in liquids or solids. Data of suitable precision are compiled on data sheets in a uniform format. The data for each system are evaluated, and where data from different sources agree sufficiently, recommended values are proposed. The evaluation sheets, recommended values, and compiled data sheets are published on consecutive pages.

Definitions

A *mixture* (1, 2) describes a gaseous, liquid, or solid phase containing more than one substance, when the substances are all treated in the same way.

A *solution* (1, 2) describes a liquid or solid phase containing more than one substance, when for convenience one of the substances, which is called the *solvent*, and may itself be a mixture, is treated differently than the other substances, which are called *solutes*. If the sum of the mole fractions of the solutes is small compared to unity, the solution is called a *dilute solution*.

The *solubility* of a substance B is the relative proportion of B (or a substance related chemically to B) in a mixture which is saturated with respect to solid B at a specified temperature and pressure. *Saturated* implies the existence of equilibrium with respect to the processes of dissolution and precipitation; the equilibrium may be stable or metastable. The solubility of a substance in metastable equilibrium is usually greater than that of the corresponding substance in stable equilibrium. (Strictly speaking, it is the activity of the substance in metastable equilibrium that is greater.) Care must be taken to distinguish true metastability from supersaturation, where equilibrium does not exist.

Either point of view, mixture or solution, may be taken in describing solubility. The two points of view find their expression in the quantities used as measures of solubility and in the reference states used for definition of activities, activity coefficients and osmotic coefficients.

The qualifying phrase "substance related chemically to B" requires comment. The composition of the saturated mixture (or solution) can be described in terms of any suitable set of thermodynamic components. Thus, the solubility of a salt hydrate in water is usually given as the relative proportion of anhydrous salt in solution, rather than the relative proportions of hydrated salt and water.

Quantities Used as Measures of Solubility

1. *Mole fraction* of substance B, x_B:

$$x_B = n_B/\sum_{s=1}^{c} n_s \qquad [1]$$

where n_s is the amount of substance of s, and c is the number of distinct substances present (often the number of thermodynamic components in the system). *Mole per cent* of B is $100\,x_B$.

2. *Mass fraction* of substance B, w_B:

$$w_B = m_B'/\sum_{s=1}^{c} m_s' \qquad [2]$$

where m_s' is the mass of substance s. *Mass per cent* is $100\,w_B$. The equivalent terms *weight fraction* and *weight per cent* are not used.

3. *Solute mole (mass) fraction* of solute B (3, 4):

$$x_{s,B} = m_B/\sum_{s=1}^{c'} m_s = x_B/\sum_{s=1}^{c'} x_s \qquad [3]$$

$$w_{s,B} = m_B'/\sum_{s=1}^{c'} m_s' = w_B/\sum_{s=1}^{c'} w_s \qquad [3a]$$

where the summation is over the solutes only. For the solvent *A*, $x_{S,A} = x_A/(1 - x_A)$, $w_{S,A} = w_A/(1 - w_A)$. These quantities are called *Jänecke mole (mass) fractions* in many papers.

4. *Molality* of solute *B* (1, 2) in a solvent *A*:

$$m_B = n_B/n_A M_A \qquad \text{SI base units: mol kg}^{-1} \qquad [4]$$

where M_A is the molar mass of the solvent.

5. *Concentration* of solute *B* (1, 2) in a solution of volume *V*:

$$c_B = [B] = n_B/V \qquad \text{SI base units: mol m}^{-3} \qquad [5]$$

The symbol c_B is preferred to [*B*], but both are used. The terms molarity and molar are not used.

Mole and mass fractions are appropriate to either the mixture or the solution point of view. The other quantities are appropriate to the solution point of view only. Conversions among these quantities can be carried out using the equations given in Table I-1 following this Introduction. Other useful quantities will be defined in the prefaces to individual volumes or on specific data sheets.

In addition to the quantities defined above, the following are useful in conversions between concentrations and other quantities.

6. *Density*: $\rho = m/V$ SI base units: kg m^{-3} [6]

7. *Relative density*: d; the ratio of the density of a mixture to the density of a reference substance under conditions which must be specified for both (1). The symbol $d_{t'}^{t}$ will be used for the density of a mixture at t°C, 1 bar divided by the density of water at t'°C, 1 bar. (In some cases 1 atm = 101.325 kPa is used instead of 1 bar = 100 kPa.)

8. *A note on nomenclature*. The above definitions use the nomenclature of the IUPAC *Green Book* (1), in which a solute is called *B* and a solvent *A* In compilations and evaluations, the first-named component (component 1) is the solute, and the second (component 2 for a two-component system) is the solvent. The reader should bear these distinctions in nomenclature in mind when comparing nomenclature and theoretical equations given in this Introduction with equations and nomenclature used on the evaluation and compilation sheets.

Thermodynamics of Solubility

The principal aims of the Solubility Data Project are the tabulation and evaluation of: (a) solubilities as defined above; (b) the nature of the saturating phase. Thermodynamic analysis of solubility phenomena has two aims: (a) to provide a rational basis for the construction of functions to represent solubility data; (b) to enable thermodynamic quantities to be extracted from solubility data. Both these are difficult to achieve in many cases because of a lack of experimental or theoretical information concerning activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve critical evaluation of a large body of data that is not directly relevant to solubility. The following is an outline of the principal thermodynamic relations encountered in discussions of solubility. For more extensive discussions and references, see books on thermodynamics, e.g., (5-12).

Activity Coefficients (1)

(a) *Mixtures*. The activity coefficient f_B of a substance *B* is given by

$$RT \ln (f_B x_B) = \mu_B - \mu_B^* \qquad [7]$$

where μ_B^* is the chemical potential of pure *B* at the same temperature and pressure. For any substance *B* in the mixture,

$$\lim_{x_B \to 1} f_B = 1 \qquad [8]$$

(b) *Solutions*.

(i) *Solute B*. The molal activity coefficient γ_B is given by

$$RT \ln(\gamma_B m_B) = \mu_B - (\mu_B - RT \ln m_B)^\infty \qquad [9]$$

where the superscript $^\infty$ indicates an infinitely dilute solution. For any solute *B*,

$$\gamma_B^\infty = 1 \qquad [10]$$

Activity coefficients y_B connected with concentrations c_B, and $f_{x,B}$ (called the *rational activity coefficient*) connected with mole fractions x_B are defined in analogous ways. The relations among them are (1, 9), where ρ^* is the density of the pure solvent:

$$f_B = (1 + M_A\sum_s m_s)\gamma_B = [\rho + \sum_s(M_A - M_s)c_s]y_B/\rho^* \qquad [11]$$

$$\gamma_B = (1 - \sum_s x_s)f_{x,B} = (\rho - \sum_s M_s c_s)y_B/\rho^* \qquad [12]$$

$$y_B = \rho^* f_{x,B}[1 + \sum_s(M_s/M_A - 1)x_B]/\rho = \rho^*(1 + \sum_s M_s m_s)\gamma_B/\rho \qquad [13]$$

For an electrolyte solute $B \equiv C_{\nu+}A_{\nu-}$, the activity on the molality scale is replaced by (9)

$$\gamma_B m_B = \gamma_\pm{}^\nu m_B{}^\nu Q^\nu \qquad [14]$$

where $\nu = \nu_+ + \nu_-$, $Q = (\nu_+{}^{\nu+}\nu_-{}^{\nu-})^{1/\nu}$, and $\gamma_\pm$ is the mean ionic activity coefficient on the molality scale. A similar relation holds for the concentration activity, $y_B c_B$. For the mole fractional activity,

$$f_{x,B}x_B = Q^\nu f_\pm{}^\nu x_\pm{}^\nu \qquad [15]$$

where $x_\pm = (x_+x_-)^{1/\nu}$. The quantities x_+ and x_- are the ionic mole fractions (9), which are

$$x_+ = \nu_+x_B/[1 + \sum_s(\nu_s - 1)x_s]; \quad x_- = \nu_-x_B[1 + \sum_s(\nu_s - 1)x_s] \qquad [16]$$

where ν_s is the sum of the stoichiometric coefficients for the ions in a salt with mole fraction x_s. Note that the mole fraction of solvent is now

$$x_A{}' = (1 - \sum_s \nu_s x_s)/[1 + \sum_s(\nu_s - 1)x_s] \qquad [17]$$

so that

$$x_A{}' + \sum_s \nu_s x_s = 1 \qquad [18]$$

The relations among the various mean ionic activity coefficients are:

$$f_\pm = (1 + M_A\sum_s \nu_s ms)\gamma_\pm = [\rho + \sum_s(\nu_s M_A - M_s)c_s]y_\pm/\rho^* \qquad [19]$$

$$\gamma_\pm = \frac{(1 - \sum_s x_s)f_\pm}{1 + \sum_s(\nu_s - 1)x_s} = (\rho - \sum_s M_s c_s)y_\pm/\rho^* \qquad [20]$$

$$y_\pm = \frac{\rho^*[1 + \sum_s(M_s/M_A - 1)xs]f_\pm}{\rho[1 + \sum_s(\nu_s - 1)x_s]} = \rho^*(1 + \sum_s M_s m_s)\gamma_\pm/\rho \qquad [21]$$

(ii) *Solvent, A*:

The *osmotic coefficient*, ϕ, of a solvent A is defined as (1):

$$\phi = (\mu_A{}^* - \mu_A)/RT\, M_A \sum_s m_s \qquad [22]$$

where $\mu_A{}^*$ is the chemical potential of the pure solvent.

The *rational osmotic coefficient*, ϕ_x, is defined as (1):

$$\phi_x = (\mu_A - \mu_A{}^*)/RT\ln x_A = \phi M_A \sum_s m_s/\ln(1 + M_A \sum_s m_s) \qquad [23]$$

The activity, a_A, or the activity coefficient, f_A, is sometimes used for the solvent rather than the osmotic coefficient. The activity coefficient is defined relative to pure A, just as for a mixture.

For a mixed solvent, the molar mass in the above equations is replaced by the average molar mass; i.e., for a two-component solvent with components J, K, M_A becomes

$$M_A = M_J + (M_K - M_J)x_{v,K} \qquad [24]$$

where $x_{v,K}$ is the solvent mole fraction of component K.

The osmotic coefficient is related directly to the vapor pressure, p, of a solution in equilibrium with vapor containing A only by (12, p.306):

$$\phi M_A \sum_s \nu_s m_s = -\ln(p/p_A{}^*) + (V_{m,A}^* - B_{AA})(p - p_A{}^*)/RT \qquad [25]$$

where $p_A{}^*$, $V_{m,A}^*$ are the vapor pressure and molar volume of pure solvent A, and B_{AA} is the second virial coefficient of the vapor.

The Liquid Phase

A general thermodynamic differential equation which gives solubility as a function of temperature, pressure and composition can be derived. The approach is similar to that of Kirkwood and Oppenheim (7); see also (11, 12). Consider a solid mixture containing *c* thermodynamic components *i*. The Gibbs-Duhem equation for this mixture is:

$$\sum_{i=1}^{c} x_i'(S_i'\mathrm{d}T - V_i'\mathrm{d}p + \mathrm{d}\mu_i') = 0 \qquad [26]$$

A liquid mixture in equilibrium with this solid phase contains *c'* thermodynamic components *i*, where *c'* > *c*. The Gibbs-Duhem equation for the liquid mixture is:

$$\sum_{i=1}^{c} x_i(S_i\mathrm{d}T - V_i\mathrm{d}p + \mathrm{d}\mu_i') + \sum_{i=c+1}^{c'} x_i(S_i\mathrm{d}T - V_i\mathrm{d}p + \mathrm{d}\mu_i) = 0 \qquad [27]$$

Subtract [26] from [27] and use the equation

$$\mathrm{d}\mu_i = (\mathrm{d}\mu_i)_{T,p} - S_i\mathrm{d}T + V_i\mathrm{d}p \qquad [28]$$

and the Gibbs-Duhem equation at constant temperature and pressure:

$$\sum_{i=1}^{c} x_i(\mathrm{d}\mu_i')_{T,p} + \sum_{i=c+1}^{c'} x_i(\mathrm{d}\mu_i)_{T,p} = 0 \qquad [29]$$

The resulting equation is:

$$RT\sum_{i=1}^{c} x_i'(\mathrm{d}\ln a_i)_{T,p} = \sum_{i=1}^{c} x_i'(H_i - H_i')\mathrm{d}T/T - \sum_{i=1}^{c} x_i'(V_i - V_i')\mathrm{d}p \qquad [30]$$

where

$$H_i - H_i' = T(S_i - S_i') \qquad [31]$$

is the enthalpy of transfer of component *i* from the solid to the liquid phase at a given temperature, pressure and composition, with H_i and S_i the partial molar enthalpy and entropy of component *i*.

Use of the equations

$$H_i - H_i^0 = -RT^2(\partial\ln a_i/\partial T)_{x,p} \qquad [32]$$

and

$$V_i - V_i^0 = RT(\partial\ln a_i/\partial p)_{x,T} \qquad [33]$$

where superscript 0 indicates an arbitrary reference state gives:

$$RT\sum_{i=1}^{c} x_i'\mathrm{d}\ln a_i = \sum_{i=1}^{c} x_i'(H_i^0 - H_i')\partial T/T - \sum_{i=1}^{c} x_i'(V_i^0 - V_i')\mathrm{d}p \qquad [34]$$

where

$$\mathrm{d}\ln a_i = (\mathrm{d}\ln a_i)_{T,p} + (\partial\ln a_i/\partial T)_{x,p} + (\partial\ln a_i/\partial p)_{x,T} \qquad [35]$$

The terms involving enthalpies and volumes in the solid phase can be written as:

$$\sum_{i=1}^{c} x_i'H_i' = H_s^* \qquad \sum_{i=1}^{c} x_i'V_i' = V_s^* \qquad [36]$$

With eqn [36], the final general solubility equation may then be written:

$$R\sum_{i=1}^{c} x_i'\mathrm{d}\ln a_i = (H_s^* - \sum_{i=1}^{c} x_i'H_i^0)\mathrm{d}(1/T) - (V_s^* - \sum_{i=1}^{c} x_i'V_i^0)\mathrm{d}p/T \qquad [37]$$

Note that those components which are not present in both phases do not appear in the solubility equation. However, they do affect the solubility through their effect on the activities of the solutes.

Several applications of eqn [37] (all with pressure held constant) will be discussed below. Other cases will be discussed in individual evaluations.

(a) *Solubility as a function of temperature.*

Consider a binary solid compound A_nB in a single solvent *A*. There is no fundamental thermodynamic distinction between a binary compound of A and B which dissociates completely or partially on melting and a solid mixture of A and B; the binary compound can be regarded as a solid mixture of constant composition. Thus, with $c = 2$, $x_A' = n/(n + 1)$, $x_B' = 1/(n + 1)$, eqn [37] becomes:

$$\mathrm{d}\ln(a_A{}^n a_B) = -\Delta H_{AB}{}^0 \mathrm{d}(1/RT) \qquad [38]$$

where

$$\Delta H_{AB}{}^0 = nH_A + H_B - (n + 1)H_s{}^* \qquad [39]$$

is the molar enthalpy of melting and dissociation of pure solid A_nB to form A and B in their reference states. Integration between T and T_0, the melting point of the pure binary compound A_nB, gives:

$$\ln(a_A{}^n a_B) = \ln(a_A{}^n a_B)_{T=T_0} - \int_{T_0}^{T} \Delta H_{AB}{}^0 \mathrm{d}(1/RT) \qquad [40]$$

(i) Non-electrolytes

In eqn [32], introduce the pure liquids as reference states. Then, using a simple first-order dependence of $\Delta H_{AB}{}^*$ on temperature, and assuming that the activitity coefficients conform to those for a simple mixture (6):

$$RT \ln f_A = wx_B{}^2 \qquad \mathrm{RT} \ln f_B = wx_A{}^2 \qquad [41]$$

then, if w is independent of temperature, eqn [32] and [33] give:

$$\ln\{x_B(1-x_B)^n\} + \ln\left\{\frac{n^n}{(1 + n)^{n+1}}\right\} = G(T) \qquad [42]$$

where

$$G(T) = -\left\{\frac{\Delta H_{AB}{}^* - T^*\Delta C_p{}^*}{R}\right\}\left\{\frac{1}{T} - \frac{1}{T^*}\right\} + \frac{\Delta C_p{}^*}{R}\ln(T/T^*) - \frac{w}{R}\left\{\frac{x_A{}^2 + nx_B{}^2}{T} - \frac{n}{(n + 1)T^*}\right\} \qquad [43]$$

where $\Delta C_p{}^*$ is the change in molar heat capacity accompanying fusion plus decomposition of the pure compound to pure liquid A and B at temperature T^*, (assumed here to be independent of temperature and composition), and $\Delta H_{AB}{}^*$ is the corresponding change in enthalpy at $T = T^*$. Equation [42] has the general form:

$$\ln\{x_B(1-x_B)^n\} = A_1 + A_2/(T/\mathrm{K}) + A_3\ln(T/\mathrm{K}) + A_4(x_A{}^2 + nx_B{}^2)/(T/\mathrm{K}) \qquad [44]$$

If the solid contains only component B, then $n = 0$ in eqn [42] to [44].

If the infinite dilution reference state is used, then:

$$\mathrm{RT} \ln f_{x,B} = w(x_A{}^2 - 1) \qquad [45]$$

and [39] becomes

$$\Delta H_{AB}{}^\infty = nH_A{}^* + H_B{}^\infty - (n + 1)H_s{}^* \qquad [46]$$

where $\Delta H_{AB}{}^\infty$ is the enthalpy of melting and dissociation of solid compound A_nB to the infinitely dilute reference state of solute B in solvent A; $H_A{}^*$ and $H_B{}^\infty$ are the partial molar enthalpies of the solute and solvent at infinite dilution. Clearly, the integral of eqn [32] will have the same form as eqn [35], with $\Delta H_{AB}{}^\infty$ replacing $\Delta H_{AB}{}^*$, $\Delta C_p{}^\infty$ replacing ΔCp^*, and $x_A{}^2 - 1$ replacing $x_A{}^2$ in the last term.

See (5) and (11) for applications of these equations to experimental data.

(ii) Electrolytes

(a) Mole fraction scale

If the liquid phase is an aqueous electrolyte solution, and the solid is a salt hydrate, the above treatment needs slight modification. Using rational mean activity coefficients, eqn [34] becomes:

$$\ln\left\{\frac{x_B{}^{\nu}(1 - x_B)^n}{[1 + (\nu - 1)x_B]^{n+\nu}}\right\} - \ln\left\{\frac{n^n}{(n + \nu)^{n+\nu}}\right\} + \ln\left\{\left[\frac{f_B}{f_B{}^*}\right]^{\nu}\left[\frac{f_A}{f_A{}^*}\right]^{n}\right\}$$

$$= -\left\{\frac{\Delta H_{AB}{}^* - T^*\Delta C_p{}^*}{R}\right\}\left\{\frac{1}{T} - \frac{1}{T^*}\right\} + \frac{\Delta Cp^*}{R}\ln(T/T^*) \qquad [47]$$

where superscript * indicates the pure salt hydrate. If it is assumed that the activity coefficients follow the same temperature dependence as the right-hand side of eqn [47] (13-16), the thermochemical quantities on the right-hand side of eqn [47] are not rigorous thermodynamic enthalpies and heat capacities, but are apparent quantities only. Data on activity coefficients (9) in concentrated solutions indicate that the terms involving these quantities are not negligible, and their dependence on temperature and composition along the solubility-temperature curve is a subject of current research.

A similar equation (with $\nu = 2$ and without the heat capacity terms or activity coefficients) has been used to fit solubility data for some MOH-H_2O systems, where M is an alkali metal (13); enthalpy values obtained agreed well with known values. The full equation has been deduced by another method in (14) and applied to MCl_2-H_2O systems in (14) and (15). For a summary of the use of equation [47] and similar equations, see (14)

(2) Molality scale

Substitution of the mean activities on the molality scale in eqn [40] gives:

$$\nu\ln\left[\frac{\gamma_{\pm}m_B}{\gamma_{\pm}{}^*m_B{}^*}\right] - \nu(m_B/m_B{}^* - 1) - \nu\{m_B(\phi - 1)/m_B{}^* - \phi^* + 1\}$$

$$= G(T) \qquad [48]$$

where $G(T)$ is the same as in eqn [47], $m_B{}^* = 1/nM_A$ is the molality of the anhydrous salt in the pure salt hydrate and $\gamma_{\pm}$ and ϕ are the mean activity coefficient and the osmotic coefficient, respectively. Use of the osmotic coefficient for the activity of the solvent leads, therefore, to an equation that has a different appearance to [47]; the content is identical. However, while eqn [47] can be used over the whole range of composition ($0 < x_B < 1$), the molality in eqn [48] becomes infinite at $x_B = 1$; use of eqn [48] is therefore confined to solutions sufficiently dilute that the molality is a useful measure of composition. The essentials of eqn [48] were deduced by Williamson (17); however, the form used here appears first in the *Solubility Data Series*. For typical applications (where activity and osmotic coefficients are not considered explicitly, so that the enthalpies and heat capacities are apparent values, as explained above), see (18).

The above analysis shows clearly that a rational thermodynamic basis exists for functional representation of solubility-temperature curves in two-component systems, but may be difficult to apply because of lack of experimental or theoretical knowledge of activity coefficients and partial molar enthalpies. Other phenomena which are related ultimately to the stoichiometric activity coefficients and which complicate interpretation include ion pairing, formation of complex ions, and hydrolysis. Similar considerations hold for the variation of solubility with pressure, except that the effects are relatively smaller at the pressures used in many investigations of solubility (5).

(b) *Solubility as a function of composition.*

At constant temperature and pressure, the chemical potential of a saturating solid phase is constant:

$$\mu_{A_nB}{}^* = \mu_{A_nB}(\mathrm{sln}) = n\mu_A + \mu_B \qquad [49]$$

$$= (n\mu_A{}^* + \nu_+\mu_+{}^{\infty} + \nu_-\mu_-{}^{\infty}) + nRT\ \ln f_Ax_A$$

$$+ \nu RT\ \ln(\gamma_{\pm}m_{\pm}Q)$$

for a salt hydrate A_nB which dissociates to water (A), and a salt (B), one mole of which ionizes to give ν_+ cations and ν_- anions in a solution in which other substances (ionized or not) may be present. If the saturated solution is sufficiently dilute, $f_A = x_A = 1$, and the quantity K_s in

$$\Delta G^{\infty} = (\nu_+\mu_+{}^{\infty} + \nu_-\mu_-{}^{\infty} + n\mu_A{}^* - \mu_{AB}{}^*)$$

$$= -RT\ \ln K_s$$

$$= -\nu RT \ln(Q\gamma_{\pm}m_B) \qquad [50]$$

is called the *solubility product* of the salt. (It should be noted that it is not customary to extend this definition to hydrated salts, but there is no reason why they should be excluded.) Values of the solubility product are often given on mole fraction or concentration scales. In dilute solutions, the theoretical behaviour of the activity coefficients as a function of ionic strength is often sufficiently well known that reliable extrapolations to infinite dilution can be made, and values of K_s can be determined. In more concentrated solutions, the same problems with activity coefficients that were outlined in the section on variation of solubility with temperature still occur. If these complications do not arise, the solubility of a hydrate salt $C_\nu A_\nu \cdot nH_2O$ in the presence of other solutes is given by eqn [50] as

$$\nu \ln\{m_B/m_B(0)\} = -\nu \ln\{\gamma_{\pm}/\gamma_{\pm}(0)\} - n \ln\{a_A/a_A(0)\} \qquad [51]$$

where a_A is the activity of water in the saturated solution, m_B is the molality of the salt in the saturated solution, and (0) indicates absence of other solutes. Similar considerations hold for non-electrolytes.

Consideration of *complex mixed ligand equilibria* in the solution phase are also frequently of importance in the interpretation of solubility equilibria. For nomenclature connected with these equilibria (and solubility equilibria as well), see (19, 20).

The Solid Phase

The definition of solubility permits the occurrence of a single solid phase which may be a pure anhydrous compound, a salt hydrate, a non-stoichiometric compound, or a solid mixture (or solid solution, or "mixed crystals"), and may be stable or metastable. As well, any number of solid phases consistent with the requirements of the phase rule may be present. Metastable solid phases are of widespread occurrence, and may appear as polymorphic (or allotropic) forms or crystal solvates whose rate of transition to more stable forms is very slow. Surface heterogeneity may also give rise to metastability, either when one solid precipitates on the surface of another, or if the size of the solid particles is sufficiently small that surface effects become important. In either case, the solid is not in stable equilibrium with the solution. See (21) for the modern formulation of the effect of particle size on solubility. The stability of a solid may also be affected by the atmosphere in which the system is equilibrated.

Many of these phenomena require very careful, and often prolonged, equilibration for their investigation and elimination. A very general analytical method, the "wet residues" method of Schreinemakers (22), is often used to investigate the composition of solid phases in equilibrium with salt solutions. This method has been reviewed in (23), where [see also (24)] least-squares methods for evaluating the composition of the solid phase from wet residue data (or initial composition data) and solubilities are described. In principle, the same method can be used with systems of other types. Many other techniques for examination of solids, in particular X-ray, optical, and thermal analysis methods, are used in conjunction with chemical analyses (including the wet residues method).

COMPILATIONS AND EVALUATIONS

The formats for the compilations and critical evaluations have been standardized for all volumes. A brief description of the data sheets has been given in the FOREWORD; additional explanation is given below.

Guide to the Compilations

The format used for the compilations is, for the most part, self-explanatory. The details presented below are those which are not found in the FOREWORD or which are not self-evident.

Components. Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The formula is given either in terms of the IUPAC or Hill (25) system and the choice of formula is governed by what is usual for most current users: i.e., IUPAC for inorganic compounds, and Hill system for organic compounds. Components are ordered according to:

(a) saturating components;
(b) non-saturating components in alphanumerical order;
(c) solvents in alphanumerical order.

The saturating components are arranged in order according to a 18-column periodic table with two additional rows:

Columns 1 and 2: H, alkali elements, ammonium, alkaline earth elements
3 to 12: transition elements
13 to 17: boron, carbon, nitrogen groups; chalcogenides, halogens
18: noble gases
Row 1: Ce to Lu
Row 2: Th to the end of the known elements, in order of atomic number.

Salt hydrates are generally not considered to be saturating components since most solubilities are expressed in terms of the anhydrous salt. The existence of hydrates or solvates is carefully noted in the text, and CA Registry Numbers are given where available, usually in the critical evaluation. Mineralogical names are also quoted, along with their CA Registry Numbers, again usually in the critical evaluation.

Original Measurements. References are abbreviated in the forms given by *Chemical Abstracts Service Source Index* (CASSI). Names originally in other than Roman alphabets are given as transliterated by *Chemical Abstracts*.

Experimental Values. Data are reported in the units used in the original publication, with the exception that modern *names* for units and quantities are used; e.g., mass per cent for weight per cent; mol dm^{-3} for molar; etc. Both mass and molar values are given. Usually, only one type of value (e.g., mass per cent) is found in the original paper, and the compiler has added the other type of value (e.g., mole per cent) from computer calculations based on 1983 atomic weights (26).

Errors in calculations and fitting equations in original papers have been noted and corrected, by computer calculations where necessary.

Method. Source and Purity of Materials. Abbreviations used in *Chemical Abstracts* are often used here to save space.

Estimated Error. If these data were omitted by the original authors, and if relevant information is available, the compilers have attempted to estimate errors from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and and reporting errors are based on the papers by Ku and Eisenhart (27).

Comments and/or Additional Data. Many compilations include this section which provides short comments relevant to the general nature of the work or additional experimental and thermodynamic data which are judged by the compiler to be of value to the reader.

References. See the above description for Original Measurements.

Guide to the Evaluations

The evaluator's task is to check whether the compiled data are correct, to assess the reliability and quality of the data, to estimate errors where necessary, and to recommend "best" values. The evaluation takes the form of a summary in which all the data supplied by the compiler have been critically reviewed. A brief description of the evaluation sheets is given below.

Components. See the description for the Compilations.

Evaluator. Name and date up to which the literature was checked.

Critical Evaluation

(a) Critical text. The evaluator produces text evaluating all the published data for each given system. Thus, in this section the evaluator reviews the merits or shortcomings of the various data. Only published data are considered; even published data can be considered only if the experimental data permit an assessment of reliability.

(b) Fitting equations. If the use of a smoothing equation is justifiable the evaluator may provide an equation representing the solubility as a function of the variables reported on all the compilation sheets.

(c) Graphical summary. In addition to (b) above, graphical summaries are often given.

(d) Recommended values. Data are *recommended* if the results of at least two independent groups are available and they are in good agreement, and if the evaluator has no doubt as to the adequacy and reliability of the applied experimental and computational procedures. Data are considered as *tentative* if only one set of measurements is available, or if the evaluator considers some aspect of the computational or experimental method as mildly undesirable but estimates that it should cause only minor errors. Data are considered as *doubtful* if the evaluator considers some aspect of the computational or experimental method as undesirable but still considers the data to have some value in those instances where the order of magnitude of the solubility is needed. Data determined by an inadequate method or under ill-defined conditions are *rejected*. However references to these data are included in the evaluation together with a comment by the evaluator as to the reason for their rejection.

(e) References. All pertinent references are given here. References to those data which, by virtue of their poor precision, have been rejected and not compiled are also listed in this section.

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in S.I. units (1, 28) when the data can be accurately converted.

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September, 1986

R. Cohen-Adad,
Villeurbanne, France

J. W. Lorimer,
London, Ontario, Canada

M. Salomon,
Fair Haven, New Jersey, U.S.A.

COMPONENTS:	EVALUATOR:
(1) Silver-cadmium 1:1; AgCd; [12002-62-9] (2) Mercury; Hg; [7439-97-6]	C. Gumiński; Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland May 1984

CRITICAL EVALUATION:

The Ag-Cd-Hg system was investigated with the use of potentiometry, first by Tammann and Jander (1) and later by Hartmann and Schölzel (2). According to them no intermetallic compounds between Ag and Cd are formed in Hg. However, further studies of Kemula and coworkers (3) with stripping voltammetry and of Zebreva (4) with amalgam polarography suggested the formation of AgCd; Zebreva and Kozlovskii (8) reported the solubility product, K_s = [Ag][Cd], as $(7.3\pm0.9)\times10^{-6}$ mol^2 dm^{-6} at 291 K. From the point of view of the remaining works this result should be rejected, because it was never confirmed. Extended studies on this system carried out by Ostapczuk and Kublik (5) with the use of electroanalytical techniques gave no evidence of intermetallic compound formation between Ag and Cd in Hg up to the solubility limit of Ag in Hg (5.1×10^{-2} mol dm^{-3} at 298 K). On the other hand, under conditions where Ag-Hg crystals are deposited on the surface of amalgam electrodes some codeposition of Cd on these crystals takes place, and this might be interpreted erroneously as a proof of the precipitation of AgCd in Hg. Also Rodgers and Meites (6) as well as Glodowski and Kublik (7) confirmed that compounds between Ag and Cd do not exist in unsaturated Ag amalgams.

The AgCd solid phase is known in the Ag-Cd binary alloys (9). In summary, at 298 K, AgCd is more soluble than Ag in Hg.

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COMPONENTS:

(1) Silver-cadmium 1:1; AgCd; [12002-62-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zebreva, A.I.

Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR 1962, *9*, 55-70.

VARIABLES:

Temperature: 291 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of AgCd in Hg at 18 °C:

$10^3c_{Cd}{}^i$ mol dm^{-3}	$10^3c_{Cd}{}^f$ mol dm^{-3}	$10^3c_{Ag}{}^i$ mol dm^{-3}	$10^3c_{Ag}{}^f$ mol dm^{-3}	10^6K_s mol^2 dm^{-6}
2.10	2.09	3.0	2.91^a 2.99^b	6.2
2.10	2.06	3.5	3.45^a 3.84^b	7.1
2.10	1.94	4.0	3.82	7.4
2.10	1.70	4.5	4.10	7.0
2.10	1.48	5.0	4.92^a 4.38^b	7.3^a 6.5^b
2.50	2.42	3.0	2.92	7.1
3.00	2.99	2.0	- 1.99^c	- 6.0^c
3.30	2.82	3.0	2.52	7.1
3.70	3.10	3.0	2.40	7.45
4.20	4.15	1.5	1.45	6.1
4.20	3.93	2.0	1.73	6.8
2.10	2.09	3.0	2.91^a	2.99^{b}6.2

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The complex Ag-Cd amalgams were obtained by simultaneous electroreduction of Ag(I) and Cd(II) solutions on a Hg cathode. The amalgams were transferred to the reservoir of a dropping amalgam electrode. This operation was carried out in a CO_2 atmosphere. Then polarographic waves of the anodic oxidation of Cd from the complex amalgams in 0.25 mol dm^{-3} Na_2SO_4 were recorded. The concentration of Cd in equilibrium was calculated using calibration curves of concentrations vs. oxidation current. K_s-values were calculated from the concentration balance of the metals.

SOURCE AND PURITY OF MATERIALS:

Nothing specified. Hg was probably (2) purified by a long equilibration with $Hg(NO)_3)_2$ solution and distillation in vacuum.

ESTIMATED ERROR:

Solubility: ± 12 %, as reported in (1); standard deviation ± 9 %, as calculated by compilers. Temperature: nothing specified.

REFERENCES:

1. Zebreva, A.I.; Kozlovskii, M.T. *Zavod. Lab.* 1964, *30*, 1193.
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COMPONENTS: (1) Silver-cadmium 1:1; AgCd; [12002-62-9] (2) Mercury; Hg; [7439-97-6]	ORIGINAL MEASUREMENTS: Zebreva, A.I. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* <u>1962</u>, *9*, 55-70.

EXPERIMENTAL VALUES (continued)

The solubility product of AgCd in Hg at 18 °C:

$10^3c_{Cd}{}^{i}$ mol dm^{-3}	$10^3c_{Cd}{}^{f}$ mol dm^{-3}	$10^3c_{Ag}{}^{i}$ mol dm^{-3}	$10^3c_{Ag}{}^{f}$ mol dm^{-3}	10^6K_s mol^2 dm^{-6}
4.20	3.74	2.5	2.04	7.6
4.20	2.40	5.0	3.20	7.7
5.50	4.65	2.5	1.55^a 1.65^b	7.2^a 7.7^b
mean value (by compilers, taking into account the corrected results)				$(7.0\pm0.6)\times10^{-6}$

[a] erroneous value

[b] corrected by compilers

[c] calculated by compilers

The stoichiometry of AgCd was established by amperometric titration of Ag amalgam with Cd. In (1) the K_s-value of $(7.3\pm0.9)\times10^{-6}$ mol^2 dm^{-6} was reported.

COMPONENTS:	EVALUATOR:
(1) Silver-tin 3:1; Ag_3Sn; [12041-38-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1984

CRITICAL EVALUATION:

Joyner and Knight (2, 9) reported solubility values of Ag and Sn in mutually saturated amalgams at temperatures ranging from 298.6 to 487.2 K; the numbers differ significantly from those in pure Hg. Gayler (10) determined melting points on the Ag_3Sn-Hg phase diagram. In spite of the Ag_3Sn phase transition at 505 K, there is a poor agreement between the results of (9) and (10), so no acceptable solubility values may be suggested.

In potentiometry and amalgam polarography experiments carried out by Kovaleva and Zebreva (1) at room temperature no interaction was found between Ag and Sn in complex amalgams containing Ag at concentrations lower than $5x10^{-2}$ mol dm^{-3}. Also Glodowski and Kublik (12) demonstrated with the use of voltammetry that any Ag-Sn compound is precipitated in the diluted complex amalgam. When the concentration of Ag is higher than its solubility in Hg, Ag_3Hg_4 solid phase may be formed. The alloy of composition Ag_3Sn is decomposed by Hg to Ag_3Hg_4 or Ag_5Hg_4 and solid Sn saturated with Hg (2-8, 11). The Ag-Sn-Hg phase diagram at 310 K is taken from (7). Near room temperature the solubility of Ag_3Sn is higher than the solubility of Ag in Hg (1-12).

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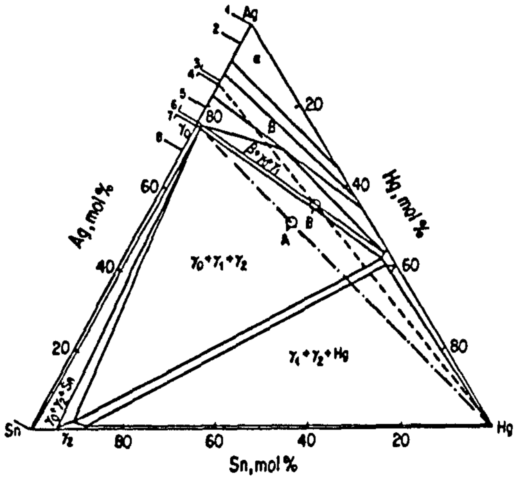

α - Ag mixed crystal
β - Ag-Hg
γ_0 - Ag_3Sn
γ_1 - Ag_3Hg_4
γ_2 - $Sn_{7-8}Hg$

COMPONENTS:

(1) Silver-tin 3:1; Ag_3Sn; [12041-38-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Joyner, R.A. *J. Chem. Soc.* 1911, 195-208.

Knight, W.A.; Joyner, R.A. *J. Chem. Soc.* 1913, 2247-62.

VARIABLES:

Temperature: 298-487 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubilities of various Ag-Sn alloys reported as the ranges of composition (including Ag_3Sn) were determined:

	Primary solid phase					
t/°C	x_{Ag}/mol %	x_{Sn}/mol %	x_{Ag}/mass %	x_{Ag}/mol %	x_{Sn}/mass %	x_{Sn}/mol %
25.40±0.01	11-91	9-89	0.045±0.005	0.083±0.010^{a}	0.751±0.008	1.26±0.01^{a}
25.40±0.01	32-62	38-68	0.043±0.003	0.080±0.006^{a}	0.753±0.004	1.26±0.01^{a}
25.60±0.01	23-81	19-77	0.041±0.003	0.076±0.006^{a}	0.758±0.006	1.27±0.01^{a}
63.05±0.15	21-81	19-79	0.181±0.003	0.330±0.006^{a}	2.56±0.04	4.24±0.07^{a}
63.10±0.05	92-95	5-8		0.06-0.36		1.82-4.16
90.0±0.2	21-81	19-79		0.53-1.00		4.2-20.6
166.5±0.5	11-89	11-89		1.41-3.57		4.6-67.1
214.0±0.5	9-57	43-91		3.8-5.1		61.4-93.2

^{a}by compilers.

The liquid is in equilibrium with the solids: Ag_3Hg_4 and Sn saturated with Hg. Equilibrium may not be attained at temperatures other than 63 °C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

An alloy of definite composition was prepared and placed in a glass tube filled with H_2. Hg was added in excess and the tube was sealed off. The tube was installed in a thermostatically controlled environment and was frequently shaken. Equilibrium was reached within a week. The tube was opened for analysis and, by means of a glass tube with a plug of glass-wool in the end, a quantity of liquid phase was withdrawn by means of a pipette. The sample was weighed, dissolved in HNO_3 (1:4) and boiled. The metastannic acid thus formed was collected and estimated in "the usual way". The filtrate was treated with NH_4Cl. AgCl was dissolved in NH_3 and then determined in the usual way.

SOURCE AND PURITY OF MATERIALS:

The best commercial Sn was used. Ag was purified by precipitation as AgCl and subsequent Hg reduction to Ag. Hg purity was not specified.

ESTIMATED ERROR:

Solubility: precision better than ± 10 %.

Temperature: precision between ± 0.01 and 0.5 K.

COMPONENTS:

(1) Silver-tin 3:1; Ag_3Sn; [12041-38-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Gayler, M.L.V.

J. Inst. Met. 1937, *60*, 379-406.

VARIABLES:

Temperature: 614-928 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Melting points from the liquidus of the Ag_3Sn-Hg phase diagram were determined by compilers and the composition was recalculated to mol %.

m_{Ag_3Sn}/mass %	x_{Ag_3Sn}/mol %	t/°C
7	3.3	341
20	10.2	412
35	19.6	455
55	35.6	510
60	40.5	551
70	51.4	565
80	64.4	600
85	72.0	622
90	80.3	648
93	85.8	640
95	89.6	657
98	95.7	655

The melting point of Ag_3Sn is 661 °C. The liquid phase is in equilibrium with a mixture of Ag_3Hg_4 and Ag_5Hg_4 for compositions up to 37 mass % of Ag_3Sn and with Ag_5Hg_4 for compositions up to 37 mass % of Ag_3Sn and with Ag_5Hg_4 for compositions over 37 mass %.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Fillings of the alloy together with the requisite amount of Hg were sealed off in a silica vessel in an atmosphere of dry H_2. Before thermal analysis was carried out, the container was heated slowly to about 460 °C, kept at this temperature for a short time, and then very slowly cooled to room temperature. Thermal analysis was performed with the use of a Pt/Pt-Rh calibrated thermocouple.

SOURCE AND PURITY OF MATERIALS:

Freshly purified and distilled Hg was used. Ag from Sheffield Smelting Co. contained 0.066 % of Cu and no more than 10^{-4} % of other impurities. Chemically pure Sn contained only traces of Fe.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:	EVALUATOR:
(1) Silver-zinc 1:1; AgZn; [12041-17-7] (2) Mercury; Hg; [7439-97-6]	C. Gumiński; Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1982

CRITICAL EVALUATION:

It was stated by Tammann and Jander (1) and later by Hartmann and Schölzel (2) that practically no interaction exists between Zn and Ag in Hg. Also Kozlovskii who used the polarographic method reported no evidence of the formation of any Ag-Zn compound. However, Kemula and coworkers (4) and Zebreva (5) in their studies with stripping voltammetry and amalgam polarography, respectively, established the formation of a compound, AgZn, in Hg. Zebreva determined its solubility product, $K_s = [Ag][Zn]$, as $(2.7 \pm 0.5) \times 10^{-6}$ mol^2 dm^{-6} at 291 K (5, 8). These papers should be rejected (5, 8) because this result was not confirmed in further detailed works.

Extended studies on this system carried out by Ostapczuk and Kublik (6) using potentiometry as well as cyclic and stripping voltammetry gave no evidence of formation of any intermetallic compounds in the Hg-rich part of the Ag-Zn-Hg system when the Ag concentration is lower than its solubility in Hg (5.1×10^{-2} mol dm^{-3} at 298 K); however, under conditions where Ag-Hg crystals were deposited on the surface of the amalgam electrodes some codeposition of Zn on such crystals occurs, and this effect might be erroneously interpreted as an evidence of precipitation of the intermetallic compound in Hg. Also Rodgers and Meites (7) by means of chronoamperometry and chronopotentiometry found no evidence for Ag-Zn compounds in the diluted complex amalgams.

AgZn is formed in the binary Ag-Zn alloys (9).

In conclusion, AgZn is more soluble in Hg than Ag in Hg, at 298 K.

References

1. Tammann, G.; Jander, W. *Z. Anorg. Chem.* 1922, *124*, 105.
2. Hartmann, H.; Schölzel, K. *Z. Phys. Chem., N. F.* 1956, *9*, 106.
3. Kozlovskii, M.T. *Rtut i Amalgamy v Elektrokhimicheskikh Metodakh Analiza*, Nauka, Alma-Ata, 1956.
4. Kemula, W.; Galus, Z.; Kublik, Z. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 1958, *6*, 661.
5. Zebreva, A.I. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1962, *9*, 55.
6. Ostapczuk, P.; Kublik, Z. *J. Electroanal. Chem.* 1977, *83*, 1.
7. Rodgers, R.S.; Meites, L. *J. Electroanal. Chem.* 1981, *125*, 167.
8. Zebreva, A.I.; Kozlovskii, M.T. *Zavod. Lab.* 1964, *30*, 1193.
9. Elliott, R.P. *Constitution of Binary Alloys*, McGraw-Hill, N.Y., 1965.

COMPONENTS:

(1) Silver-zinc 1:1; AgZn; [12041-17-7]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zebreva, A.I.

Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR 1962, *9*, 55-70.

VARIABLES:

Temperature: 291 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of AgZn in Hg at 18 °C:

$10^3c_{Zn}^i$ mol dm^{-3}	$10^3c_{Zn}^f$ mol dm^{-3}	$10^3c_{Ag}^i$ mol dm^{-3}	$10^3c_{Ag}^f$ mol dm^{-3}	10^6K_s mol^2 dm^{-6}
1.40	0.98	3.00	2.68^a 2.58^b	2.6^a 2.5^b
1.90	1.83	1.50	1.42^a 1.43^b	2.6
1.91	1.20	2.50	1.79	2.2
1.91	1.15	3.00	2.25^a 2.24^b	2.6
1.91	0.86	4.50	3.45	2.9
2.70	1.58	3.00	2.02^a 1.88^b	3.2^a 3.0^b
3.00	1.76	3.00	1.76	3.1^a 3.0^b
3.80	3.78	0.50	- 0.48	- 0.24 (rejected)
3.80	3.22	1.50	0.98^a 0.92	3.0
3.85	2.55	2.50	1.15^a 1.20	2.9^a 3.1^b
3.85	2.30	3.00	1.45	3.3
3.95	2.28	3.00	1.33	3.0

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The complex Ag-Zn amalgams were prepared by simultaneous electroreduction of Ag(I) and Zn(II) solutions on an Hg cathode. The amalgams were transferred to the reservoir of a dropping amalgam electrode. Such operations were carried out in a CO_2 atmosphere. Then polarographic waves for the anodic oxidation of Zn from the amalgams in 0.25 mol dm^{-3} Na_2SO_4 were recorded. The equilibrium concentration of Zn was calculated from a corresponding calibration plot: concentration vs. oxidation current. K_s-values were calculated from the concentra-tion balance.

SOURCE AND PURITY OF MATERIALS:

Nothing specified. Hg was probably (2) purified by a long equilibration with $Hg(NO_3)_2$ solution and distillation in vacuum.

ESTIMATED ERROR:

Solubility: ± 12 %, as reported in (1); standard deviation ± 9%, as found by compilers. Temperature: nothing specified.

REFERENCES:

1. Zebreva, A.I.; Kozlovskii, M.T. *Zavod. Lab.* 1964, *30*, 1193.
2. Kozlovskii, M.T. *Rtut i Amalgamy v Elektrokhimicheskikh Metodakh Analiza*, Nauka, Alma-Ata, 1956.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver-zinc 1:1; AgZn; [12041-17-7] (2) Mercury; Hg; [7439-97-6]	Zebreva, A.I. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* <u>1962</u>, *9*, 55-70.

EXPERIMENTAL VALUES (continued)

The solubility product of AgZn in Hg at 18 °C:

$10^3 c_{Zn}{}^{i}$ mol dm^{-3}	$10^3 c_{Zn}{}^{f}$ mol dm^{-3}	$10^3 c_{Ag}{}^{i}$ mol dm^{-3}	$10^3 c_{Ag}{}^{f}$ mol dm^{-3}	$10^6 K_s$ mol^2 dm^{-6}
4.30	2.52	3.00	1.23[a] 1.22	3.1
5.25	3.45	2.50	0.80[a] 0.70[b]	2.8[a] 2.4[b]
5.50	3.78	2.50	0.78	2.9
mean value (by compilers, taking into account the corrected results)				(2.8±0.3)x10^{-6}

[a] erroneous value

[b] corrected by compilers

The stoichiometry of AgZn was determined by the amperometric titration of Ag amalgam with Cd. In (1) the K_s-value of (2.7±0.5)x10^{-6} mol^2 dm^{-6} was reported.

COMPONENTS:	EVALUATOR:
(1) Gold-cadmium 3:1; Au_3Cd; [12006-68-7] (2) Mercury; Hg; [7439-97-6]	C. Gumiński; Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland March 1986

CRITICAL EVALUATION:

When more than a twofold excess of Au in regard to Cd is present in Hg then Au_3Cd may be formed. The formation of Au_3Cd was observed for the first time by Kozin and coworkers (1) who showed that the solubility product, $K_s = [Au]^3[Cd]$, is constant while the corresponding equilibrium constant, $K = [Au_3Cd]/[Au]^3[Cd]$, changes with concentrations of the parent metals. The experiments were performed in the temperature range 293-343 K. The formation of Au_3Cd was confirmed in the subsequent works of Palyska (6) at 278 to 348 K and of Ostapczuk and Kublik (2) at 298 K.

However, Mikheeva and Stromberg (3), based on their own mathematical analysis of the results (1), suggested the formation of Au_2Cd under these experimental conditions; see also the critical evaluation of solubility of AuCd in Hg. Rodgers and Meites (4) found no evidence of Au_3Cd formation in Hg. Nevertheless Au_3Cd is a stable phase of the Au-Cd binary system (5) and in the amalgam, as it was found by chemical analysis in (1). The temperature dependence of pK_s, based on the least square method, was constructed taking into account the results of (1, 2) and (6):

$$pK_s = -6.68 + 4.64 \times 10^3\ T^{-1}; \quad r = 0.959, \text{ concentration in mol dm}^{-3},\ T \text{ in K}$$

The K_s-values from different sources, (1), (2), and (6), at the same temperature are somewhat divergent, for example at 298 K: 9.0×10^{-10}, 4.4×10^{-9} and 1.3×10^{-9} mol^4 dm^{-12}, respectively, so it is difficult to give the recommended value. Reference (1) seems to be the most precise determination.

Values of Au_3Cd solubility in Hg (tentative)

T/K	$10^9 K_s$/mol^4 dm^{-12}	10^3soly/mol dm^{-3} ^{a}	ref.
298	1	2.5	1, 6
343	80	7.4	1

^{a}calculated by evaluators from K_s.

References

1. Kozin, L.F.; Cherkasova, G.F.; Erdenbaeva, M.I. *Izv. Akad. Nauk Kaz. SSR Ser. Khim.* 1969, no. 3, 42.
2. Ostapczuk, P.; Kublik, Z. *J. Electroanal. Chem.* 1977, *83*, 1.
3. Mikheeva, N.P.; Stromberg, A.G. *Zh. Anal. Khim.* 1978, *33*, 1726.
4. Rodgers, R.S.; Meites, L. *J. Electroanal. Chem.* 1981, *125*, 167.
5. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
6. Palyska, D. *M. Sc. Thesis*, University of Warsaw, 1975, *77*, 87.

COMPONENTS:

(1) Gold-cadmium 3:1; Au_3Cd; [12006-68-7]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kozin, L.F.; Cherkasova, G.F.;
Erdenbaeva, M.I.

Izv. Akad. Nauk Kaz. SSR, Ser. Khim. 1969, no. 3, 42-9.

VARIABLES:

Temperature: 293-343 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Au_3Cd is treated as a sparingly soluble compound in Hg. The equilibrium is well described by the solubility product, $K_s = [Au]^3[Cd]$. The dissociation constant, $K_d = [Au]^3[Cd]/[Au_3Cd]$, was also calculated to show its variance. The initial Au concentration was 4.91×10^{-4} mol fraction in all experiments.

t/°C	$10^5 x_{Cd}{}^i$	$10^5 x_{Cd}{}^r$	$10^4 x_{Au}{}^f$	$10^{17} K_s$/(mol fr.)^4	$10^{12} K_d$/(mol fr.)^3
20	0.102	0.0292	4.886	2.88^a 3.40^{b,c}	80.62^a 46.5^b
	0.428	0.0234	4.789	2.58	6.36
	1.194	0.0275	4.560	2.61	2.24
	2.295	0.0302	4.231	2.29	1.01
	4.304	0.0426	3.632	2.04	0.48
	5.130	0.0467	3.385	1.82	0.36
	6.544	0.0537	2.963	1.40	0.23
25	0.133	0.0380	4.885	4.42	46.6
	0.398	0.0407	4.805	4.52	12.61
	1.275	0.0489	4.541	4.58	3.70

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Amalgams of Au and Cd were separately prepared from the pure metals. They were mixed in various proportions. Differences of potentials of the complex Au-Cd and simple Cd amalgams were measured for 45-60 min for the following cell: Au-Cd(Hg)|0.2 mol dm^{-3} $CdSO_4$ 0.5 mol dm^{-3} $(NH_4)_2SO_4$, 3 mol dm^{-3} NH_3, 50-60 g dm^{-3} $N_2H_4 \cdot H_2SO_4$|Cd(Hg). The concentration of Cd in the right half cell was always constant. The solubility products were calculated from the potential differences. The experiments were performed in pure H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

High purity chemicals were used; "Cd-DD" and Hg was chemically purified and vacuum distilled.

ESTIMATED ERROR:

Solubility product: precision no better than ± 10 %.

Temperature: precision ± 0.2 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-cadmium 3:1; Au_3Cd; [12006-68-7] (2) Mercury; Hg; [7439-97-6]	Kozin, L.F.; Cherkasova, G.F.; Erdenbaeva, M.I. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* <u>1969</u>, no. 3, 42-9.

EXPERIMENTAL VALUES (continued)

t/°C	$10^5 x_{Cd}^{i}$	$10^5 x_{Cd}^{f}$	$10^4 x_{Au}^{f}$	$10^{17}K_s$/(mol fr.)^4	$10^{12}K_d$/(mol fr.)^3
	2.297	0.0551	4.239	4.09^{a} 4.19^{b}	1.82
	3.147	0.0690	3.989	4.38	1.42
	5.130	0.0893	3.400	3.51	0.696
	7.467	0.1257	2.474	2.47^{a} $1.90^{b,c}$	0.337^{a} 0.259^{b}
45	0.558	0.448	4.8/6	51.9	472.0
	1.324	0.479	4.638	47.8	56.6
	1.818	0.491	4.511	45.1	34.0
	2.652	0.584	4.289	46.1	22.3
	3.590	0.668	4.032	43.8	15.0
	5.125	0.786	3.507	34.0	7.8
	7.132	1.048	3.084	31.6^{a} 30.7^{b}	5.2
70	7.260	5.140	4.264	398	1880
	10.220	6.770	3.865	391	1130
	12.870	7.860	3.397	309	614
	18.650	10.480	2.449	154^{c}	188

[a] erroneous value

[b] corrected by compilers

[c] rejected

t/°C	K_s/(mol fraction)^4	K_s/mol^4 dm^{-12}
20	$(2.16\pm0.41)\times 10^{-17}$	$(4.6\pm0.9)\times 10^{-10}$
25	$(4.25\pm0.40)\times 10^{-17}$	$(9.0\pm0.9)\times 10^{-10}$
35	7.63×10^{-17}	1.6×10^{-9}
45	$(4.29\pm0.81)\times 10^{-16}$	$(9.0\pm1.7)\times 10^{-9}$
60	1.94×10^{-15}	4.1×10^{-8}
70	$(3.66\pm0.49)\times 10^{-15}$	$(7.7\pm1.0)\times 10^{-8}$

standard deviations and K_s expressed in mol^4 dm^{-12} are calculated by by compilers. Experiments were also performed at 5 °C but no numerical data are reported.

The temperature dependence of pK_s, based on the weighted least-square fit of linear correlation may be given by the equation:

$pK_s = (-6.57\pm0.67) + (4.67\pm0.20)\times10^3\ T^{-1}$; T in K and K_s in mol^4 dm^{-12} (by compilers).

COMPONENTS:

(1) Gold-cadmium 3:1; Au_3Cd; [12006-68-7]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Palyska, D.

M. Sc. Thesis, University of Warsaw 1975.

VARIABLES:

Temperature: 278-348 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product values of Au_3Cd in Hg are reported. The initial concentration of Au was always 7.0×10^{-2} mol dm^{-3} and the initial concentration of Cd was changed in the range 7.1×10^{-3} - 1.9×10^{-2} mol dm^{-3}.

t/°C	K_s/mol^4 dm^{-12}
5.0	$(1.8 \pm 0.4) \times 10^{-10}$
15.0	$(5.0 \pm 0.5) \times 10^{-10}$
25.0	$(1.3 \pm 0.3) \times 10^{-9}$
35.0	$(2.8 \pm 1.1) \times 10^{-9}$
45.0	$(7.7 \pm 2.3) \times 10^{-9}$
55.0	$(6.0 \pm 1.5) \times 10^{-8}$
65.0	$(1.6 \pm 0.5) \times 10^{-7}$
75.0	$(6.1 \pm 0.9) \times 10^{-7}$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Au amalgam was prepared by dissolution of the metal in Hg. Proper amounts of Cd were introduced into Hg and Au amalgam electrodes by constant current electrolysis. Potentials of both electrodes after the introduction of Cd were measured in 0.1 mol dm^{-3} $Cd(NO_3)_2$ vs. SCE. The difference of potentials of the electrodes at times longer than 600 s was constant and this was assumed to correspond to equilibrium conditions. Then equilibrium concentration of Cd was found and of Au calculated from mass balance and K_s by their multiplication.
The experiments were performed in an H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

99.99 % pure Au from Polish Mint, doubly distilled Hg after chemical purification with $Hg_2(NO_3)_2$, analytically pure $Cd(NO_3)_2$ from POCh and triply distilled H_2O were used. Solutions of Cd(II) were electrolyzed on an Hg cathode at -0.5 V vs. SCE.

ESTIMATED ERROR:

Solubility product: standard deviation higher than ± 10 %.

Temperature: precision ± 0.2 K.

COMPONENTS: (1) Gold-cadmium 3:1; Au_3Cd; [12006-68-7] (2) Mercury; Hg; [7439-97-6]	ORIGINAL MEASUREMENTS: Ostapczuk, P.; Kublik, Z. *J. Electroanal. Chem.* 1977, *83*, 1-17.
VARIABLES: Temperature: 298 K	PREPARED BY: C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Au_3Cd as a sparingly soluble compound in Hg has the following solubility product at 25 °C:

initial concn of Au/mol dm^{-3}	initial concn of Cd/mol dm^{-3}	K_s/mol^4 dm^{-12}
8.23×10^{-2}	1.0×10^{-4} - 2.0×10^{-3}	$(4.6 \pm 1.0) \times 10^{-9}$ [a]
4.7×10^{-2}	1.5×10^{-4} - 7.4×10^{-4}	$(4.3 \pm 0.8) \times 10^{-9}$ [a]

[a] the standard deviations are from a private communication by P. Ostapczuk.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Au amalgam was prepared by dissolution of Au in Hg. Cd was introduced by electrolysis into the hanging mercury drop electrode and into a hanging gold amalgam drop electrode in equal amounts. Potentials of the electrodes were measured vs. SCE. From the potential differences the solubility products were calculated. The experiments were carried out in an Ar atmosphere.	SOURCE AND PURITY OF MATERIALS: 99.99 % pure Au (from Polish Mint), doubly distilled Hg, triply distilled water and analytically pure reagents (from POCh) were used. ESTIMATED ERROR: Solubility products: precision ± 15 % (private communication). Temperature: precision ± 0.1 K.

COMPONENTS:	EVALUATOR:
(1) Gold-cadmium 1:1; AuCd; [12044-73-4] (2) Mercury; Hg; [7439-97-6]	C. Gumiński; Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland March 1982

CRITICAL EVALUATION:

Early, in calorimetric experiments (1), an interaction was found between Au and Cd in about 0.2 mol % amalgam at 363 K. However in potentiometric measurements (16) performed in the same laboratory no diminution of Cd activity in the Au-Cd amalgam was observed for atom product equal to or less than 1.4×10^{-6} mol^2 dm^{-6} at 289 K. It was found later that the compound AuCd is formed in Hg when its components are present in similar and appropriately high concentrations (2-10). When the concentration of Au exceeds that of Cd by a factor of three or more, then Au_3Cd may also form (4, 6, 13).

Hartmann and Schölzel (2) reported formation of soluble AuCd in Hg. Its instability constant, $K = [Au][Cd]/[AuCd]$, depends on both metal concentrations. Zebreva (11) recalculated the data of (2) showing that the solubility product, $K_s = [Au][Cd]$, has a constant value, which suggests that this compound formed in Hg medium has a crystalline form. The value of K_s reported by Zebreva (11), 2.5×10^{-9} mol^2 dm^{-6} at 293 K, was not correct since she did not transform mole fractions of the metals to molar concentrations. Similarly, the erroneous result of K_s equal to $(2.62 \pm 0.13) \times 10^{-9}$ mol^2 dm^{-6} was obtained later by Maryanov (12), who applied his own method of mathematical treatment of the data in (2). The formation of insoluble AuCd in Hg was experimentally confirmed in subsequent work (3-7, 13, 15, 17), and the solubility product determined (4-7, 13, 15, 17). The results (2, 5-7, 17) were obtained at room temperature; in (4, 13, 15) the temperature was changed in the ranges: 293-343, 278-348 and 293-363 K, respectively. Quantitative agreement of these data is good within errors of the methods used. The results of Palyska (13) seem to be slightly high. No numerical result is presented in (3). However the state of aggregation of AuCd in Hg is still open to discussion.

Mesyats and Mikheeva (8), based on their stripping analysis experiments, suggested that at concentrations below 10^{-4} mol dm^{-3} the compound AuCd is soluble in Hg, but slightly dissociated, with an instability constant equal to 1×10^{-5} mol dm^{-3} at 293 K. Nazarov (9) reported a result of $(8-20) \times 10^{-5}$ mol dm^{-3} in similar experiments at room temperature. Based on unpublished EMF experiments of Mesyats, his collaborators (10) found that when the concentrations of the components were about 10^{-4} mol dm^{-3} a soluble form of AuCd is formed with the dissociation constant equal to 2×10^{-5} mol dm^{-3} at 289 K. This work (9, 10) is not compiled, because it is not known whether equilibria were reached during the measurements; moreover the information given on the experimental conditions is scanty.

Another problem arose after mathematic analysis of the results of (2, 4, 5, 10). Mikheeva and Stromberg (10) recalculated all primary data of (2, 4, 5, 10) proposing another formula (10) and solubility product values for compounds formed in the Au-Cd-Hg system with the following result:

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Gold-cadmium 1:1; AuCd; [12044-73-4] (2) Mercury; Hg; [7439-97-6]	C. Gumiński; Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland March 1982

CRITICAL EVALUATION (continued)

ref.	proposed formula	equilibrium const./mol dm^{-3}		T/K	- log c_{Au} mol dm^{-3}	- log c_{Cd} mol dm^{-3}
10	AuCd	1.2×10^{-5}	(K)	289	3.8	3.2 - 4.6
2	AuCd	1.0×10^{-5}	$(K_s)^a$	293	1.9	1.2 - 4.2
2	Au_3Cd_2	$(1.7 \times 10^{-6})^2$	$(K_s)^a$	293	1.6	1.3 - 3.2
5	Au_3Cd_2	$(2.2 \times 10^{-6})^2$	$(K_s)^a$	298	1.7	1.8 - 2.7
4	AuCd	7.3×10^{-6}	$(K_s)^a$	293	1.5	1.5 - 1.8
4	Au_2Cd	1.5×10^{-8}	$(K_s)^a$	293	1.5	2.4 - 4.2
4	AuCd	1.1×10^{-5}	$(K_s)^a$	298	1.5	1.5 - 2.5
4	Au_2Cd	4.0×10^{-8}	$(K_s)^a$	298	1.5	2.3 - 4.1

^{a}units as indicated by proposed formula.

Nevertheless it seems reasonable that a better criterion for the composition of a compound being precipitated in Hg is a point of inflection on the ΔE vs. log (c_{Cd}/c_{Au}) dependence. The stoichiometry of the AuCd and Au_3Cd solid phases isolated from the complex amalgam was confirmed by chemical analysis (4). Moreover, in the intermediate composition range of the amalgams a formation of mixed AuCd and Au_3Cd crystals is possible, and the slow attainment of such equilibrium may partly explain the observed discrepancies. AuCd is a stable compound formed in the Au-Cd binary system (14). According to (10) the equilibrium in this complex heterogeneous Au-Cd amalgam may be characterized by the following scheme:

$$\text{Au} + \text{Cd} \rightleftharpoons \text{AuCd}_{sol} \rightleftharpoons \text{AuCd}\downarrow$$

The existence of $AuCd_{sol}$ is then detectable at the concentration level of about 10^{-4} mol dm^{-3}. Nevertheless one should remember that the decrease of Cd-activity at low concentrations of Cd may be caused also by corrosion of the amalgam. When the concentration product of [Au] and [Cd] is lower than K_s, as in the experiments of (2, 4, 6, 7, 16), then no potential differences, within experimental errors, is observed for the same input concentration of Cd in Hg as well as in the diluted Au amalgam. Temperature dependence of pK_s, based on the least square method, was constructed using the results of works (2, 4-7, 15, 17) as

$$pK_s = -2.94 + 2.30 \times 10\ T^{-1}\ ;\ r = 0.985 \qquad (T/K) \quad (K_s/\text{mol}^2\ \text{dm}^{-6})$$

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Gold-cadmium 1:1; AuCd; [12044-73-4] (2) Mercury; Hg; [7439-97-6]	C. Gumiński; Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland March 1982

CRITICAL EVALUATION (continued)

Values of AuCd solubility in Hg

T/K	K_s/mol^2 dm^{-6}	Soly/mol dm^{-3} [a]	Refer.
298	1.7×10^{-5} [b]	4.1×10^{-3}	(2, 4-7, 15, 17) mean value
323	7×10^{-5} [c]	8×10^{-3}	(15)
343	1.6×10^{-4} [c]	1.3×10^{-2}	(4, 15) interpolated
363	4×10^{-4} [c]	2×10^{-2}	(15)

[a] calculated by evaluators from K_s.

[b] recommended.

[c] tentative.

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16. Tammann, G.; Jander, W. *Z. Anorg. Chem.* 1922, *124*, 105.
17. Gumiński, C. *Ph.D. Thesis*, University of Warsaw, 1975.

COMPONENTS:

(1) Gold-cadmium 1:1, AuCd; [12044-73-4]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Hartmann, H.; Schölzel, K.

Z. Phys. Chem., N. F. 1956, *9*, 106-26.

VARIABLES:

Temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

AuCd is treated by the authors as a soluble compound in Hg, the equilibrium is described by a dissociation constant, $K = [Au][Cd]/[AuCd]$, which is equal to 2×10^{-5} mol fraction at 20 °C for equal Au and Cd concentrations. The initial Au concentration was 1.82×10^{-4} or 3.94×10^{-4} mol fraction and Cd concns were changed in the ranges 8.9×10^{-7} - 1.0×10^{-3} and 1.0×10^{-6} - 1.0×10^{-3} mol fraction, respectively. The results are presented on graphs and only for 182×10^{-4} mol fraction Au are in numerical form as reproduced below.

$10^5 x_{Cd}^{i}$	$10^5 x_{Cd}^{f}$	$10^5 K$(mol. fr.)	$10^9 K_s$(mol. fr.)^2	$10^5 K_s$/mol^2 dm^{-6} [a]
0.089	0.064	46[a]	11.5[b]	--
0.357	0.317	14[a]	5.8[b]	--
0.892	0.827	230[a]	1.5[b]	--
3.569	1.36	9.9	2.2	1.0
6.681	2.16	6.4	2.9	1.3
13.21	3.04	2.4	2.4	1.1
16.43	4.23	2.1	2.5	1.15
19.63	5.87	1.9	2.5	1.15

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Au and Cd amalgams were prepared by dissolution of the metals in Hg. Differences of potential of the complex Au-Cd and simple Cd amalgams were measured in the cells Au-Cd(Hg)/$CdSO_4$ aq./Cd(Hg) for a few hours. K-values were calculated from the equilibrium potentials. The experiments were performed in an H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

99.95 % pure or higher.

ESTIMATED ERROR:

Nothing specified. Precision of K_s no better than ± 10 % (by compilers).

REFERENCES:

1. Zebreva, A.I. *Vestn. Akad. Nauk Kaz. SSR* 1958, no. 11, 88; *Zh. Fiz. Khim.* 1961, *35*, 948; *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1962, *9*, 55.
2. Gumiński, C.; Galus, Z. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 1972, *20*, 1037.
3. Maryanov, B.M. *Elektrokhimia* 1975, *11*, 1808.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-cadmium 1:1, AuCd; [12044-73-4] (2) Mercury; Hg; [7439-97-6]	Hartmann, H.; Schölzel, K. *Z. Phys. Chem., N. F.* 1956, *9*, 106-26.

EXPERIMENTAL VALUES (continued)

$10^5 x_{Cd}^{i}$	$10^5 x_{Cd}^{f}$	10^5K(mol. fr.)	$10^9 K_s$(mol. fr.)^2	$10^5 K_s$/mol^2 dm^{-6} [a]
26.77	11.05	1.8	2.6	1.2
101.02	82.52	1.4[a]	2.5	1.15
			mean value	1.15±0.1

[a] calculated by compilers.

[b] rejected.

On the basis of these experimental results a solubility product, which is the correct thermodynamic value for the system, was calculated by a few authors (1-3). The values reported in (1) and (3) are erroneously recalculated concerning the concentration unit (see Critical Evaluation). The compilers' correction of the original data presented above yields K_s = (1.2±0.1)x10^{-5} mol^2 dm^{-6} (2).

COMPONENTS:

(1) Gold-cadmium 1:1; AuCd; [12044-73-4]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kozin, L.F.; Cherkasova, G.F.; Erdenbaeva, M.I.

Izv. Akad. Nauk Kaz. SSR, Ser. Khim. 1969, no. 3, 42-9.

VARIABLES:

Temperature: 298-343 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

AuCd is treated as a sparingly soluble compound in Hg; the equilibrium is described by the solubility product, K_s. However, a dissociation constant, K_D = [Au][Cd]/[AuCd], was also calculated by the authors. Initial Au concentration in all experiments was 4.91x10^{-4} mol fraction.

	t/°C	$10^5x_{Cd}{}^i$	$10^5x_{Cd}{}^f$	$10^4x_{Au}{}^f$	10^9K_s/(mol fr.)^2	10^3K_D/(mol fr.)
	20	25.61	0.886	2.438	2.16	0.874
		28.83	0.933	2.130	1.99	0.710
		32.58	0.998	1.752	1.75	0.554
$10^5x_{Cd}{}^i$		36.35	1.259	1.401	1.76	0.502
		40.70	1.839	1.024	1.88	0.495
		44.60	2.333	0.683	1.59	0.376
	25	25.61	1.850	2.534	4.72	2.07
		32.39	2.16	2.274	4.91	1.62
		36.36	2.34	1.510	3.53	1.03
		40.80	2.84	1.116	3.15	0.83

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgams were prepared by dissolution of the metals. Differences between the potentials of the complex Au-Cd and simple Cd amalgams were measured for 45-60 min for the following cell: Au-Cd(Hg)|0.2 mol dm^{-3} $CdSO_4$, 0.5 mol dm^{-3} $(NH_4)_2SO_4$, 3 mol dm^{-3} NH_3, 50-60 g dm^{-3} $N_2H_4 \cdot H_2SO_4$|Cd(Hg). The concentration of Cd in the right half cell was always constant. The solubility products were calculated from the potential differences. The experiments were performed in a pure H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

"High purity" chemicals were used: "Cd-00" and Hg were purified and vacuum distilled.

ESTIMATED ERROR:

Solubility product: precision no better than ± 10 %.

Temperature: precision ± 0.2 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-cadmium 1:1; AuCd; [12044-73-4] (2) Mercury; Hg; [7439-97-6]	Kozin, L.F.; Cherkasova, G.F.; Erdenbaeva, M.I. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* <u>1969</u>, no. 3, 42-9.

EXPERIMENTAL VALUES (continued)

t/°C	$10^5x_{Cd}^{i}$	$10^5x_{Cd}^{f}$	$10^4x_{Au}^{f}$	10^9K_s/(mol fr.)^2	10^3K_D/(mol fr.)
	45.20	3.71	0.763	2.83	0.68
	51.30	3.82	0.174	0.665^a	0.14
45	20.400	4.280	3.297	14.6^b 14.1^c	9.01
	25.110	6.530	3.051	19.8	10.70
	34.100	6.780	2.177	14.7	5.39
	43.20	8.340	1.723	11.8^b 14.1^c	3.39
	54.23	10.030	0.489	4.9^a	1.10
70	26.19	12.71	3.586	45.6	34.5
	37.5	14.09	2.659	37.4	16.0
	51.29	19.99	1.770	35.4	11.3
	56.03	22.78	1.575	35.8	10.8
	60.80	25.39	1.359	34.6	9.7
	71.59	32.39	0.980	31.8	8.1
	86.21	44.40	0.719	31.8	7.6
	103.59	59.30	0.521	31.0	7.1

[a] rejected.

[b] erroneous value.

[c] corrected by compilers.

t/°C	K_s/(mol fraction)^2 ^{b}	K_s/mol^2 dm^{-6} $^{a\ b}$
20	$(1.86 \pm 0.20) \times 10^{-9}$	$(8.5 \pm 0.9) \times 10^{-6}$
25	$(3.83 \pm 0.94) \times 10^{-9}$	$(1.8 \pm 0.4) \times 10^{-5}$
35	6.57×10^{-9}	3.0×10^{-5}
45	$(1.52 \pm 0.33) \times 10^{-8}$	$(7.0 \pm 1.5) \times 10^{-5}$
60	2.38×10^{-8}	1.1×10^{-4}
70	$(3.54 \pm 0.27) \times 10^{-8}$	$(1.6 \pm 0.12) \times 10^{-4}$

Some experiments were also carried out at 5 °C but no numerical data are reported.

[a] recalculated by compilers.

[b] standard deviations by compilers.

For smaller Cd concentrations Au_3Cd formation may be observed.
The dependence of pK_s on temperature, which is based on the method of weighed linear least squares regression, is expressed by the equation (by compilers):

$$pK_s = (-3.72 \pm 0.47) + (2.56 \pm 0.15) \times 10^3\ T^{-1} \quad (T/K)(K_s/\text{mol}^2\ \text{dm}^{-6})$$

COMPONENTS:

(1) Gold-cadmium 1:1; AuCd; [12044-73-4]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Gumiński, C.; Galus, Z.

Bull. Acad. Polon. Sci., Ser. Sci. Chim. 1972, *20*, 1037-44.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

AuCd is considered as sparingly soluble in Hg; the equilibrium is described by the solubility product. The initial concentration of Au was 2.00x10^{-2} mol dm^{-3} and the temperature was 25.0 °C.

$10^3c_{Cd}{}^i$/mol d $^{-3}$	$c_{Cd}{}^f$/mol dm^{-3} *b*	$c_{Au}{}^f$/mol dm^{-3} *b*	10^5K_s/mol dm^{-3}	$10^{-2}K$/mol^{-1}dm^3
15.9	1.47	6.5	0.95	19.3
9.26	0.72	11.4	0.82	10.4
7.94	0.80	12.9	1.0	6.9
6.62	0.72	14.1	1.0	5.8
8.70	1.34	12.6	1.7	4.4
7.83	1.48	13.7	2.1	2.4
6.09	1.53	15.4	2.3	1.9
4.35	1.35	17.0	2.3	1.3
4.50	1.22	16.7	2.0	1.6
3.40	1.25	17.8	2.2	1.0

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equal portions of Cd were introduced by constant current electrolysis into a hanging mercury drop electrode and into a hanging drop electrode filled with gold amalgam prepared by dissolution of Au in Hg). Potentials of the electrodes were measured vs. SCE for 30 min in the same solution of 0.1 mol dm^{-3} $CdCl_2$. The solubility products were calculated from the potential differences and mass balance. The experiments were carried out in a H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

99.999 % pure Au (from Polish Mint), triply distilled water, doubly distilled Hg after chemical purification with $Hg_2(NO_3)_2$, $CdCl_2$ "for analysis" (from POCh) were used. Solutions of $CdCl_2$ were electrolyzed cathodically for one day at -0.45 V before use.

ESTIMATED ERROR:

Solubility: precision no better than ± 25 %. Temperature: ± 0.2 K.

REFERENCES:

1. Gumiński, C. *Ph. D. Thesis*, University of Warsaw, 1975.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-cadmium 1:1; AuCd; [12044-73-4] (2) Mercury; Hg; [7439-97-6]	Gumiński, C.; Galus, Z. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* <u>1972</u>, *20*, 1037-44.

EXPERIMENTAL VALUES (continued)

$10^3c_{Cd}{}^{i}$/mol dm^{-3}	$c_{Cd}{}^{f}$/mol dm^{-3} [b]	$c_{Au}{}^{f}$/mol dm^{-3} [b]	10^5K_s/mol dm^{-3}	$10^{-2}K$/mol^{-1}dm^3
2.72	0.90	18.2	1.6	1.1
2.38	0.94	18.5	1.7	0.9
		mean value	1.6 ± 0.5[a]	

[a] standard deviation calculated by compilers

[b] calculated by compilers

In another set of experiments using 5.00×10^{-2} mol dm^{-3} Au amalgam and changing the Cd concentration in the range 1.74×10^{-2}-4.35×10^{-2} mol dm^{-3}, K_s was determined to be $(2.1 \pm 0.7) \times 10^{-5}$ mol^2 dm^{-6} at 25.0 °C. It was shown that the formally calculated equilibrium constant (K) changed monotonically with initial concentrations of the metals. Also the second order rate constant of the formation of AuCd in Hg depends on concentrations of the metals. These are additional proofs that AuCd crystals precipitate in Hg medium.

Gumiński (1) repeated the measurements for 5.00×10^{-2} mol dm^{-3} Au amalgam, changing concentration of Cd in the range 1.74×10^{-2}-4.35×10^{-2} mol dm^{-3}, and found K_s equal to $(1.7 \pm 0.4) \times 10^{-5}$ mol^2 dm^{-6} at 25.0 °C. The same experimental procedure was applied.

COMPONENTS:

(1) Gold-cadmium 1:1; AuCd; [12044-73-4]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Palyska, D.

M. Sc. Thesis, University of Warsaw, 1975.

VARIABLES:

Temperature: 278-348 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product values of AuCd in Hg are reported. The initial concentration of Au was always 7.0×10^{-2} mol dm^{-3} and the initial concentration of Cd was changed in the range 2.7×10^{-2}-7.6×10^{-2} mol dm^{-3}.

$t/°C$	$K_s/mol^2\ dm^{-6}$
5.0	$(1.2\pm0.2)\times10^{-5}$
15.0	$(2.3\pm0.4)\times10^{-5}$
25.0	$(4.0\pm0.9)\times10^{-5}$
35.0	$(6.1\pm1.0)\times10^{-5}$
45.0	$(1.1\pm0.2)\times10^{-4}$
55.0	$(1.8\pm0.2)\times10^{-4}$
65.0	$(2.4\pm0.2)\times10^{-4}$
75.0	$(3.9\pm0.1)\times10^{-4}$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Au amalgam was prepared by dissolution of the metal in Hg. Cd was introduced in proper amounts into Hg and Au amalgam electrodes by constant current electrolysis. Potentials of both electrodes after the introduction of Cd were measured in 0.1 mol dm^{-3} $Cd(NO_3)_2$ vs. SCE. The potential difference of the electrodes at times longer than 600 s was constant and this was assumed to correspond to equilibrium. The final concentration of Cd was found from the potential difference, the concentration of Au was calculated from mass balance, and K_s by their multiplication. Experiments were carried out in an H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

99.99 % pure Au from Polish Ming, doubly distilled Hg after chemical purification with $Hg_2(NO_3)_2$, analytically pure $Cd(NO_3)_2$ from POCh and triply distilled H_2O were used. Solutions of Cd(II) were electrolyzed on Hg cathode at -0.5 V vs. SCE.

ESTIMATED ERROR:

Solubility product: standard deviation higher than ± 10 %.

Temperature: precision ± 0.2 K.

COMPONENTS:

(1) Gold-cadmium 1:1; AuCd; [12044-73-4]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Mesyats, N.A.; Mikheeva, N.I.

Izv. Tomsk. Politekh. Inst. **1975**, *197*, 43-5.

VARIABLES:

Temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

It was found that AuCd formed in Hg and exists in a soluble form. The dissociation constant of the compound was determined to be 1x10^{-5} mol dm^{-3} at 293 K.

The amalgam seems to be unsaturated with respect to AuCd. The ratio of the ion concentrations of Cd(II) to Au(III) in the solution was changed from 2 to 0.33.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The complex amalgam was obtained by simultaneous electroreduction of Cd and Au ions on a Hg electrode from a solution of 0.1 mol dm^{-3} $(NH_4)_2SO_4$. Concentrations of Cd(II) and Au(III) were equal to 5x10^{-5} mol dm^{-3} and the time of the electrolysis was changed in the range 6-18 min. The oxidation of Cd from the complex amalgam was carried out under voltammetric conditions. The dissociation constant was calculated from the charge corresponding to the oxidation of Cd and mass balance of the reagents.

SOURCE AND PURITY OF MATERIALS:

Nothing specified. Probably, concentrations of other heavy metals in the solution were below 10^{-8} mol dm^{-3}, as it was in other papers from this laboratory (compilers).

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:

(1) Gold-cadmium 1:1; AuCd; [12044-73-4]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Dergacheva, M.B.

Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR 1975, *11*, 36-42.

VARIABLES:

Temperature: 298-363 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubilities of AuCd in Hg are reported:

t/°C	solubility/mol dm^{-3}	K_s/mol^2 dm^{-6} [a]
20	2.93×10^{-3}	8.6×10^{-6}
50	8.7×10^{-3}	7.6×10^{-5}
75	1.37×10^{-2}	1.88×10^{-4}
90	1.91×10^{-2}	3.6×10^{-4}

[a] calculated by compilers

Initial concentrations of Au and Cd are 3.04×10^{-2} and 3.04×10^{-3}-3.55×10^{-2} mol dm^{-3}, respectively.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

No details are described but it seems that the method of EMF was used and the procedure was essentially the same as reported in (1); see corresponding data sheet.

SOURCE AND PURITY OF MATERIALS:

Nothing specified, but probably the purity was the same as in (1).

ESTIMATED ERROR:

Solubility: nothing specified; no better ± 5 % (compilers).

Temperatures: precision ± 0.2 K.

REFERENCES:

1. Kozin, L.F.; Cherkasova, G.F.; Erdenbaeva, M.I. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1969, no. 3, 42-9.

COMPONENTS:

(1) Gold-cadmium 1:1; AuCd; [12044-73-4]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Ostapczuk, P.; Kublik, Z.

J. Electroanal. Chem. 1977, *83*, 1-17.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

AuCd as a sparingly soluble compound in Hg has a solubility product, K_s at 25.0 °C:

$c_{Au}{}^{l}$/ mol dm^{-3}	$c_{Cd}{}^{l}$/ mol dm^{-3}	K_s/ mol^2 dm^{-6}
1.05×10^{-2}	3.0×10^{-3} - 3.0×10^{-2}	$(2.4\pm0.4)\times10^{-5}$
4.1×10^{-2}	2.2×10^{-2} - 4.0×10^{-2}	$(2.7\pm0.2)\times10^{-5}$ [a]
8.2×10^{-2}	1.8×10^{-2} - 4.5×10^{-2}	$(2.6\pm0.4)\times10^{-5}$ [a]

[a] private communication of P. Ostapczuk to the compilers

Perhaps 3 min was not enough time to reach equilibrium in the system, and therefore these results are slightly overstated.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Au amalgam was prepared by Au dissolution in Hg. Cd was introduced by constant current electrolysis into a hanging mercury drop electrode and into a hanging gold amalgam drop electrode. Potentials of the electrodes were measured after 3 min vs. SCE and the solubility products were calculated from their differences. The experiments were performed in an Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

99.99 % pure Au (from Polish Mint), triply distilled water, twicely distilled Hg and analytically pure reagents (from POCh) were used.

ESTIMATED ERROR:

Solubility: precision no better than ± 15%. Temperature: precision ± 0.2 K.

COMPONENTS:

(1) Gold-cadmium 1:1; AuCd; [12044-73-4]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Rodgers, R.S.; Meites, L.

J. Electroanal. Chem. 1981, *125*, 167-76.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of AuCd in Hg at 298.2 K is:

10^3c^i/mol dm^{-3}		10^3c^f/mol dm^{-3}			10^5K_s/mol^2 dm^{-6}
Cd	Au	Cd	Au		
12.91	12.11	4.71	3.91		1.84
	7.29	7.97	2.35		1.87
	2.49	11.77	1.35		1.59
6.71	5.00	5.03	3.32		1.67
	2.49	6.51	2.29		1.49
3.40	7.37	2.74	6.71		1.84
	4.91	3.37	4.88		1.65
	2.49	3.40	2.49		-- (no precipitation occurred)
	1.23	3.40	1.23		-- (no precipitation occurred)
3.31	12.11	1.49	10.29		1.53
	9.63	2.23	8.55		1.91
				Mean:	1.71 ± 0.14

No evidence of Au_3Cd formation was obtained in these experiments.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The complex Au-Cd amalgams were obtained by electroreduction which was carried out under potentiostatic conditions. Stock solutions of the metal ions were standardized by conventional techniques. Then the complex amalgams were oxidized with constant current and potential changes were recorded. Complementary experiments by stripping chronoamperometry were also performed. The solubility product was calculated from the oxidation charge of Cd, found from chronopotentiograms, and mass balance.

SOURCE AND PURITY OF MATERIALS:

Reagent grade chemicals were used.

ESTIMATED ERROR:

Solubility product: standard deviation ± 8%. Temperature: precision ± 0.05 K.

COMPONENTS:

(1) Gold-copper 1:1; AuCu; [12006-51-8]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

August 1984

CRITICAL EVALUATION:

Sennechales (3), during investigations of amalgamation of Au-Cu alloys, reported that certain compositions of these alloys are more resistive to dissolution in Hg. Kaplin and coworkers (4) investigated the equilibrium of formation of a compound between Au and Cu in Hg by stripping voltammetry on a thin film electrode. However, no numerical results are reported in papers (3) and (4).

Sasim and coworkers (1, 5-7) investigated quantitatively the Au-Cu-Hg system by potentiometry Formation of AuCu solid in Hg was observed; such a compound is formed also in the Au-Cu binary alloys (2). The solubility product, $K_s = [Au][Cu]$, values were determined over the temperature range 278 - 308 K. Dependence of K_s on temperature, using a weighted linear least-squares fit, may be expressed by the following equation:

$$pK_s = (-0.67 \pm 0.63) + (1.35 \pm 0.18) \times 10^3 \; T^{-1}$$

Previously the formation of Au_3Cu and $AuCu_3$ in Hg was also suggested (5, 6) for excesses of Au or Cu respectively. However, detailed analysis of the potentiometric experiments (1) showed that only AuCu is formed in the complex diluted amalgams. An excess of Cu leads to the precipitation of Cu_7Hg_6 (which is 3 times more soluble than AuCu in Hg; see the Cu-Hg system) along with AuCu.

Value of the solubility (tentative)

The solubility product of AuCu in Hg at 298 K, according to work (1), is:

$$7\text{x}10^{-6}\ \text{mol}^2\ \text{dm}^{-6}$$

and the solubility

$$2.7\text{x}10^{-3}\ \text{mol dm}^{-3}$$ (calculated by evaluators)

References

1. Sasim, D.; Srudka, M.; Gumiński, C. *Monatsh. Chem.* 1984, *115*, 45.
2. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, N. Y., 1958.
3. Sennechales, M. *Ing. Chim.* 1935, *19*, 70; as cited from *Chem. Abstr.* 1936, *30*, 2153^8.
4. Kaplin, A.A.; Ryashentseva, T.F.; Stromberg, A.G.; Anisimova, A.S.; Pikula, N.P. *Sbor. Annot. Nauch.-Issled, Rabot Tomsk. Politekh. Inst., Tomsk* 1975, no. 6, 75.
5. Sasim, D. *M. Sc. Thesis*, University of Warsaw, Warsaw, 1974.
6. Gumiński, C. *Ph.D. Thesis*, University of Warsaw, Warsaw, 1975.
7. Srudka, M. *M. Sc. Thesis*, University of Warsaw, Warsaw, 1978.

COMPONENTS:

(1) Gold-copper 1:1; AuCu; [12006-51-8]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Sasim, D.; Srudka, M.; Gumiński, C.

Monatsh. Chem. 1984, *115*, 45-56.

VARIABLES:

Temperature: 278-308 K

PREPARED BY:

C. Gumiński; Z Galus

EXPERIMENTAL VALUES:

Solubility products and dissociation constants of AuCu in mercury obtained with initial gold concentration $7.0\cdot10^{-2}$ mol dm^{-3} at 298 K:

t/s	i/μA	c_{Cu}^{i}/mol dm^{-3}	ΔE/mV	c_{Cu}^{b}/mol dm^{-3}	$10^6 K_s$/mol^2 dm^{-6}	K_d/mol dm^{-3}
50	4.0	$1.53\cdot10^{-3}$	35	$1.42\cdot10^{-3}$	6.9	$4.9\cdot10^{-3}$
60	5.0	$2.3\cdot10^{-3}$	40	$2.2\cdot10^{-3}$	6.7	$3.0\cdot10^{-3}$
50	10.0	$3.8\cdot10^{-3}$	48	$3.7\cdot10^{-3}$	6.3	$1.7\cdot10^{-3}$
40	20	$6.1\cdot10^{-3}$	54	$6.0\cdot10^{-3}$	6.2	$1.0\cdot10^{-3}$
60	20	$9.2\cdot10^{-3}$	60	$9.1\cdot10^{-3}$	5.6	$6.2\cdot10^{-4}$
40	50	$1.53\cdot10^{-2}$	65	$1.51\cdot10^{-2}$	5.7	$3.8\cdot10^{-4}$
60	50	$2.3\cdot10^{-2}$	68	$2.3\cdot10^{-2}$	5.9	$2.6\cdot10^{-4}$
50	100	$3.8\cdot10^{-2}$	64	$3.8\cdot10^{-2}$	8.2	$2.2\cdot10^{-4}$
40	200	$6.1\cdot10^{-2}$	57	$6.1\cdot10^{-2}$	7.1	$1.2\cdot10^{-4}$
60	200	$9.2\cdot10^{-2}$	46	$8.9\cdot10^{-2}$	--	--
50	400	$1.53\cdot10^{-1}$	11	$8.8\cdot10^{-2}$	--	--
100	400	$3.1\cdot10^{-1}$	2	$4.0\cdot10^{-2}$	--	--
200	400	$6.1\cdot10^{-1}$	0	0	--	--
				mean value:	6.7 ± 0.8	

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Experiments were performed in a pure H_2 atmosphere. Equal portions of Cu were introduced by electrolysis with constant current into hanging drop electrodes filled with Hg or Au amalgam (prepared by dissolution of Au foil in Hg). Potential differences of the electrodes were measured for 2000 s in a solution of 0.1 mol dm^{-3} $CuSO_4$, pH = 2. Equilibrium concentrations of Cu were measured and the solubility product was calculated from mass balance.

SOURCE AND PURITY OF MATERIALS:

99.999 % pure Au (from Polish Mint), doubly distilled Hg after chemical purification with acidic $Hg_2(NO_3)_2$, triply distilled water and other chemicals of analytic purity (from POCh) were used. The solutions were additionally purified by a cathodic electrolysis.

ESTIMATED ERROR:

Solubility product: precision ± 15 % (at best). Temperature: ± 0.1 K.

REFERENCES:

1. Stromberg, A.G.; Mesyats, N.A.; Mikheeva, N.P. *Zh. Fiz. Khim.* 1971, *45*, 1521.
2. Srudka, M. *M. Sc. Thesis*, University of Warsaw, 1978.
3. Sasim, D. *M. Sc. Thesis*, University of Warsaw, 1974.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-copper 1:1; AuCu; [12006-51-8] (2) Mercury; Hg; [7439-97-6]	Sasim, D.; Srudka, M.; Gumiński, C. *Monatsh. Chem.* 1984, *115*, 45-56.

EXPERIMENTAL VALUES (continued)

Solubility products (K_s) and dissociation constants (K_d) of AuCu in mercury at 298 K:

$c_{Au}{}^{i}$/mol dm^{-3}	$c_{Cu}{}^{i}$/mol dm^{-3}	$10^6 K_s$/mol^2 dm^{-6}	$10^6 K_s$/mol^2 dm^{-6} [c]	K_d/mol dm^{-3}
$6.0\cdot10^{-3}$	$1.21\cdot10^{-3}$-$9.20\cdot10^{-3}$	7.3 ± 0.6	7.0	$7.3\cdot10^{-2}$-$1.9\cdot10^{-3}$
$8.0\cdot10^{-3}$	$1.21\cdot10^{-3}$-$6.10\cdot10^{-3}$	7.6 ± 0.8 [a]	8.0	$3.0\cdot10^{-2}$-$1.5\cdot10^{-3}$
$1.0\cdot10^{-2}$	$2.3\cdot10^{-3}$-$7.6\cdot10^{-3}$	11.1 ± 5.4 [b]	15.0	$2.7\cdot10^{-2}$-$6.0\cdot10^{-4}$
$2.0\cdot10^{-2}$	$2.3\cdot10^{-3}$-$1.15\cdot10^{-2}$	4.3 ± 1.2 [b]	4.6	$2.8\cdot10^{-3}$-$2.8\cdot10^{-4}$
$5.0\cdot10^{-2}$	$7.6\cdot10^{-4}$-$4.6\cdot10^{-2}$	6.9 ± 1.9 [b]	5.9	$1.8\cdot10^{-2}$-$1.1\cdot10^{-4}$
$7.0\cdot10^{-2}$	$1.53\cdot10^{-3}$-$6.1\cdot10^{-2}$	6.7 ± 0.8 [a]	5.4	$4.9\cdot10^{-2}$-$1.2\cdot10^{-4}$
$9.0\cdot10^{-2}$	$1.30\cdot10^{-3}$-$2.3\cdot10^{-2}$	8.6 ± 1.8 [a]	6.7	$8.9\cdot10^{-2}$-$2.4\cdot10^{-4}$
	mean value:	7.1 ± 1.5		

[a] also reported in (2).

[b] also reported in (3).

[c] obtained by method of (1).

Temperature dependence of K_s for initial Au concentration equal to 5.0×10^{-2} mol dm^{-3}

T/K	K_s/mol^2 dm^{-6}
278	$(3.0\pm0.6)\times10^{-6}$
288	$(4.2\pm0.4)\times10^{-6}$
298	$(7.1\pm1.5)\times10^{-6}$ [a]
308	$(9.4\pm2.0)\times10^{-6}$

[a] mean value for various Au concentrations.

COMPONENTS:	EVALUATOR:
(1) Gold-gallium 1:1; AuGa; [12006-53-0] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland August 1984

CRITICAL EVALUATION:

Palyska (1) determined a value of the solubility product, $K_s = [Au][Ga]$, of AuGa in Hg equal to $2x10^{-8}$ mol^2 dm^{-6} at 298 K. This value was also reported in (2, 3). Although AuGa is a moderately stable compound in the Au-Ga binary system (4), the composition of the intermetallic compound formed in the amalgam has been given as AuGa (1-3, 5, 6) and also as $Ga_4Au_5Hg_x$ (7). Moreover, there are divergent opinions on equilibrium in the Hg-rich corner of the Au-Ga-Hg system. The formation of a poorly soluble compound was found in (1-3, 7). Based on stripping voltammetry, Stromberg and coworkers (6) concluded that the soluble form of AuGa is present in Hg, whereas Stepanova (5), using the same method, postulated formation of AuGa in both forms according to the equation:

$$Au + Ga \rightleftharpoons AuGa_{sol} \rightleftharpoons AuGa \downarrow$$

Value of the solubility (tentative)

The solubility product of AuGa in Hg at 298 K, according to (1), is:

$$2x10^{-8}\ mol^2\ dm^{-6}$$

and the solubility, as calculated by evaluators, is:

$$1.4x10^{-4}\ mol\ dm^{-3}$$

References

1. Palyska, D. *M. Sc. Thesis*, University of Warsaw, Warsaw, 1975.
2. Gumiński, C. *Ph.D. Thesis*, University of Warsaw, Warsaw, 1975.
3. Sasim, D.; Srudka, M.; Gumiński, C. *Monatsh. Chem.* 1984, *115*, 45.
4. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, NY, 1958.
5. Stepanova, O.S. *Izv. Tomsk. Politekh. Inst.* 1966, *151*, 14.
6. Stromberg, A.G.; Zakharov, M.S.; Mesyats, N.A.; Zaichko, L.F.; Stepanova, O.S. *Teoria i Praktika Amalgamnykh Protsesov*, Alma-Ata, 1966, p. 68.
7. Lysenko, V.I. *Metallurgia Tsvetnykh Metallov i Metody ikh Analiza* 1962, *7*, 303.

COMPONENTS:

(1) Gold-gallium 1:1; AuGa; [12006-53-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Palyska, D.

M. Sc. Thesis, University of Warsaw, Warsaw, 1975.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of AuGa in Hg at 298.2 K:

$10^2c_{Ga}{}^l$/mol dm^{-3}	$10^2c_{Au}{}^l$/mol dm^{-3}	10^8K_s/mol^2 dm^{-6}
1.12 - 9.9	9.0	2.2±1.0
0.50 - 1.50	7.0	1.6±0.6
0.50 - 2.0	5.0	1.3±0.9
0.50 - 2.0	2.0	2.4±0.8
	mean value	2±1

The same result was reported in (1, 2).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equal portions of Ga were introduced by electrolysis into hanging drop electrodes filled with Au amalgam (prepared by dissolution of Au foil in Hg) and Hg. Potentials of the electrodes vs. SCE were measured for 1000 s in a solution of 1.0x10^{-2} mol dm^{-3} Ga(NO$_3$)$_3$, 7.5 mol dm^{-3} KSCN. Equilibrium concentrations of Ga were obtained from the potential differences and the solubility product was calculated from mass balance. The experiments were carried out in a H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

99.999 % pure Au (from Polish Mint), doubly distilled Hg (from POCh) after chemical purification with acidic $Hg_2(NO_3)_2$, triply distilled water and analytically pure reagents (from POCh) were used. The solutions were additionally purified by cathodic electrolysis at -0.8 V vs. SCE for one day.

ESTIMATED ERROR:

Solubility product: precision ± 50 %.

Temperature: precision ± 10.2 K.

REFERENCES:

1. Gumiński, C. *Ph.D. Thesis*, University of Warsaw, Warsaw, 1975.
2. Sasim, D.; Srudka, M.; Gumiński, C. *Monatsh. Chem.* 1984, *115*, 45-56.

COMPONENTS:	EVALUATOR:
(1) Gold-indium 3:1; Au_3In; [12598-23-1] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1985

CRITICAL EVALUATION:

Formation of a slightly soluble intermetallic compound, Au_3In, in Hg was reported first by Zebreva and Levitskaya (1). They estimated the solubility product, $K_s = [Au]^3[In]$, equal to 7×10^{-12} mol^4 dm^{-12} at 293 K by means of amalgam polarography. Existence of Au_3In in Hg was confirmed later, and it was established that its formation needs more than a two-fold excess of Au over In in the amalgam. Kozin and Dergacheva (2) determined the solubility product in the temperature range 289-348 K (for example 4.1×10^{-9} mol^4 dm^{-12} at 289 K). The solubility product value of 1.1×10^{-8} mol^4 dm^{-12} at 298 K was found by Sas[illegible] (6) and was also reported in (7). The results of (2) and (6) are in good agreement; they are several orders of magnitude higher than those of Zebreva and Levitskaya (1) and seem to be satisfactorily precise; thus the value of (1) should be rejected.

Stromberg and Baev (3) reported the solubility product of Au_3In as 7.7×10^{-8} mol^4 dm^{-12} at 328 K, based on their recalculations of an unpublished result of Dergacheva obtained by means of potentiometry. In subsequent work, Stromberg and coworkers (4) recalculated the results of (2) using their own mathematical procedure; the results at 289 and 308 K were practically the same as the original ones but those at 328 and 348 K were more than two and more than three times higher, respectively; this makes the pK_s vs. T^{-1} relation steeper. The phase Au_3In is formed in the Au-In system (5), and the same phase was identified in the amalgam (2).

Based on the results of (2, 6) the temperature dependence of the solubility product was found by the linear least squares method:

$$pK_s = 1.225 + 2059 \times T^{-1}\ (T/K) \qquad (K_s/mol^4\ dm^{-12});\quad r = 0.96$$

Values of the solubility product of Au_3In in Hg

The correction of the results of (2) made in (4) should lead to a quite different equation. So we may suggest only doubtful values of the solubility product. Solubility of Au_3In in Hg:

T/K	K_s/mol^4 dm^{-12}	Solubility^a/mol dm^{-3}	Reference
289	4×10^{-9}	3.6×10^{-3}	(2)
308	1×10^{-8}	4.4×10^{-3}	(2)
348	9×10^{-8}	8×10^{-3}	(2)

^{a}calculated by evaluators from K_s.

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Gold-indium 3:1; Au_3In; [12598-23-1] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1985

CRITICAL EVALUATION (continued)

References

1. Zebreva, A.I.; Levitskaya, S.A. *Zh. Fiz. Khim.* 1962, *36*, 2799.
2. Kozin, L.F.; Dergacheva, M.B. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1971, *2*, 73.
3. Stromberg, A.G.; Baev, V.S. *Sborn. Tr. Molod. Uchen. Tomsk. Politekhn. Inst.* 1973, no. 1, 13.
4. Stromberg, A.C ; Mikheeva, N.P.; Belousov, Yu.P. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1974, *7*, 42.
5. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
6. Sasim, D. *M. Sc. Thesis*, University of Warsaw, 1974.
7. Gumiński, C. *Ph.D. Thesis*, University of Warsaw, Warsaw, 1975.

COMPONENTS:

(1) Gold-indium 3:1; Au_3In; [12598-23-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zebreva, A.I.; Levitskaya, S.A.

Zh. Fiz. Khim. 1962, *36*, 2799-2803.

VARIABLES:

Temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of Au_3In in Hg at 20 °C:

$10^3 c_{Au}^{i}$/mol dm^{-3}	$10^3 c_{In}^{i}$/mol dm^{-3}	$10^3 c_{In}^{f}$/mol dm^{-3}	$10^3 c_{Au}^{f}$/mol dm^{-3}	K_s/mol^4 dm
3.0	1.14	0.82	2.04	7
2.5	1.14	1.04	2.2	13[a] 11[b]
2.0	0.92	0.7	1.34	1[a] 2
			mean value:	7

[a] erroneous value.

[b] corrected by compilers.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The experiments were performed in an inert gas atmosphere - a mixture of N_2 and H_2 from hydrazine decomposition. Amalgams of In were obtained by electroreduction of $In_2(SO_4)_3$ in 10 % NaCl, pH ≈ 3, on a Hg cathode at -0.8 V vs. SCE. Content of In in the amalgam was found by polarographic oxidation. Au amalgams were prepared by electroreduction of $HAuCl_4$ in 1 mol dm^{-3} HCl. Both amalgams were mixed and then polarized anodically. A decrease of anodic current of In in the presence of Au is due to formation of Au_3In in Hg. Knowing the active concentration of In and using mass balance, the solubility product of Au_3In was calculated.

SOURCE AND PURITY OF MATERIALS:

Hg was purified by electrolysis and vacuum distilled.

ESTIMATED ERROR:

Nothing specified. Determination of K_s with an error ± 50 % or more (compilers).

COMPONENTS:

(1) Gold-indium 3:1; Au_3In; [12598-23-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kozin, L.F.; Dergacheva, M.B.

Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR 1971, *2*, 73-83.

VARIABLES:

Temperature: 289-348 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubility products of Au_3In as a sparingly soluble compound in Hg are reported for different temperatures. Initial Au concentration in all experiments was 1.01×10^{-1} mol dm^{-3}.

$t/°C$	$10^2 c_{In}^i$/mol dm^{-3}	$10^4 c_{In}^f$/mol dm^{-3}	$10^2 c_{Au}^f$/mol dm^{-3}	$10^9 K_s$/$mol^4 dm^{-12}$
16	0.337	0.0675	7.95	3.39
	0.425	0.0687	7.95	3.46
	0.535	0.0756	7.95	3.80
	0.675	0.0868	7.95	4.36
	0.844	0.0992	7.92	4.94
	1.067	0.131	7.25	4.99
	1.342	0.169	6.43	4.48
	1.685	0.280	5.40	4.40
	2.122	0.560	4.11	3.89
			mean value	$(4.1 \pm 0.7)^a$
35	0.25	0.119	9.25	9.41
	0.328	0.134	9.02	9.91^d

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method of Au amalgam preparation is not known. The element In was introduced into Au amalgam or Hg by electroreduction of In(III). Differences of potentials between Au-In amalgam and In amalgam electrodes in solutions of 1 mol dm^{-3} $InCl_3$, 200 g dm^{-3} NH_4Cl, 50 g dm^{-3} $C_4H_5O_6Na$ and 50 g dm^{-3} $N_2H_4 \cdot HCl$ were measured for 15-30 min, enabling the calculation of equilibrium concentrations of In and consequently the solubility product of Au_3In.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: precision ± 20 %.

Temperature: probably ± 0.2 K.

REFERENCES:

1. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1974, 7, 42.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-indium 3:1; Au_3In; [12598-23-1] (2) Mercury; Hg; [7439-97-6]	Kozin, L.F.; Dergacheva, M.B. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1971, *2*, 73-83.

EXPERIMENTAL VALUES (continued)

t/°C	$10^2 c_{In}{}^{i}$/mol dm^{-3}	$10^4 c_{In}{}^{f}$/mol dm^{-3}	$10^2 c_{Au}{}^{f}$/mol dm^{-3}	$10^9 K_s$/mol^{4}dm^{-12}
	0.573	0.169	8.44	10.0[d]
	0.786	0.193	7.80	9.55[d]
	0.866	0.233	7.41	9.64[d]
	0.972	0.268	7.10	9.35[d]
	1.17	0.337	6.52	9.91[d]
	1.34	0.455	6.01	9.90[d]
	1.50	0.615	5.44	9.65[d]
	1.73	0.824	4.84	9.91[d]
			mean value	(9.8±0.4)[a]
55	0.186	0.294	9.53	25.4
	0.325	0.369	9.12	28.0
	0.602	0.445	8.29	25.4
	0.810	0.523	7.67	23.4
	0.952	0.642	7.24	24.3
	1.235	0.884	6.40	23.2
	1.59	1.47	5.34	22.4
	1.945	2.34	4.32	18.9
			mean value	(23±5)[a]
75	0.226	0.81	9.32	66.0[c]
	0.368	1.225	9.02	90.0
	0.584	1.58	8.27	90.0
	0.664	1.77	8.14	95.6
	0.744	1.895	7.90	98.2[d]
	0.932	2.50	7.26	96.3
	1.10	3.01	6.78	94.0
	1.26	3.62	6.42	96.2
			mean value	(94±4)[a]

[a] Recalculated values as reported in (1) are 3.85, 10, 56, and 37.8 mol^4 dm^{-12}, respectively.

[b] Values calculated from $c_{In}{}^{f}$ and $c_{Au}{}^{f}$ by compilers.

[c] Rejected by authors.

[d] Values recalculated by compilers are 9.83, 10.1, 9.16, 9.48, 9.59, 9.33, 9.88, 9.90, 9.34, and 9.34 mol^4 dm^{-12}, respectively.

Au amalgam used at 16 °C was not homogeneous which could lead to a small error. In the phase separation experiments, not described in detail, the solubility of Au_3In in Hg at 21 °C is found to be 8x10^{-4} mol dm^{-3}. This value is only 1/5 of the value obtained in the potentiometric experiments.

COMPONENTS:

(1) Gold-indium 3:1; Au_3In; [12598-23-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Sasim, D.

M. Sc. Thesis, University of Warsaw
Warsaw, 1974.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of Au_3In in Hg at 298.2 K. Initial concentration of Au equals 9.0×10^{-2} mol dm^{-3}.

$10^4 c_{In}{}^i$/mol dm^{-3}		$10^8 K_s$/mol^4 dm^{-12}
5.1		1.3
10.2		1.1
25.5		1.2
38.0		1.1
51		1.8
76		1.1
102		1.0
153		0.8
178		0.8
204		0.5
	mean value	1.1±0.4

The result was also reported in (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Au amalgam was prepared by dissolution of the metal in Hg. Equal portions of In were electrolytically introduced into the hanging drop electrodes filled with pure Hg as well as Au amalgam. Changes of potential with time (10 min) in 0.1 mol dm^{-3} $In(NO_3)_3$ vs. SCE were measured after the electrolysis was stopped. From the stable potential differences the concentration of In in the Au-In amalgam was found and this allowed calculation of the solubility product of Au_3In in Hg using mass balance.

SOURCE AND PURITY OF MATERIALS:

99.999 % pure Au (Polish Mint), triply distilled water, twice distilled Hg (POCh) after chemical purification with $Hg_2(NO_3)_2$ and other chemicals of analytical purity (POCh) were used. The solution of $In(NO_3)_3$ was cathodically electrolyzed for one day at -0.5 V vs. SCE.

ESTIMATED ERROR:

Solubility product: standard deviation ± 30 %. Temperature: ± 0.2 K.

REFERENCES:

1. Gumiński, C. *Ph. D. Thesis*, University of Warsaw, Warsaw, 1975.

COMPONENTS:	EVALUATOR:
(1) Gold-indium 1:1; AuIn; [12006-55-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1985

CRITICAL EVALUATION:

Formation of insoluble intermetallic compounds between Au and In in Hg was first reported by Zebreva and Levitskaya (1). They found that two compounds, AuIn and Au_3In, are formed in this system. Polarographic measurements (1) indicated that the solubility product, K_s = [Au][In], of AuIn at 293 K is $1.9x10^{-6}$ mol^2 dm^{-6}, whereas in potentiometric experiments a value of $1.8x10^{-7}$ mol^2 dm^{-6} was determined. These results should be rejected due to the discrepancy in the results and lack of data in the paper. Mesyats (10) determined a K_s value of $9x10^{-6}$ mol^2 dm^{-6} at room temperature by stripping voltammetry, but details are not known to the evaluators. Subsequently Kozin and Dergacheva (2) confirmed the formation of AuIn and Au_3In by potentiometric experiments in the temperature range 289-348 K. The corresponding solubility products were determined and these values are suggested as tentative. Sasim (8) confirmed the results of (2) at 298 K (K_s of AuIn equal to $4.4x10^{-5}$ mol^2 dm^{-6}); the result of (8) was also reported in (9). Stromberg and Baev (5) reported a solubility product value of $5.6x10^{-5}$ mol^2 dm^{-6} at 328 K, which is derived from their recalculation using unpublished potentiometric measurements of Dergacheva. In another work, Stromberg and coworkers (6) recalculated the data of (2) using their own mathematical procedure; at 289 K the result obtained is one-half of the primary one. The rest of the numbers agree with the primary results of (2); moreover they fit better to a straight line relating pK_s to reciprocal temperature.

Because of some difference between potentiometric and phase separation experiments (2), it was later suggested by the same authors that AuIn is sparingly soluble and partially dissociated in Hg according to (3, 4):

$$Au + In \rightleftharpoons AuIn \rightleftharpoons AuIn\downarrow$$

The compound AuIn is a stable phase formed in the binary Au-In system (7) as well as in the amalgam (2) as found by chemical analysis. By the method of weighted linear least squares regression one may express the temperature dependence of K_s from (2, 8, 10) with:

$$pK_s = -1.977 + 1.982\ T^{-1} \qquad r=0.91 \qquad (T/K,\ K_s/mol^2\ dm^{-6})$$

Values of the solubility of AuIn in Hg (tentative)[a]

T/K	$K_s/mol^2\ dm^{-6}$	Solubility/mol dm^{-3}	reference
289	$2x10^{-5}$	$4.5x10^{-3}$	(2)
308	$3x10^{-5}$	$6x10^{-3}$	(2)
348	$2x10^{-4}$	$1.4x10^{-2}$	(2)

[a] calculated by evaluators from K_s.

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Gold-indium 1:1; AuIn; [12006-55-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1985

CRITICAL EVALUATION (continued)

References

1. Zebreva, A.I.; Levitskaya, S.A. *Zh. Fiz. Khim.* 1962, *36*, 2799.
2. Kozin, L.F.; Dergacheva, M.B. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1971, *2*, 73.
3. Kozin, L.F.; Dergacheva, M.B. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1972, *3*, 31.
4. Dergacheva, M.B. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 197 *11*, 36.
5. Stromberg, A.G.; Baev, V.S. *Sborn. Tr. Molod. Uchen. Tomsk. Politekhn. Inst.* 1973, no. 1; 13.
6. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1974, *7*, 42.
7. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
8. Sasim, D. *M. Sc. Thesis*, University of Warsaw, 1974.
9. Gumiński, C. *Ph.D. Thesis*, University of Warsaw, Warsaw, 1975.
10. Mesyats, N.A. *Ph.D. Thesis*, Tomsk. Politekhn. Inst., Tomsk., 1968, as cited in (2).

COMPONENTS:

(1) Gold-indium 1:1; AuIn; [12006-55-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zebreva, A.I.; Levitskaya, S.A.

Zh. Fiz. Khim. **1962**, *36*, 2799-2803.

VARIABLES:

Temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of AuIn in Hg at 20 °C determined by amalgam polarography:

$10^3c_{Au}{}^{i}$/mol dm^{-3}	$10^3c_{In}{}^{i}$/mol dm^{-3}	$10^3c_{In}{}^{f}$/mol dm^{-3}	$10^3c_{Au}{}^{f}$/mol dm^{-3}	10^6K_s/mol^2 dm^{-6}
2.0	1.30	0.92	1.62	1.49
2.0	1.62	1.04	1.42	1.48
2.0	2.21	1.9	1.44	2.30
2.5	1.95	1.10	1.65	1.82
2.5	2.21	1.30	1.59	2.03
2.5	2.47	1.46	1.49	2.14
3.0	1.62	1.10	2.48	2.71
3.0	2.21	1.30	2.09	2.72
3.0	2.47	1.24	1.77	2.18
3.0	3.06	1.14	1.08	1.26
3.0	3.32	1.26	0.94	1.20
3.0	3.57	1.58	1.01	1.74
			mean value	1.92±0.51[a]

[a]standard deviation calculated by compilers.

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgams of Au and In were separately prepared by an electroreduction on Hg from corresponding salts. They were mixed in various proportions and oxidized in polarographic conditions. In the presence of Au a decrease of the oxidation current of In was observed and this allowed one to find its equilibrium concentration and consequently K_s. In potentiometric experiments In was introduced into Au amalgam by electroreduction in successive steps. Potentials of the cell: In(Hg)|$In_2(SO_4)_3$ 8.8 g dm^{-3}, 10 % NaCl, pH = 3.4-4.0|Au-In(Hg) were measured for 30-40 min. The concentration of free In was found from the potential differences. The K_s-values were calculated from mass balance. All experiments were performed in an atmosphere of N_2 and H_2 from hydrazine decomposition.

SOURCE AND PURITY OF MATERIALS:

Hg was purified by electrolysis and vacuum distilled.

ESTIMATED ERROR:

Solubility product: standard deviation of ± 25 % (polarography) as calculated by compilers. Temperature: nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-indium 1:1; AuIn; [12006-55-2] (2) Mercury; Hg; [7439-97-6]	Zebreva, A.I.; Levitskaya, S.A. *Zh. Fiz. Khim.* 1962, *36*, 2799-2803.

EXPERIMENTAL VALUES (continued)

The solubility product of AuIn in Hg at 20 °C determined by potentiometry:

$10^3c_{Au}{}^{i}$/mol dm^{-3}	$10^3c_{In}{}^{i}$/mol dm^{-3}	$10^3c_{In}{}^{f}$/mol dm^{-3}	$10^3c_{Au}{}^{f}$/mol dm^{-3}	10^7K_s/mol^2 dm^{-6}
1.01	1.14	0.525	0.385	2.07
1.0	1.03	0.432	0.405	1.75
1.0	1.01	0.392	0.381	1.50
0.8	0.83	0.495	0.465	1.82
0.8	0.78	0.452	0.472	2.10
0.8	0.76	0.375	0.415	1.55
0.9	0.97	0.510	0.460	2.23
0.9	0.95	0.434	0.384	1.68
0.9	0.21	0.370	0.360	1.70
			mean value	1.82±0.26[a]

[a] standard deviation calculated by compilers.

The discrepancy of the results obtained by the different methods may be explained by the possibility of partial oxidation of solid AuIn under polarographic conditions, thus leading to a higher value of K_s. However, it is difficult to find a reason why both values are too low compared with subsequent papers on the same system. Only corrosion of the amalgam would explain this.

COMPONENTS:

(1) Gold-indium 1:1; AuIn; [12006-55-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kozin, L.F.; Dergacheva, M.B.

Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR 1971, *2*, 73-83.

VARIABLES:

Temperature: 289-348 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubility products of AuIn as a sparingly soluble compound in Hg are reported. Initial Au concentration in all experiments was 1.01×10^{-1} mol dm^{-3}.

t/°C	$10^2 c_{In}^{i}$/mol dm^{-3}	$10^2 c_{In}^{f}$/mol dm^{-3}	$10^2 c_{Au}^{f}$/mol dm^{-3}	$10^5 K_s$/mol^2 dm^{-6} [a]
16	6.79	7.61	3.74	2.85
	7.60	7.96	2.93	2.33
	8.54	8.15	2.0	1.63
	8.94	12.3	1.64	2.02
	9.15	14.2	1.45	2.06
	9.59	17.8	1.04	1.85
	9.80	22.4	0.88	1.97
	10.0	25.8	0.71	1.83
			mean value	(2.2±0.6)
35	7.98	17.0	2.21	3.74
	8.54	19.1	1.65	3.15
	8.74	21.4	1.48	3.16

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Au amalgam was prepared by an unknown method. The In was introduced to Au amalgam or Hg by electrolysis. Differences of potential between Au-In amalgam and In amalgam electrodes in a solution of 1 mol dm^{-3} $InCl_3$, 200 g dm^{-3} NH_4Cl, 50 g dm^{-3} $C_4H_5O_6Na$, 50 g dm^{-3} $N_2H_4 \cdot HCl$ were measured for 15-30 min and in consequence Au and In equilibrium concentrations could be calculated, and K_s by their multiplication.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: precision no better than ± 0.2 K.

REFERENCES:

1. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1974, *7*, 42.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-indium 1:1; AuIn; [12006-55-2] (2) Mercury; Hg; [7439-97-6]	Kozin, L.F.; Dergacheva, M.B. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1971, *2*, 73-83.

EXPERIMENTAL VALUES (continued)

t/°C	$10^2 c_{In}{}^{i}$/mol dm^{-3}	$10^2 c_{In}{}^{f}$/mol dm^{-3}	$10^2 c_{Au}{}^{f}$/mol dm^{-3}	$10^5 K_s$/mol^2 dm^{-6} [a]
	8.94	23.0	1.29	2.96
	9.15	26.4	1.12	2.96
	9.58	30.3	0.72	2.18
	9.8	36.4	0.57	2.08
				(2.9±0.8)
55	7.10	30.3	3.29	9.96
	7.79	34.8	2.64	9.18
	7.96	38.2	2.41	9.21
	8.54	42.8	1.87	8.0
	8.74	45.9	1.80	8.26
	8.95	50.3	1.64	8.25
	9.15	53.9	1.37	7.38
				(8.7±1.3)
75	6.94	56.5	3.61	20.4
	7.44	64.9	3.29	21.3
	7.97	76.1	2.78	21.1
	8.54	93.6	2.48	23.2
	9.58	115.0	1.55	17.8
	10.0	129.0	1.27	16.4
				(20±3)

[a] average values recalculated by the authors of paper (1) using their own mathematical procedure are 1.25, 2.5, 7.7, and 21.5 mol^2 dm^{-6}, respectively.

The Au amalgam used at 16 °C was not homogeneous before addition of In, which may lead to a negligible error. The solubility of AuIn in Hg at 21 °C, 3x10^{-3} mol dm^{-3}, was also determined in the phase separation experiment; however no details are given in the paper.

COMPONENTS:

(1) Gold-indium 1:1; AuIn; [12006-55-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Sasim, D.

M. Sc. Thesis, University of Warsaw
Warsaw, 1974.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of AuIn in Hg at 298.2 K. Initial Au concentration was 9.0x10^{-2} mol dm^{-3}.

$10^2 c_{In}{}^{i}$/mol dm^{-3}		$10^5 K_s$/mol^2 dm^{-6}
2.80		3.2
3.06		3.0
3.57		5.8
4.08		5.7
4.59		4.3
5.10		3.7
6.12		5.1
	mean value	4.4 ± 1.1

This result was also reported in (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Au amalgam was prepared by dissolution of the metal in Hg. Equal portions of In were electrolytically introduced into the hanging drop electrodes filled with pure Hg or Au amalgam. Changes of potential in time in 0.1 mol dm^{-3} $In(NO_3)_3$ vs. SCE were measured for 10 min after the electrolysis was stopped. From the stable potential differences the concentration of In in the Au-In amalgam was found. Then with the use of mass balance the solubility product was calculated. The experiments were performed in a H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

99.999 % pure Au (Polish Mint), triply distilled water, twice distilled Hg (POCh) after chemical purification with $Hg_2(NO_3)_2$ and other chemicals of analytic purity (POCh) were used. The solution of $In(NO_3)_3$ was cathodically polarized on Hg for one day at -0.5 V vs. SCE.

ESTIMATED ERROR:

Solubility product: standard deviation ± 25 %. Temperature: precision ± 0.2 K.

REFERENCES:

1. Gumiński, C. *Ph.D. Thesis*, University of Warsaw, 1975.

COMPONENTS: (1) Gold-magnesium 1:1; AuMg; [12256-45-0] (2) Mercury; Hg; [7439-97-6]	EVALUATOR: C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1985

CRITICAL EVALUATION:

Loomis observed that the concentration of Mg in the liquid phase of Au amalgam was immeasureably small (3). Dergacheva and Kozin (1) investigated the Au-Mg-Hg system with the use of potentiometry and phase separation techniques. Tye concluded that AuMg is formed in Hg; similarly AuMg is a stable phase occurring in the Au-Mg binary alloys (2). Since the solubility products, $K_s = [Au][Mg]$, calculated from the phase separation experiments are higher than those obtained from potentiometric measurements, the authors of (1) suggest that the solid phase of AuMg is in equilibrium with a soluble form of this compound according to the reaction:

$$Au + Mg = AuMg = AuMg\downarrow$$

The temperature dependence of K_s obtained by weighted least square linear regression may be expressed by the equation (fitted by the evaluators):

$$pK_s = (-2.88 \pm 1.39) + (3.06 \pm 0.42) \times 10^3 \quad T^{-1}(T/K,\ K_s/mol^2\ dm^{-6})$$

The equation is valid for the temperature range 285 - 328 K. The formation of $AuMg_2$ and $AuMg_3$ was also found in the Au-Mg-Hg system (4), but the stability of these compounds is unknown.

Value of the solubility (tentative)

Solubility product of AuMg in Hg at 293 K is:

$$3 \times 10^{-8}\ mol^2\ dm^{-6}$$

and the solubility:

$$1.7 \times 10^{-4}\ mol\ dm^{-3}$$

References

1. Dergacheva, M.B.; Kozin, L.F. *Vestn. Akad. Nauk Kaz. SSR* 1974, no. 6, 56.
2. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, N.Y., 1958.
3. Loomis, A.G. *J. Am. Chem. Soc.* 1922, 44, 8.
4. Daams, J.L.C.; van Vucht, J.H.N. *Philips J. Res.* 1984, *39*, 275.

COMPONENTS:

(1) Gold-magnesium 1:1; AuMg; [12256-45-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Dergacheva, M.B.; Kozin, L.F.

Vestn. Akad. Nauk Kaz. SSR 1974, no. 6, 56-60.

VARIABLES:

Temperature: 285-328 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubility products of AuMg in Hg at different temperatures are determined. Initial Au and Mg concentrations were changed in the ranges 5.07×10^{-4} - 8.35×10^{-3} mol dm^{-3} and 3×10^{-4} - 4×10^{-1} mol dm^{-3} respectively.

t/°C	$10^8 K_s$/mol^{2}dm^{-6}	soly/mol dm^{-3}
12	(1.9±0.4)	1.4×10^{-4}
20	(2.8±0.6)	1.7×10^{-4}
30	(6.0±1.0)	2.4×10^{-4}
35	(7.1±1.0)	2.6×10^{-4}
55	(50±10)	7.0×10^{-4}

The solubility of AuMg in Hg obtained from phase separation analysis at 20 °C is $(4\pm1)\times10^{-3}$ mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Au amalgam was prepared by reduction of Au(III) on a Hg electrode in a separate cell. Proper amounts of Mg(II) were reduced on Au amalgam or Hg electrodes by electrolysis with constant current from $MgBrC_2H_5$ etheric solutions. Differences of potentials between Mg and Au-Mg amalgams in such solutions were measured and the solubility product calculated from the active concentration of Mg and mass balance. For the phase separation analysis known amounts of Au amalgam and metallic Mg were placed in a glass tube. The tube was sealed under vacuum and conditioned at 873 K for 3 hours. In the presence of an inert gas the amalgam was transferred into a vertical capillary for conditioning at 293 K for 4-47 hours. Various fractions of the amalgam in the capillary were analyzed for the metal contents with unspecified procedures.

SOURCE AND PURITY OF MATERIALS:

Purified Mg was used. Nothing more specified.

ESTIMATED ERROR:

Solubility product: precision no better than ± 15 % (potentiometry); solubility: precision ± 25 % (phase separation analysis). Temperature: nothing specified.

COMPONENTS:	EVALUATOR:
(1) Gold-manganese 1:1; AuMn; [12256-46-1] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry, University of Warsaw Warsaw, Poland May 1979

CRITICAL EVALUATION:

The Au-Mn amalgams were investigated by Dowgird and Galus (1) with various electrochemical methods. They found that an intermetallic compound, which forms in this system, has the composition AuMn. The equilibrium was described by the solubility product, $K_s = [Au][Mn]$, and the experiments were performed in the temperature range 278 - 328 K. It was not easy to obtain reproducible results because of the distinct reactivity of Mn amalgams. Better reproducibility of the results was detected for relatively larger concentrations of both metals in Hg, and when the Mn concentration was higher than that of Au. Therefore on the basis of these experiments it is rather impossible to exclude the formation of other compounds with greater Au content. The compound AuMn is a stable phase formed in the Au-Mn binary system (2). The evaluators found the temperature dependence of K_s, which may be expressed by the equation obtained with weighted linear least squares regression:

$$pK_s = (6.4 \pm 0.7) + (-0.31 \pm 0.22) \times 10^3 \quad T^{-1} | (T/K,\ K_s/\text{mol}^2\ \text{dm}^{-6})$$

However, one should remember that apparent changes of K_s are more or less masked by the effect of corrosion observed in the case of Mn amalgams.

Value of the solubility (tentative)

Solubility product of AuMn in Hg at 298 K is:

$$3 \times 10^{-6}\ \text{mol}^2\ \text{dm}^{-6}$$

and the solubility as calculated by evaluators from K_s:

$$1.7 \times 10^{-3}\ \text{mol dm}^{-3}$$

References

1. Dowgird, A.; Galus, Z. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 1978, *26*, 701.
2. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, N.Y., 1958.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-manganese 1:1; AuMn; [12256-46-1] (2) Mercury; Hg; [7439-97-6]	Dowgird, A.; Galus, Z. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 1978, *26*, 701-8.
VARIABLES:	PREPARED BY:
Temperature: 278-328 K	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubility products of AuMn as a sparingly soluble compound in Hg are reported for different temperatures. Initial concentrations of Au and Mn were changed in the ranges 1.00×10^{-4} - 8.7×10^{-3} mol dm^{-3} and 1.00×10^{-4} - 9.00×10^{-2} mol dm^{-3} respectively.

t/°C	K_s/ mol^2 dm^{-6}
5	$(5.4\pm2.1)\times10^{-6}$
15	$(5.5\pm1.9)\times10^{-6}$
25	$(3.1\pm1.5)\times10^{-6}$
35	$(3.3\pm1.1)\times10^{-6}$
45	$(4.3\pm0.6)\times10^{-6}$
55	$(2.4\pm0.6)\times10^{-6}$

Because of corrosion of the Mn amalgam in 0.1 mol dm^{-3} KCl as a base electrolyte, the result obtained for the solubility product was as low as $(9.3\pm1.7)\times10^{-7}$ mol^2 dm^{-6} at 25 °C. The higher value obtained with the use of ammonium buffer (see the table) should be more nearly correct, because influenced by corrosion to a smaller degree.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equal portions of Mn were introduced by electrolysis into a hanging mercury drop electrode and into a hanging drop electrode filled with Au amalgam (prepared by dissolution of Au in Hg). In the same solution (1×10^{-2} mol dm^{-3} $MnCl_2$, 1 mol dm^{-3} NH_4Cl and NH_3) potentials of the electrodes were measured vs. SCE. From the potential differences the solubility products were calculated. The experiments were carried out in an atmosphere of pure H_2.

SOURCE AND PURITY OF MATERIALS:

99.99 % pure Au, twice distilled Hg after chemical purification with $Hg_2(NO_3)_2$, triply distilled water and reagents of analytical quality were used. The base electrolyte was cathodically electrolyzed at -1.2 V for one day.

ESTIMATED ERROR:

Solubility product: precision no better than ± 20 %.

Temperature: ± 0.2 K.

COMPONENTS:	EVALUATOR:
(1) Gold-nickel 1:1; AuNi; [12044-85-8] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland March 1979

CRITICAL EVALUATION:

An interaction between Au and Ni in Hg was found by Gumiński and Galus (1). They performed voltammetric and potentiometric experiments using hanging mercury drop electrodes. A soluble compound is formed at lower concentrations of the metals. At higher concentrations of both metals a crystalline compound is formed. In the Au-Ni binary system the following compounds may be formed: Au_3Ni, AuNi and $AuNi_3$ (3). These molecules are not very stable so Hg may stabilize them or Hg may be the third component of a compound formed.

Assuming that the stoichiometry is 1:1 for the compound between Au and Ni in Hg, the corresponding equilibrium constant, $K = [AuNi]/[Au][Ni]$, and solubility product, $K_s = [Au][Ni]$, were estimated. The process described runs parallel to the reaction of Ni with Hg, therefore the stoichiometry cannot be determined precisely. The solubility of the compound is higher than the solubility of $NiHg_3$ in Hg, taken as 4×10^{-6} mol dm^{-3} (2).

Values of K and K_s (doubtful)

Stability constant of a compound formed in the Au-Ni-Hg system at 298 K is:

$$2 \text{ mol}^{-1} \text{ dm}^{3}$$

Solubility product of this compound is:

$$2 \times 10^{-7} \text{ mol}^{2} \text{ dm}^{-6}$$

assuming that the Au:Ni ratio is unity in both forms of the compound.

References

1. Gumiński, C.; Galus, Z. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 1978, *26*, 127.
2. Barański, A.; Galus, Z. *J. Electroanal. Chem.* 1973, *46*, 289.
3. Elliot, R.P. *Constitution of Binary Alloys*, 1st Supplement, McGraw-Hill, N.Y., 1965.

COMPONENTS:

(1) Gold-nickel 1:1; AuNi; [12044-85-8]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Gumiński, C.; Galus, Z.

Bull. Acad. Polon. Sci., Ser. Sci. Chim. 1978, *26*, 127-34.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

It was assumed that the stoichiometry of the Au-Ni compound is 1:1. Because of the complexity of the system it was very difficult to determine the ratio precisely. The investigations were performed for 9.00×10^{-2} mol dm^{-3} Au amalgam and 1.5×10^{-4} - 5.4×10^{-4} mol dm^{-3} Ni amalgam. Soluble AuNi is formed in Hg and the equilibrium constant at 298 K is:

$$(2 \pm 1)\ mol^{-1}\ dm^{3}$$

When the initial Ni concentrations is increased to over 7.0×10^{-4} mol dm^{-3} a crystalline compound is formed with the solubility product:

$$(2 \pm 1) \times 10^{-7}\ mol^{2}\ dm^{-6}$$

It was assumed that the concentration of free Ni in Hg is 4×10^{-6} mol dm^{-3} at 298 K, as reported for the solubility of $NiHg_3$ in Hg (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Au amalgam was prepared by dissolution of Au in Hg. In all experiments 0.2 mol dm^{-3} $NiCl_2$ in 5.5 mol dm^{-3} $CaCl_2$ was used. In the potentiometric experiments equal portions of Ni were introduced by electrolysis into the hanging gold amalgam drop electrode and the hanging mercury drop electrode. Potentials of the electrodes were measured vs. SCE. The corresponding constants were calculated from stable potential differences. The solubility product was estimated after determination of the unbound Au by means of the voltammetric pre-peak formation method (2). The experiments were performed in an H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

99.99 % pure Au, doubly distilled Hg after chemical purification with $Hg_2(NO_3)_2$, triply distilled H_2O and analytical grade reagents were used. The solution of $NiCl_2$ in $CaCl_2$ was purified by cathodic electrolysis.

ESTIMATED ERROR:

Solubility product: precision no better than ± 50 %. Temperature: ± 0.2 K.

REFERENCES:

1. Barański, A.; Galus, Z. *J. Electroanal. Chem.* 1973, *46*, 289.
2. Gumiński, C., Galus, Z. *J. Electroanal. Chem.* 1977, *83*, 139.

COMPONENTS:	EVALUATOR:
(1) Gold-antimony 1:1; AuSb; [36369-49-0] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland July 1982

CRITICAL EVALUATION:

The mercury rich part of the Au-Sb-Hg system was investigated by Zakharov and coworkers (1, 2, 4) by stripping voltammetry. Although $AuSb_2$ is the only stable compound found in the Au-Sb binary system (3), the authors (1, 2, 4) stated that an insoluble AuSb is formed in Hg. The mean estimated solubility product, $K_s = [Au][Sb]$, is 2.5×10^{-9} mol^2 dm^{-6} (1). This value seems to be rather rough, and a further study on the system is needed.

Value of solubility of AuSb in Hg (doubtful)

The solubility product of AuSb in Hg at room temperature is:

$$3 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$$

and the solubility, as calculated by evaluators,

$$5 \times 10^{-5} \text{ mol dm}^{-3}$$

References

1. Zakharov, M.S.; Zaichko, L.F. *Izv. Tomsk. Politekhn. Inst.* 1967, *164*, 183.
2. Zaichko, L.F.; Zakharov, M.S. *Izv. Tomsk. Politekhn. Inst.* 1971, *174*, 66.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, N.Y., 1958.
4. Stromberg, A.G.; Zakharov, M.S.; Mesyats, N.A.; Zaichko, L.F.; Stepanova, O.S. *Teoria i Praktika Amalgamnykh Protsesov*, Alma-Ata, 1966, p. 68.

COMPONENTS:

(1) Gold-antimony 1:1; AuSb; [36369-49-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zakharov, M.S.; Zaichko, L.F.

Izv. Tomsk. Politekhn. Inst. 1967, *164*, 183-6.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

AuSb is treated as a sparingly soluble compound in Hg. The equilibrium is described by the solubility product, and it was determined to be 2.1×10^{-9} and 2.8×10^{-9} mol^2 dm^{-6} in two experiments for which Sb(III) concentration in the solution was 2.0×10^{-5} and 2.6×10^{-5} mol dm^{-3}, respectively.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Stripping voltammetry with accumulation (5 min) on the hanging mercury drop electrodes was performed on solutions of Sb(III) and Sb(III)-Au(III) in 2 mol dm^{-3} KOH at -1.65 V vs. SCE. The time interval between accumulation and stripping was 1 min. The reference electrode was the SCE. The solubility product was calculated from the current integral under the peak, which corresponded to the active concentration of Sb, and a mass balance.

SOURCE AND PURITY OF MATERIALS:

Content of heavy metal ions impurities in the solution was below 5×10^{-8} mol dm^{-3}.

ESTIMATED ERROR:

Nothing specified. The error of the solubility product determine should not be smaller than ± 20 % (compilers).

COMPONENTS:	EVALUATOR:
(1) Gold-tin 1:1; AuSn; [12006-60-9] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1986

CRITICAL EVALUATION:

The formation of an intermetallic compound in the Au-Sn complex amalgam was primarily reported by Tammann and Ohler (1), who found a heat evolution during the dissolution of Sn in Au amalgam. Later Griengl and Baum (2) measured potentials of Au-Sn-Hg alloys for various compositions of the metals. However, the previously suggested formation of AuSn and $AuSn_2$ in Hg was not confirmed experimentally.

Kovaleva and Zebreva (3), using potentiometry and amalgam polarography, detected formation of $AuSn_2$, insoluble in Hg. Subsequently, Kemula and coworkers (4), i opposition to Kovaleva and Zebreva, reported formation of AuSn on the basis of amalgam polarography experiments. However evidence of $AuSn_2$-formation was seen also on the corresponding curve in the paper. The authors (4) found that AuSn is insoluble in Hg, and they determined solubility products, $K_s^{II} = [Sn_2][Au]^2$ and $K_s^{I} = [Sn][Au]$; both products were strongly dependent on the concentrations of Au and Sn: $(0.5\text{-}8.9)\times10^{-9}$ mol^3 dm^{-9} and $(0.96\text{-}12)\times10^{-6}$ mol^2 dm^{-6}, respectively. The mean value of K_s^{I} seems to be overstated and the equilibrium expressed by K_s^{II} was not confirmed later. It should be mentioned here that the amalgam polarography technique may supply erroneous results due to partial oxidation of a solid phase from an amalgam.

Independently, Kozin and Dergacheva (5) concluded that solid AuSn is formed in Hg and its solubility product (K_s^{I}) is only slightly dependent on the Au concentration in the amalgam. The solubility product extrapolated to zero Au concentration is equal to 8.9×10^{-7} mol^2 dm^{-6} at 298 K. In the opinion of these authors the existence of $AuSn_2$ and $AuSn_4$ in the amalgam is also possible when the proper excess of Sn is present, but formation of these compounds is not evident on potentiometric curves since stability of these compounds is similar. In the second work of Kovaleva and Zebreva (6), carried out using amalgam polarography, the authors arrived at the conclusion that two compounds, AuSn and $AuSn_2$, are formed in this system, depending on the initial concentration ratio of Sn to Au. The solubility product of AuSn is 1.7×10^{-6} mol^2 dm^{-6} at 293 K (probably), in agreement with the mean unextrapolated result of (5). A solubility product value of 8.7×10^{-7} mol^2 dm^{-6} at 298 K was determined by Dowgird (12) by means of potentiometry. This value agrees well with the extrapolated result of (5).

In a review on intermetallic compounds in Hg Kozin and Dergacheva (7) suggested that the solid AuSn in the amalgam is in equilibrium with a soluble form of this compound according to the equation:

$$Au + Sn \rightleftarrows AuSn \rightleftarrows AuSn\downarrow$$

Stromberg and coworkers (8, 10), using their mathematical-graphical procedure, calculated solubility products of AuSn, $AuSn_2$ and Au_4Sn_5 compounds in Hg on the basis of the earlier

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Gold-tin 1:1; AuSn; [12006-60-9] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1986

CRITICAL EVALUATION (continued)

results (3, 5) and the unpublished thesis of Zebreva (13). The existence of Au_4Sn_5 is unlikely. The recalculated results (denoted with (?)) are absurdly high. All the data are inserted in the table below.

Formulae and K_s-values of Au-Sn compounds in Hg according to (8, 10)

Reference	T/K	orig. formula	orig. $K_s/(\mathrm{mol\ dm^{-3}})^x$	calc. formula	calc. $K_s/(\mathrm{mol\ dm^{-3}})^x$
3	293	$AuSn_2$	2.5×10^{-10}	AuSn	8.0×10^{-7}
3	293	$AuSn_2$	2.5×10^{-10}	$AuSn_2$	1.6×10^{-5} (?)[a]
13	293	$AuSn_2$	3.1×10^{-10}	Au_4Sn_5	2.5×10^{-6} (?)[b]
13	293	$AuSn_2$	3.1×10^{-10}	$AuSn_2$	1.6×10^{-5} (?)[a]
5	289	AuSn	8.9×10^{-7}	AuSn	8.5×10^{-7}
5	328	AuSn	1.6×10^{-5}	AuSn	1.2×10^{-5}

[a] Probably exponent should be 2.

[b] Probably exponent should be 5.

The AuSn solid phase is the most stable in the Au-Sn binary system (11); it was identified after separation from the amalgam (5). According to Winterhager and Schlösser (9), Hg decomposes a solid Au-Sn alloy (80 mass % Au) and new solid phases $AuHg_2$ and AuSn are formed there. There is rough agreement between K_s-values obtained in (3, 5, 6, 12) by various techniques and at various temperatures, in the range 289-328 K. Changes of K_s with temperature, based on potentiometric results (3, 5, 12) are expressed by an equation established by linear least squares (by evaluators):

$$pK_s = -5.58 + 3431\,T^{-1} \qquad r = 0.98 \qquad (K_s/\mathrm{mol^2\ dm^{-6}};\ T/\mathrm{K})$$

<u>Values of the solubility of AuSn in Hg</u>

T/K	$K_s/\mathrm{mol^2\ dm^{-6}}$	Soly/mol $\mathrm{dm^{-3}}$ [a]	Refer.
298	9×10^{-7} [b]	9.5×10^{-4}	(3, 5, 8, 12)
323	9×10^{-6} [c]	3×10^{-3}	(3)

[a] calculated from K_s by evaluators.

[b] recommended.

[c] tentative.

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Gold-tin 1:1; AuSn; [12006-60-9] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1986

CRITICAL EVALUATION (continued)

References

1. Tammann, G.; Ohler, E. *Z. Anorg. Chem.* 1924, *135*, 118.
2. Griengl, F.; Baum, R. *Monatsh. Chem.* 1932, *61*, 330.
3. Kovaleva, L.M.; Zebreva, A.I. *Elektrokhimia* 1965, *1*, 1084.
4. Kemula, W.; Dowgird, A.; Galus, Z. *Elektrokhimia* 1968, *4*, 1058.
5. Kozin, L.F.; Dergacheva, M.B. *Ukr. Khim. Zh.* 1967, *33*, 787.
6. Kovaleva, L.M.; Zebreva, A.I. *Elektrokhimia* 1971, *7*, 911.
7. Kozin, L.F.; Dergacheva, M.B. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1972, *3*, 31.
8. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Zh. Fiz. Khim.* 1974, *48*, 2243.
9. Winterhager, W.; Schlösser, W. *Metall.* 1960, *14*, 1, 396.
10. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1974, *7*, 42.
11. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
12. Dowgird, A. *Ph.D. Thesis*, University of Warsaw, 1972; cited also by Gumiński, C. *Z. Metallk.* 1986, *77*, 87.
13. Zebreva, A.J. *Ph.D. Thesis*, University of Kazakhstan, Alma-Ata, 1968; as cited in 10.

COMPONENTS:

(1) Gold-tin 1:1; AuSn; [12006-60-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kovaleva, L.M.; Zebreva, A.I.

Elektrokhimia 1965, *1*, 1084-8.

VARIABLES:

Temperature: 293-323 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Although the authors originally calculated only the solubility product of $AuSn_2$ in Hg (see the $AuSn_2$-Hg system), it was shown by Stromberg et al. (1) and confirmed by the compilers that, for a sufficiently concentrated Au amalgam, the solubility product of AuSn in Hg is:

t/°C	Conditions	Method	K_s/mol^2 dm^{-6} [a]	Source
20	Au concn 3.5×10^{-3} mol dm^{-3}	potentiometry	7.9×10^{-7}	ref. (1)
20	$c_{Au}^{i}/c_{Sn}^{i} \geq 1$	potentiometry	$(6.7 \pm 1.6) \times 10^{-7}$	compilers
50	$c_{Au}^{i}/c_{Sn}^{i} \geq 1$	potentiometry	$(9.2 \pm 1.9) \times 10^{-6}$	compilers
17-20	$c_{Au}^{i}/c_{Sn}^{i} \geq 1$	polarography	$(2.7 \pm 0.8) \times 10^{-6}$	compilers

[a] standard deviations calculated by compilers.

The overstating of the polarographic results is most probably due to kinetically controlled dissolution of solid AuSn during electrolysis.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Proper amounts of Sn were reduced on Au amalgam and Hg electrodes. Differences of potentials between the electrodes in $SnCl_2$ in 2 mol dm^{-3} KCl + HCl (pH ≈ 1.3) were measured. In the amalgam polarography studies, the Au-Sn and Sn amalgams were oxidized in 0.5 mol dm^{-3} NaF solution. The limiting oxidation currents from Au-Sn and Sn amalgams were compared and corresponding constants were calculated.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: precision no better than ± 20 % (compilers).

Temperature: nothing specified.

REFERENCES:

1. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Zh. Fiz. Khim.* 1974, *48*, 2243.

COMPONENTS:

(1) Gold-tin 1:1; AuSn; [12006-60-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kozin, L.F.; Mergacheva, M.B.

Ukr. Khim. Zh. 1967, *33*, 787-93.

VARIABLES:

Temperature:

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of AuSn was determined in Hg. The experiments were performed at 16, 25, 35, 45 and 55 °C; however, numerical results are only given for 25 °C. In addition to the solubility product (K_s) the dissociation constant (K_d) was calculated by the authors to show its variability.

$10^3 c_{Au}{}^i$/mol dm^{-3}	$10^3 c_{Sn}{}^i$/mol dm^{-3}	$10^6 K_s$/mol^{2}dm^{-6}	$10^4 K_d$/mol dm^{-3}
9.88	3.98	2.22	5.98
9.88	4.69	2.36	5.49
9.88	5.04	2.34	4.97
9.88	5.98	2.22	4.02
9.88	6.45	2.15	3.6
9.88	7.36	2.07	3.05
9.88	7.81	2.04	2.85
9.88	8.27	1.93	2.54
9.88	9.21	2.12	2.62
9.88	10.10	2.24	2.62
9.88	11.10	2.35	2.66
	mean value	2.18	

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Proper amounts of Sn were reduced on Au distilled amalgam or Hg electrodes with constant current. Differences of potential between the Sn amalgam and Au-Sn amalgam in the complex electrolyte 1 mol dm^{-3} $SnCl_2$, 2 mol dm^{-3} $Na_2C_4H_4O_6$ and 5 % $N_2H_4 \cdot HCl$ were measured. From the potential differences the solubility products were calculated. The Au amalgam was prepared by electroreduction of Au(III) on Hg in a separate cell. All experiments were carried out in a H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

Hg was chemically purified and distilled in vacuum. Sn was 99.999 % pure.

ESTIMATED ERROR:

Solubility product: precision no better than ± 10 %. Temperature: nothing specified; probably ± 0.2 K (compilers).

REFERENCES:

1. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Zh. Fiz. Khim.* 1974, *48*, 2243.

COMPONENTS:

(1) Gold-tin 1:1; AuSn; [12006-60-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kovaleva, L.M.; Zebreva, A.I.

Elektrokhimia 1965, *1*, 1084-8.

EXPERIMENTAL VALUES (continued)

$10^3 c_{Au}{}^{1}$/mol dm^{-3}	$10^3 c_{Sn}{}^{1}$/mol dm^{-3}	$10^6 K_s$/mol^{2}dm^{-6}	$10^4 K_d$/mol dm^{-3}
4.97	1.13	1.29	15.6
4.97	1.66	1.31	10.0
4.97	2.80	1.51	6.7
4.97	4.07	1.45	4.45
4.97	4.71	1.40	3.82
4.97	5.15	1.40	3.60
4.97	6.04	1.34	3.14
4.97	6.50	1.18	2.68
4.97	7.40	1.38	3.07
4.97	7.88	1.48	3.25
4.97	8.35	1.46	3.16
	mean value	1.4	

After extrapolation of mean K_s values to $c_{Au}{}^{1} = 0$ the K_s value is equal to 8.9×10^{-7} mol^2 dm^{-6} at 25 °C was obtained (by authors). Stromberg and coworkers (1) calculated K_s values at other temperatures based on graphical plots of the potential difference vs. logarithm of $c_{Sn}{}^{1}$ presented in the paper compiled.

t/°C	K_s/mol^2 dm^{-6}
16	8.5×10^{-7}
55	1.6×10^{-5}

COMPONENTS:

(1) Gold-tin 1:1; AuSn; [12006-60-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kemula, W.; Dowgird, A.; Galus, Z.

Elektrokhimia 1968, 4, 1058-62.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL RESULTS:

It was shown that AuSn precipitates in Hg, however $AuSn_2$ tends to form when Sn is in excess. The dissociation constant, $K = [Au][Sn]/[AuSn]$, and solubility products, $K_s^I = [Au][Sn]$ or $K_s^{II} = [Au]^2[Sn_2]$, are calculated at 25 °C.

c_{Sn}^i/mol dm^{-3}	c_{Au}^i/mol dm^{-3}	K/mol dm^{-3}	K_s^I/mol^2 dm^{-6}	K_s^{II}/mol^3 dm^{-9}	$K_s^{AuSn_2}$/ mol^3 dm^{-9} [a]
10^{-2}	$1.5x10^{-2}$	$1.7x10^{-4}$	$1.7x10^{-6}$	$0.44x10^{-8}$	--
10^{-2}	$1.25x10^{-2}$	$1.8x10^{-4}$	$1.7x10^{-5}$	$0.26x10^{-8}$	--
10^{-2}	$1.00x10^{-2}$	$1.1x10^{-4}$	$0.96x10^{-6}$	$0.05x10^{-8}$	--
10^{-2}	$0.75x10^{-2}$	$6.2x10^{-4}$	$4.0x10^{-6}$	$0.22x10^{-8}$	$1.4x10^{-8}$
10^{-2}	$0.65x10^{-2}$	$1.0x10^{-3}$	$5.5x10^{-6}$	$0.33x10^{-8}$	$2.5x10^{-8}$
10^{-2}	$0.35x10^{-2}$	$5.9x10^{-3}$	$1.2x10^{-5}$	$0.89x10^{-8}$	$9.6x10^{-8}$
10^{-2}	$0.25x10^{-2}$	$5.7x10^{-3}$	$8.5x10^{-6}$	$0.42x10^{-8}$	$7.2x10^{-8}$

[a] calculated by compilers from K_s^I and K_s^{II}.

Every result is a mean value of 3 measurements.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Au amalgam was prepared by dissolution of Au foil in Hg. The Sn was introduced into the amalgam or pure Hg by electroreduction of Sn(II) in a glass container from H_2SO_4 solution as a supporting electrolyte. The amalgams were transferred into a separate reservoir with a polarographic capillary at the bottom. The capillary was placed in a cell containing 0.1 mol dm^{-3} HCl. The anodic dissolution polarograms were recorded for Au-Sn and Sn amalgams. All operations were carried out in a H_2 atmosphere. The constants which could characterize an equilibrium of the system can be calculated from concentration balance if one knows initial concentrations of Au and Sn and the final concentration of Sn as calculated from the oxidation current.

SOURCE AND PURITY OF MATERIALS:

The Au (from Polish Mint) was 99.99 % pure. The Hg (from POCh) was chemically purified and twice distilled under vacuum. The $SnCl_2$ was Analar-BDH Anal. pure HCl (from POCh) was purified by isopiezic distillation. Triply distilled H_2O was used.

ESTIMATED ERROR:

Nothing specified. Concentrations of the metals could not be determined more precisely than ± 5 %. Temperature ± 0.5 K (private communication to compilers).

COMPONENTS:

(1) Gold-tin 1:1; AuSn; [12006-60-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kovaleva, L.M.; Zebreva, A.I.

Elektrokhimia 1971, 7, 911-2.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of AuSn in Hg at probably 20 °C was found to be:

$10^3c_{Sn}{}^i$/ mol dm^{-3}	$10^3c_{Sn}{}^f$/ mol dm^{-3}	$10^3c_{Au}{}^i$/ mol dm^{-3}	$10^6K_s{}^{AuSn}$/ mol^{2}dm^{-6}	$10^9K_s{}^{AuSn_2}$/ mol^{3}dm^{-9}
4.1	2.5	1.2	--	2.5
4.1	1.9	1.9	--	2.9
4.1	0.9	2.7	--	0.9
4.1	1.7	3.1	1.2	--
4.1	1.2	4.7	2.1	--
4.1	0.7	6.0	1.8	--
5.0	3.5	1.0	--	3.0
5.0	3.2	1.5	--	6.1
5.0	3.2	2.0	0.6	11.2
5.0	2.6	3.0	1.6	--
5.0	1.9	4.0	1.7	--
5.0	1.3	5.0	1.7	--
5.0	0.9	6.0	1.7	--
10.0	5.4	2.5	--	5.8

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Sn was introduced into Hg and Au amalgams by electroreduction of Sn(II) in NaF solution. Then polarographic oxidations of the Au-Sn and Sn amalgams in 0.5 mol dm^{-3} NaF solution were carried out. The currents recorded were compared and the solubility product was calculated from final Sn concentration found and mass balance.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: precision better than ± 25 %.

Temperature: nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-tin 1:1; AuSn; [12006-60-9]	Kovaleva, L.M.; Zebreva, A.I.
(2) Mercury; Hg; [7439-97-6]	*Elektrokhimia* 1971, 7, 911-2.

EXPERIMENTAL VALUES (continued)

$10^3 c_{Sn}^{i}$/ mol dm^{-3}	$10^3 c_{Sn}^{f}$/ mol dm^{-3}	$10^3 c_{Au}^{i}$/ mol dm^{-3}	$10^6 K_s^{AuSn}$/ mol^{2}dm^{-6}	$10^9 K_s^{AuSn_2}$/ mol^{3}dm^{-9}
10.0	4.5	3.0	--	5.1
10.0	5.8	4.0	--	65
10.0	5.3	5.0	1.6	--
10.0	4.0	6.5	2.0	--
10.0	2.7	7.8	1.4	--
10.0	1.4	10.0	2.0	--
1.0	0.9	3.1	2.7	--
1.5	0.8	3.1	1.9	--
2.5	0.9	3.1	1.4	--
3.0	1.1	3.1	1.3	--
4.1	1.7	3.1	1.2	--
6.1	1.4	3.1	--	1.8
7.1	2.0	3.1	--	2.0
8.4	3.3	3.1	--	5.4
9.2	3.5	3.1	--	2.4
10.2	4.2	3.1	--	1.8
			mean value for AuSn:	1.7±0.4

COMPONENTS:

(1) Gold-tin 1:1; AuSn; [12006-60-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Dowgird, A.

Ph.D. Thesis, University of Warsaw, 1972.

VARIABLES:

One temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

AuSn is treated as a sparingly soluble compound in Hg; the equilibrium is described by the solubility product which at 25.0 °C is:

$c_{Au}{}^{i}$/mol dm^{-3}	$c_{Sn}{}^{i}$/mol dm^{-3}	K_s/mol^2 dm^{-6}
5.0×10^{-3}	9.75×10^{-4}-3.9×10^{-3}	$(9.0\pm1.0)\times10^{-7}$
2.0×10^{-2}	3.62×10^{-3}-1.31×10^{-2}	$(8.5\pm1.5)\times10^{-7}$
7.0×10^{-2}	2.40×10^{-3}-2.62×10^{-2}	$(8.5\pm1.3)\times10^{-7}$
	mean value	8.7×10^{-7}

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Au amalgam was prepared by dissolution of this metal in Hg. Equal portions of Sn were introduced electrolytically into a hanging mercury drop electrode and into a hanging drop electrode filled with Au amalgam. The electrolyte contained 5.0×10^{-2} mol dm^{-3} Sn(II) in 1 mol dm^{-3} KF. Potentials of the electrodes were measured for 18 min in the same electrolyte vs. SCE. Stable difference of potentials was reached after at least 12 min. The equilibrium concentration of Sn in the Au-Sn amalgam was determined and the solubility product calculated from mass balance. All operations were performed in a H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

99.99 % pure Au, triply distilled H_2O, twice distilled Hg after chemical purification with $Hg_2(NO_3)_2$ and analytically pure reagents (from POCh) were used.

ESTIMATED ERROR:

Solubility product: precision no better than ± 15 %.

Temperature: precision ± 0.2 K.

COMPONENTS:	EVALUATOR:
(1) Gold-tin 1:2; $AuSn_2$; [12256-54-1] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1978

CRITICAL EVALUATION:

The formation of $AuSn_2$, in addition to AuSn, in Hg was first suggested, but not experimentally proven, by Griengl and Baum (1). This compound was later detected by Kovaleva and Zebreva (2, 3, 9) who determined its solubility product, $K_s = [Au][Sn]^2$, using amalgam polarography and potentiometry at 293 and 323 K. Polarographic results in (3) show larger spread than in (2). According to Kozin and Dergaczeva (4) formation of $AuSn_2$ is possible in the Sn-rich Au-Sn amalgams but its formation is not so evident on potentiometric curves. An indication of formation of $AuSn_2$ was also seen on polarographic curves by Kemula and coworkers (8). No numerical results are inserted in (4) and (8). Stromberg and coworkers (5, 6) using their own mathematical procedure, on the basis of the potentiometric results of (2, 9), obtained some proof that $AuSn_2$ exists in the complex Au-Sn amalgams with over two-fold higher concentrations of Sn than that of Au. The solubility products reported by the last authors (5, 6) are inserted in the table given in the critical evaluation of the AuSn-Hg system. The results calculated are a few orders of magnitude higher than the primary values of Kovaleva and Zebreva (2, 9). It seems that a misprint exists in the papers (5, 6), or the table inserted needs extra explanation. Thermodynamic stability of AuSn and $AuSn_2$ in Hg seems to be similar, which causes experimental difficulties in their differentiation. Finally we give preference to the potentiometric results. $AuSn_2$ is formed also in the Au-Sn binary system (7).

Values of the solubility product of $AuSn_2$ in Hg according to (2, 9) by potentiometry (tentative)

T/K	K_s/mol^3 dm^{-9}	Solubility/mol dm^{-3} ^{a}	Ref.
293	3×10^{-10}	4×10^{-4}	(2, 9)
323	1.8×10^{-8}	1.6×10^{-3}	(2)

^{a} calculated from K_s by evaluators.

References

1. Griengl, F.; Baum, R. *Monatsh. Chem.* 1932, *61*, 330.
2. Kovaleva, L.M.; Zebreva, A.I. *Elektrokhimia* 1965, *1*, 1084.
3. Kovaleva, L.M.; Zebreva, A.I. *Elektrokhimia* 1971, *7*, 911.
4. Kozin, L.F.; Dergacheva, M.B. *Ukr. Khim. Zh.* 1967, *33*, 787.
5. Stromberg, A.G.; Mukheeva, N.P.; Belousov, Yu.P. *Zh. Fiz. Khim.* 1974, *48*, 2243.
6. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1974, *7*, 42.
7. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
8. Kemula, W.; Dowgird, A.; Galus, Z. *Electrokhimia* 1968, *4*, 1058.
9. Zebreva, A.J. *Ph.D. Thesis*, University of Kazakhstan, Alma-Ata, 1968; as cited in 6.

COMPONENTS:

(1) Gold-tin 1:2; $AuSn_2$; [12256-54-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kovaleva, L.M.; Zebreva, A.I.

Elektrokhimia 1965, *1*, 1084-8.

VARIABLES:

Temperature: 290-323 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound $AuSn_2$ is treated as sparingly soluble in Hg. Results of the potentiometric experiments are:

t/°C	$10^3c_{Au}^{i}$/ mol dm^{-3}	$10^3c_{Sn}^{i}$/ mol dm^{-3}	$10^3c_{Sn}^{f}$/ mol dm^{-3}	$10^3c_{Au}^{f}$/ mol dm^{-3}	$10^9K_s^{AuSn2}$/ mol^3 dm^{-9}	$10^6K_s^{AuSn}$/ mol^2 dm^{-6} ^{a}
20	0.628	0.866	0.642	0.516	0.21^b	0.33
	0.628	1.20	0.737	0.397	0.22^b	0.30
	0.628	1.546	0.907	0.309	0.25^b	0.28
	0.628	1.065	0.720	0.456	0.24^b	0.33
	1.26	0.539	0.434	1.209	0.23	0.52^c
	1.26	0.877	0.510	1.077	0.28	0.55^c
	1.26	1.215	0.547	0.926	0.28	0.51^c
	1.26	0.689	0.488	1.160	0.28	0.57^c
	1.26	1.067	0.535	0.994	0.28	0.53^c
	2.51	0.363	0.282	2.470	0.20	0.69^c
	2.51	0.738	0.347	2.315	0.28	0.80^c
	2.51	0.852	0.324	2.246	0.24	0.72^c

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

All experiments were performed in an inert gas atmosphere. In the potentiometric measurements proper amounts of Sn were introduced into Au amalgam or mercury by electrolysis. Differences of potentials between these amalgams in the solution of $SnCl_2$ in 2 mol dm^{-3} KCl+HCl (pH ≈ 1.3) were measured. In the amalgam polarography experiments the Au-Sn and Sn amalgams were oxidized in the solution of Sn(II) with 0.5 mol dm^{-3} NaF background electrolyte. The currents or potentials were recorded, compared and K_s values calculated from mass balance.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: precision no better than ± 10 % (compilers).

Temperature: nothing specified.

REFERENCES:

1. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Zh. Fiz. Khim.* 1974, *48*, 2243.
2. Kovaleva, L.M.; Zebreva, A.I. *Elektrokhimia* 1971, *7*, 911.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-tin 1:2; $AuSn_2$; [12256-54-1] (2) Mercury; Hg; [7439-97-6]	Kovaleva, L.M.; Zebreva, A.I. *Elektrokhimia* 1965, *1*, 1084-8.

EXPERIMENTAL VALUES (continued)

t/°C	$10^3 c_{Au}^{i}$/ mol dm^{-3}	$10^3 c_{Sn}^{i}$/ mol dm^{-3}	$10^3 c_{Sn}^{f}$/ mol dm^{-3}	$10^3 c_{Au}^{f}$/ mol dm^{-3}	$10^9 K_s^{AuSn2}$/ mol^3 dm^{-9}	$10^6 K_s^{AuSn}$/ mol^2 dm^{-6} [a]
	3.51	0.313	0.253	3.470	0.22	0.88[c]
	3.51	0.579	0.284	3.363	0.27	0.95[c]
					mean value	0.25
50	3.51	2.696	2.394	3.359	19	8.0[c]
	3.51	3.797	2.686	2.955	21[b]	7.9
	3.51	4.901	3.306	2.713	29[b]	8.9
	3.51	3.306	2.595	3.155	21	8.2[c]
	7.09	1.652	1.042	6.785	7	7.1[c]
	7.09	2.332	1.142	6.495	8	7.4[c]
	7.09	3.304	1.281	6.08	1.0	7.8[c]
	7.09	4.956	1.651	5.44	1.5	9.0[c]
	7.09	7.708	2.127	3.35	1.5[b]	7.1
	10.57	1.08	0.842	10.45	0.8	8.8[c]
	10.57	2.706	1.085	9.76	1.2	10.6[c]
	10.57	4.334	1.246	9.026	1.4	11.2[c]
	10.57	6.506	1.681	8.16	2.3	13.7[c]
					mean value	1.5

[a] Calculated by compilers.

[b] Compilers think $AuSn_2$ is formed.

[c] Compilers think AuSn is formed.

Stromberg and coworkers (1), also showed on the basis of these potentiometric results that AuSn is formed in the range of higher concentrations of Au. Results of polarographic experiments, also reported in (2), are (at 17-20 °C):

$10^3 c_{Au}^{i}$/ mol dm^{-3}	$10^3 c_{Sn}^{i}$/ mol dm^{-3}	$10^3 c_{Sn}^{f}$/ mol dm^{-3}	$10^3 c_{Au}^{f}$/ mol dm^{-3}	$10^9 K_s^{AuSn2}$/ mol^3 dm^{-9}	$10^6 K_s^{AuSn}$/ mol^2 dm^{-6} [a]
3.09	1.01	0.90	3.035	2.5	2.7[c]
3.09	1.52	0.78	2.72	1.6	2.1[c]
4.15	1.94	0.73	3.54	1.9	2.6[c]
0.56	2.03	1.40	0.25	0.5	0.35
1.12	2.03	1.25	0.73	1.1[b]	0.91
3.09	2.54	0.90	2.27	1.8	2.0[c]
1.16	2.63	1.45	0.57	1.2[b]	0.82

(continued next page)

COMPONENTS:

(1) Gold-tin 1:2; $AuSn_2$; [12256-54-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kovaleva, L.M.; Zebreva, A.I.

Elektrokhimia 1965, *1*, 1084-8.

EXPERIMENTAL VALUES (continued)

$10^3 c_{Au}{}^i$/ mol dm^{-3}	$10^3 c_{Sn}{}^i$/ mol dm^{-3}	$10^3 c_{Sn}{}^f$/ mol dm^{-3}	$10^3 c_{Au}{}^f$/ mol dm^{-3}	$10^9 K_s{}^{AuSn2}$/ mol^3 dm^{-9}	$10^6 K_s{}^{AuSn}$/ mol^2 dm^{-6} [a]
3.09	3.04	1.0	2.07	2.1	2.1[c]
1.16	4.07	2.60	0.42	2.9[b]	1.1
1.88	4.07	1.90	0.80	2.9[b]	1.5
2.72	4.07	0.80	1.09	0.7[b]	0.87
3.09	4.07	1.55	1.83	4.4[b]	2.8
4.70	4.07	1.20	3.27	4.7	3.9[c]
6.79	4.07	0.70	5.11	2.5	3.6[c]
1.26	6.11	3.70	0.55	0.7[b]	2.0
3.77	6.28	1.40	1.33	2.6[b]	1.9
3.09	9.17	3.45	0.23	2.7[b]	0.8
3.09	10.20	4.05	0.02	0.3[b]	0.8

[a] Calculated by compilers.

[b] Compilers think $AuSn_2$ is formed.

[c] Compilers think AuSn is formed.

COMPONENTS:

(1) Gold-tin 1:2; $AuSn_2$; [12256-54-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kovaleva, L.M.; Zebreva, A.I.

Elektrokhimia 1971, *7*, 911-2.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of $AuSn_2$ in Hg at probably 20 °C was determined as well as the solubility product of AuSn at corresponding concentrations of the components.

$10^3 c_{Sn}^{i}$/mol dm^{-3}	$10^3 c_{Sn}^{f}$/mol dm^{-3}	$10^3 c_{Au}^{i}$/mol dm^{-3}	$K_s^{AuSn_2}$/mol^3 dm^{-9}
4.1	2.5	1.2	2.5
4.1	1.9	1.9	2.9
4.1	0.9	2.7	0.9
5.0	3.5	1.0	3.0
5.0	3.2	1.5	6.1
5.0	3.2	2.0	11.2
10.0	5.4	2.5	5.8
10.0	4.5	3.0	5.1
10.0	5.8	4.0	65
6.1	1.4	3.1	1.8
7.1	2.0	3.1	2.0
8.4	3.3	3.1	5.4
9.2	3.5	3.1	2.4
10.2	4.2	3.1	1.8

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The experimental details were essentially the same as in paper (1); see the previous data sheet.

SOURCE AND PURITY OF MATERIALS:

As in (1).

ESTIMATED ERROR:

As in (1).

REFERENCES:

1. Kovaleva, L.M.; Zebreva, A.I.
Elektrokhimia 1965, *1*, 1084.

COMPONENTS:	EVALUATOR:
(1) Gold-zinc 1:1; AuZn; [12006-63-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland March 1982

CRITICAL EVALUATION:

AuZn is formed in Hg by mixing simple Zn and Au amalgams as was originally found by Tammann and Jander (1) using potentiometry. The first (1) and the next work (2), also using potentiometry, both assumed that AuZn is soluble in Hg, and therefore the stability constant, K = [AuZn]/[Au][Zn], of this compound was calculated. However, these "constants" were dependent on both metal concentrations. Zebreva (3) recalculated data of Hartmann and Schölzel (2), showing that the solubility product, K_s = [Au][Zn], has an almost constant value. Nevertheless, the absolute value given by Zebreva (3), 2.5×10^{-12} $mol^2\ dm^{-6}$ at 363 K, is not correct. Stromberg and coworkers (4, 11, 12), using a mathematical procedure elaborated by themselves, recalculated data of Hartmann and Schölzel (2) and obtained a mean value of K_s equal to 1.4×10^{-7} $mol^2\ dm^{-6}$ at 363 K, which corresponds very well to the results of (5) or (9). Further electrochemical work (5-9) on this system supports the view that AuZn exists in Hg as a sparingly soluble compound. All values from (5) are reported also in (9). Several results at temperatures between 278 and 363 K are reported. There is good agreement among results of (5, 6, 8, 9) at 298 K and results of (4, 7) at 363 K. However, values reported in (7) at 348, 323 and 298 K are much too low, most probably due to corrosion of free Zn in the Au-Zn amalgams. The value of the solubility product of AuZn can be affected by the presence of Cd or In in the amalgam (7), but no quantitative data on this influence can be recommended. Temperature dependence of K_s, based on: (1), as calculated by compilers; (2), as calculated in (4, 11, 12) at 363 K and by compilers at 293 K; (5), (6), (7) at 363 K; and (8), obtained by the least squares method is expressed by the equation:

$$pK_s = -3.72 + 3.82\times10^3\ T^{-1} \qquad r = 0.991 \qquad (K_s/mol^2\ dm^{-6};\ T/K)$$

One obtains a quite similar equation using only data of work (5) or (9) (see the corresponding data sheet). AuZn is the most stable compound formed in the Au-Zn binary system (10).

<u>Values of solubility of AuZn in Hg</u>

T/K	$K_s/mol^2\ dm^{-6}$	Soly/mol dm^{-3} ^{a}	Refer.
278	9×10^{-11} ^{c}	9×10^{-6}	(5) extrapolation with the fitting equation
298	6.9×10^{-10} ^{b}	2.6×10^{-5}	(5, 6, 8)
328	1.3×10^{-9} ^{c}	3.6×10^{-5}	(5)
348	5.5×10^{-8} ^{c}	2.4×10^{-4}	(5)
363	1.6×10^{-7} ^{c}	4.0×10^{-4}	(2, 4, 7, 11, 12)

^{a} calculated by evaluators from K_s.

^{b} recommended.

^{c} tentative.

(continued next page)

COMPONENTS:

(1) Gold-zinc 1:1; AuZn; [12006-63-2]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

March 1982

CRITICAL EVALUATION (continued)

References

1. Tammann, G.; Jander, W. *Z. Anorg. Chem.* 1922, *124*, 105.
2. Hartmann, H.; Schölzel, K. *Z. Phys. Chem., N. F.* 1956, *9*, 106.
3. Zebreva, A.I. *Vestn. Akad. Nauk Kaz. SSR* 1958, no. 11, 88; *Zh. Fiz. Khim.* 1961, *35*, 948.
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6. Rodgers, R.S.; Meites, L. *J. Electroanal. Chem.* 1972, *38*, 359.
7. Dergacheva, M.B. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1975, *11*, 36.
8. Ostapczuk, P.; Kublik, Z. *J. Electroanal. Chem.* 1977, *83*, 1.
9. Gumiński, C. *Ph.D. Thesis*, University of Warsaw, Warsaw, 1968.
10. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
11. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Zh. Fiz. Khim.* 1974, *48*, 2243.
12. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1974, *7*, 42.

COMPONENTS:

(1) Gold-zinc 1:1; AuZn; [12006-63-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Tammann, G.; Jander, W.

Z. Anorg. Chem. 1922, *124*, 105-22.

VARIABLES:

One temperature: 289 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

AuZn is treated as a compound soluble in Hg and the equilibrium at 16 °C is described by the stability constant; the solubility product value was calculated by the compilers. Initial Au concentration was 3.24×10^{-3} mass % in all experiments.

c_{Zn}^{i}/mass %	K/(mol fraction)$^{-1}$	c_{Zn}^{f}/mol dm^{-3} ^{a}	c_{Au}^{f}/mol dm^{-3} ^{a}	K_s/mol^2 dm^{-6} ^{a}
$1.271 \cdot 10^{-4}$	--	--	--	--
$2.542 \cdot 10^{-4}$	--	--	--	--
$3.813 \cdot 10^{-4}$	--	--	--	--
$5.084 \cdot 10^{-4}$	--	$2.09 \cdot 10^{-8}$	$1.18 \cdot 10^{-3}$	$2.47 \cdot 10^{-11}$ ^{b}
$6.355 \cdot 10^{-4}$	$4.7 \cdot 10^{7}$	$7.97 \cdot 10^{-8}$	$9.2 \cdot 10^{-4}$	$7.33 \cdot 10^{-11}$ ^{b}
$7.625 \cdot 10^{-4}$	$1.6 \cdot 10^{7}$	$3.20 \cdot 10^{-7}$	$6.5 \cdot 10^{-4}$	$2.08 \cdot 10^{-10}$
$8.863 \cdot 10^{-4}$	$2.2 \cdot 10^{7}$	$6.00 \cdot 10^{-7}$	$4.0 \cdot 10^{-4}$	$2.40 \cdot 10^{-10}$
$1.017 \cdot 10^{-3}$	$3.3 \cdot 10^{7}$	$1.31 \cdot 10^{-6}$	$1.3 \cdot 10^{-4}$	$1.73 \cdot 10^{-10}$
$1.144 \cdot 10^{-3}$	$5.4 \cdot 10^{7}$	$1.32 \cdot 10^{-4}$	--	--
$1.271 \cdot 10^{-6}$	$2.2 \cdot 10^{7}$	$3.84 \cdot 10^{-4}$	--	--
$1.398 \cdot 10^{-3}$	--	$4.38 \cdot 10^{-4}$	--	--

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Au amalgam was prepared by dissolution of the metal in Hg. The Zn amalgam was prepared by electroreduction from $ZnSO_4$ solution. The amalgams were mixed in various proportions and potentials of the complex Au-Zn amalgam as well as the simple Zn amalgam in a solution of $ZnSO_4$ were measured versus the calomel electrode with 0.5 mol dm^{-3} KCl. The stability constant was calculated from the potential differences. The experiments were performed in a H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified. Precision of the solubility product estimation is not better than ±25 % (by compilers).

REFERENCES:

1. Gumiński, C.; Galus, Z. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 1971, *19*, 771.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-zinc 1:1; AuZn; [12006-63-2] (2) Mercury; Hg; [7439-97-6]	Tammann, G.; Jander, W. *Z. Anorg. Chem.* 1922, *124*, 105-22.

EXPERIMENTAL VALUES (continued)

$c_{Zn}{}^{i}$/mass %	K/(mol fraction)$^{-1}$	$c_{Zn}{}^{f}$/mol dm^{-3} [a]	$c_{Au}{}^{f}$/mol dm^{-3} [a]	K_s/mol^2 dm^{-6} [a]
$1.525\cdot10^{-3}$	--	$5.40\cdot10^{-4}$	--	--
$1.652\cdot10^{-3}$	--	$6.35\cdot10^{-4}$	--	--
mean value	$3.4\cdot10^{7}$		mean value	$(2.1\pm0.5)\cdot10^{-10}$ [a]

[a] calculated by compilers.

[b] rejected by compilers.

A K_s-value three times higher was reported in (1); however we recognize it as incorrect because it was calculated from the mean value of K (as originally reported by the authors of this paper).

COMPONENTS:

(1) Gold-zinc 1:1; AuZn; [12006-63-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Hartmann, H.; Schölzel, K.

Z. Phys. Chem., *N. F.* 1956, *9*, 106-26.

VARIABLES:

Temperature: 293-363 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

AuZn is treated as a compound soluble in Hg; the equilibrium is described by the dissociation constant, K_d = [Au][Zn]/[AuZn]. The K_d-values are $5x10^{-10}$ and $2.5x10^{-7}$ mol fraction at 293 and 363 K respectively; they are calculated for equal Au and Zn concentrations. The Au concentration in the experiments was either $6.05x10^{-4}$ or $5.5x10^{-5}$ mol fraction and Zn concentrations were changed in the ranges $3x10^{-3}$ - $6x10^{-7}$ and $6x10^{-4}$ - $6x10^{-7}$ mol fraction, respectively.

On the basis of these experimental results a solubility product, K_s = [Au][Zn], which is the correct thermodynamic value for the system, was calculated by several authors (1-4). The value ($2.5x10^{-12}$ mol^2 dm^{-6} at 363 K) reported by Zebreva (1) is erroneously calculated. Stromberg and coworkers (2, 4) using their own mathematical-graphical procedure obtained, at 363 K, $1.2x10^{-7}$ and $1.6x10^{-7}$ mol^2 dm^{-6} for Au concentrations $3.7x10^{-3}$ and $4.1x10^{-2}$ mol dm^{-3} respectively. The compilers' (3) recalculations of the original data for equimolar concentrations of the parent metals give the values of $6.8x10^{-7}$ and $1.3x10^{-9}$ mol^2 dm^{-6} at 363 and 293 K, respectively. However, Stromberg's approach seems to be more exact than ours (3), since his method takes into account all experimental points given on the figures in the paper.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The experiments were carried out in a H_2 atmosphere. The Au and Zn amalgams were prepared by dissolution of the metals in Hg. The simple amalgams were mixed in various proportions. Differences of potential between the complex Au-Zn and simple Zn amalgams in a $ZnSO_4$ solution were measured. The corresponding constant was calculated from potential differences when the analytical concentration of Zn in both half cells was equal.

SOURCE AND PURITY OF MATERIALS:

All materials had high purity: Zn 99.95% pure (from Merck); Au 99.98% pure (from Degussa) and analytically pure $ZnSO_4$ (from Merck).

ESTIMATED ERROR:

Nothing specified. Precision of determination is not better than ± 10 % (by compilers).

REFERENCES:

1. Zebreva, A.I. *Vestn. Akad. Nauk Kaz. SSR* 1958, no. 11, 88; *Zh. Fiz. Khim.* 1961, *35*, 948.
2. Stromberg, A.G.; Mesyats, N.A.; Mikheeva, N.P. *Zh. Fiz. Khim.* 1971, *45*, 1521.
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4. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Zh. Fiz. Khim.* 1974, *48*, 2243; *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1974, *7*, 42.

COMPONENTS:

(1) Gold-zinc 1:1; AuZn; [12006-63-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Gumiński, C.; Galus, Z.

Bull. Acad. Polon. Sci., Ser. Sci. Chim. 1971, *19*, 771-6.

VARIABLES:

Temperature: 278-348 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

AuZn is treated as a sparingly soluble compound in Hg and its solubility products are reported.

Potentiometric results at 298 K

Initial concentration of Au 5.0x10^{-2} mol dm^{-3}; in addition to K_s, the stability constant was calculated by the authors.

$10^3c_{Zn}{}^1$/mol dm^{-3}	$10^{10}K_s$/mol^2 dm^{-6}	$10^{-7}K$/mol^{-1} dm^3
40.8	7.5	6.5
39.3	9.2	3.5
36.4	7.9	4.6
34.0	6.6	7.4
31.9	6.8	4.7
27.5	5.8	4.7
26.3	4.8	5.4
24.1	5.8	4.1
19.3	6.8	2.8
14.9	4.5	3.4

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equal portions of Zn were introduced by electrolysis into the hanging mercury drop electrode and into the hanging drop electrode filled with Au amalgam (prepared by dissolution of the metal in Hg). In the same solution of 0.1 mol dm^{-3} $ZnCl_2$, the potentials of the electrodes were measured versus SCE for 10 min. Also coulometric charges of the oxidation of Zn from the complex Au-Zn amalgams under chronoamperometric conditions were recorded. The solubility products were calculated from the potential differences and from the oxidation charge of the free Zn using mass balance. All experiments were performed in a H_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

99.999 % pure Au from Polish Mint, triply distilled H_2O, twice distilled Hg after chemical purification with $Hg_2(NO_3)_2$, $ZnCl_2$ from POCh were used. Solutions of $ZnCl_2$ were electrolyzed cathodically one day at -0.85 V vs. SCE before use.

ESTIMATED ERROR:

Solubility product: precision no better than ± 15 %.

Temperature: ± 0.2 K.

REFERENCES:

1. Gumiński, C. *Ph.D. Thesis*, University of Warsaw, Warsaw, 1975.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-zinc 1:1; AuZn; [12006-63-2] (2) Mercury; Hg; [7439-97-6]	Gumiński, C.; Galus, Z. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 1971, *19*, 771-6.

EXPERIMENTAL VALUES (continued)

$10^3c_{Zn}{}^i$/mol dm^{-3}	$10^{10}K_s$/mol^2 dm^{-6}	$10^{-7}K$/mol^{-1} dm^3
14.4	7.4	2.0
11.9	6.5	1.8
9.6	5.6	1.9
8.9	5.3	1.7
7.2	3.7	1.9
5.9	4.2	1.4
4.8	2.4	2.0
3.0	2.2	1.3
3.3	1.9	2.4
mean value	(5.4±2.0)	

$c_{Au}{}^i$/mol dm^{-3}	$c_{Zn}{}^i$/mol dm^{-3}	$10^{10}K_s$/mol^2 dm^{-6}
7.0×10^{-2}	2.3×10^{-2} - 5.5×10^{-2}	8.6±2.0 [a]
5.0×10^{-2}	3.0×10^{-3} - 4.0×10^{-2}	5.4±2.0
3.0×10^{-3}	7.1×10^{-4} - 2.4×10^{-3}	7.1±1.0 [a]
1.0×10^{-3}	6.7×10^{-4} - 1.0×10^{-3}	5.0±1.2 [a]
5.0×10^{-4}	2.1×10^{-4} - 5.4×10^{-4}	8.5±2.0 [a]
	mean value	6.9±1.6

Potentiometric results at various temperatures. The initial concentrations of Au: 5.0×10^{-2} mol dm^{-3} and of Zn: 2.7×10^{-2} - 5.4×10^{-2} mol dm^{-3} (except at 298 K). The results are presented on a graph and numerically in (1).

T/K	K_s/mol^2 dm^{-6}
278	$(8\pm5)\times10^{-11}$ [a]
288	$(3.5\pm2.0)\times10^{-10}$
298	$(6.9\pm1.6)\times10^{-10}$
308	$(2.6\pm0.6)\times10^{-9}$
318	$(6.1\pm0.6)\times10^{-9}$
328	$(1.3\pm0.1)\times10^{-8}$
338	$(2.6\pm0.4)\times10^{-8}$
348	$(5.7\pm1.6)\times10^{-8}$

[a] presented only in (1).

These data may be expressed by compilers' equation obtained using the method of weighed linear least squares regression:

(continued next page)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-zinc 1:1; AuZn; [12006-63-2] (2) Mercury; Hg; [7439-97-6]	Gumiński, C.; Galus, Z. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 1971, *19*, 771-6.

EXPERIMENTAL VALUES (continued)

$$pK_s = (-3.37\pm0.34) + (3.70\pm0.11)\times10^3/T \quad (K_s/\text{mol}^2\ \text{dm}^{-6};\ T/\text{K})$$

Coulometric results at 298 K

Solubility products of AuZn in mercury for 1.00×10^{-3} mol dm^{-3} Au amalgam

$q_{Zn}^{i}/\mu C$	$q_{Zn}^{f}/\mu C$	$10^{10}K_s/mol^2\ dm^{-6}$
3.25	0.38	2.4
	0.39	2.6
31.5	0.18	4.5
	0.15	3.6
28.0	0.04	2.2
	0.055	3.1
	mean result	(3.1±0.9)

COMPONENTS:

(1) Gold-zinc 1:1; AuZn; [12006-63-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Rodgers, R. S.; Meites, L.

J. Electroanal. Chem. 1972, *38*, 359-65.

VARIABLES:

Room temperature measurement (298 K)

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of slightly soluble AuZn in Hg at 298 K (probably) is $(7.1\pm0.6)\times10^{-10}$ mol^2 dm^{-6}. Detailed results are given in the table.

Solubility products for AuZn[a]

$10^6n_{e,Zn}^i$/mol	$10^6n_{e,Au}^i$/mol	$10^2P/s^{-1}$	10^{10} K_s/mol^2 dm^{-6}	10^6n_e/mol		Range of times k/P
				exptl	calcd	
279	16.6	1.88	6.6	248	251	0.6-3.0
277	41	1.54	8.9	204	202	0.9-13.0
283	83	1.76	5.6	152	136	5.5-21.5
			7.4	137	147	1.5-10.0
278	125	1.64	7.2	44.5	46.5	1.2-16.0

[a] from $i(t)^{-1} = (2n_{e,Au}^i - n_{e,Zn}^i + n_e + n_e(t) + i(t)P^{-1})(4K_sV^2P)^{-1}$, where n_e is the mols of electrons, i the current, $V = 35$ cm^3, and $P = \partial \ln i(t)/\partial t$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Au amalgam was prepared by electrolysis of $AuCl_3$ solution at a mercury pool cathode at -0.8 V. The Zn(II) was then reduced at the Au amalgam from 0.1 mol dm^{-3} ammonium citrate and 0.2 mol dm^{-3} NH_3 saturated with NaCl at potential -1.35 V. Subsequently stripping of Zn from the Au-Zn amalgam was carried out at -0.25 V. The currents were integrated and the solubility product was calculated from the equation given.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: standard deviation 8 %.

Temperature: nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold-zinc 1:1; AuZn; [12006-63-2] (2) Mercury; Hg; [7439-97-6]	Dergacheva, M.B. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1975, *11*, 36-42.
VARIABLES:	**PREPARED BY:**
Temperature: 323-363 K Addition of In or Cd	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubility products of AuZn in Hg at various temperatures:

t/°C	$c_{Au}{}^{i}$/mol dm^{-3}	$c_{Zn}{}^{i}$/mol dm^{-3} [a]	Soly/mol dm^{-3} [b]	K_s/mol^2 dm^{-6}
50	3.04×10^{-3}	1.9×10^{-3} - 1.5×10^{-1}	2.23×10^{-5}	4×10^{-10}
	3.04×10^{-2}	1.0×10^{-4} - 8.0×10^{-2}		5.9×10^{-10}
75	3.04×10^{-3}	3.0×10^{-3} - 1.5×10^{-1}	8.35×10^{-5}	8.1×10^{-9}
	3.04×10^{-2}	1.6×10^{-4} - 6.0×10^{-2}		6.6×10^{-9}
90	3.04×10^{-3}	3.0×10^{-3} - 1.5×10^{-1}	4.46×10^{-4}	2.5×10^{-7}
	3.04×10^{-2}	1.5×10^{-4} - 6.0×10^{-2}		1.0×10^{-7}

[a] values were read from figures.

[b] solubilities are not simply related to reported values of K_s.

Only the solubility product at 363 K is reliable. At lower temperatures the results are too low. The most probable cause of these errors lies in corrosion of Zn in the amalgams tested.

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Proper amounts of Zn were introduced into Au amalgam or Hg electrodes by electrolysis. Differences of potentials between Zn amalgam and Au-Zn amalgam in complex 0.2 mol dm^{-3} $ZnSO_4$, 0.5 mol dm^{-3} $(NH_4)_2SO_4$, 3 mol dm^{-3} NaOH, 50 g dm^{-3} $N_2H_4\cdot H_2SO_4$ electrolyte were measured. The solubility products were calculated from the potential differences and mass balance. In one experimental series In was introduced to the Au-Zn amalgam and the solubility product was found without addition of In. All other details as in paper (1).

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Kozin, L.F.; Dergacheva, M.B. *Ukr. Khim. Zh.* 1967, *33*, 787, see the AuSn-Hg system.

COMPONENTS:

(1) Gold-zinc 1:1; AuZn; [12006-63-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Dergacheva, M.B.

Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR 1975, *11*, 36-42.

EXPERIMENTAL VALUES (continued)

K_s-values of AuZn in Hg

Temperature: 75 °C; $c_{Au}^{i} = 3.04 \times 10^{-2}$ mol dm^{-3}

c_{Zn}^{i}/mol dm^{-3}	c_{Zn}^{f}/mol dm^{-3}	c_{Au}^{f}/mol dm^{-3}	K_s/mol^{2}dm^{-6}	c_{Au}^{f*}/mol dm^{-3}	K_s^*/mol^{2}dm^{-6}
5.12×10^{-4}	4.7×10^{-7}	2.9×10^{-2}	1.4×10^{-8}	1.3×10^{-2}	6.1×10^{-9}
2.10×10^{-3}	4.7×10^{-7}	2.8×10^{-2}	1.4×10^{-8}	1.2×10^{-2}	5.6×10^{-9}
3.6×10^{-3}	7.5×10^{-7}	2.7×10^{-2}	2.0×10^{-8}	1.0×10^{-2}	7.5×10^{-9}
6.7×10^{-3}	8.4×10^{-7}	2.4×10^{-2}	2.0×10^{-8}	7.4×10^{-3}	6.2×10^{-9}
1.27×10^{-2}	1.65×10^{-6}	1.7×10^{-2}	2.8×10^{-8}	2.0×10^{-3}	3.3×10^{-9}
		mean values:	$(1.9 \pm 0.6) \times 10^{-8}$ [a]		5.75×10^{-9}

[a] the mean value and standard deviation calculated by the compilers.

* values corrected for presence of AuIn.

Influence of In or Cd on the equilibrium in the Au-Zn amalgam being investigated is an interesting phenomenon, although the results may serve only as a qualitative information (due to corrosion); K_s agrees better with results of other papers than K_s^*; this is opposite to what should be expected.

COMPONENTS:

(1) Gold-zinc 1:1; AuZn; [12006-63-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Ostapczuk, P.; Kublik, Z.

J. Electroanal. Chem. 1977, *83*, 1-17.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubility products of slightly soluble AuZn in Hg at 298.2 K are:

$c_{Au}{}^{i}$/mol dm^{-3}	$c_{Zn}{}^{i}$/mol dm^{-3}	K_s/mol^2 dm^{-6}
3.3×10^{-3}	2.0×10^{-4} - 2.0×10^{-3}	$(4.1\pm1.0)\times10^{-10}$
1.1×10^{-2}	3.0×10^{-3} - 1.0×10^{-2}	$(5.5\pm1.5)\times10^{-10}$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Au amalgam was prepared by Au dissolution in Hg and conditioning for 5 days. The Zn was introduced electrolytically into the hanging gold amalgam drop electrode. Potentials of the electrodes in a solution containing Zn(II) were measured vs. SCE. The solubility products were calculated from the potential differences and mass balance. The experiments were performed in an Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Au was 99.99 % pure from Polish Mint, twice distilled Hg, triply distilled H_2O and all other reagents were analytically pure from POCh.

ESTIMATED ERROR:

Solubility product: precision no better than ± 15 % (private communication to the compilers). Temperature: precision ± 0.1 K.

COMPONENTS:

(1) Barium-cadmium 1:1; BaCd; [37190-17-3]

(2) Mercury; Hg; [7439-97-6]

ORGINAL MEASUREMENTS:

Filippova, L.M.; Zhumakanov, V.Z.; Klyukas, Yu.E.; Zebreva, A.I.

Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 1984, *27*, 1241-2.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of BaCd in Hg at 25 °C, K_s = [Ba][Cd], is 0.42 mol^2 dm^{-6}, and the solubility 0.64 mol dm^{-3}, as calculated by compilers. Concentrations of Ba and Cd were changed in the ranges 0.2 - 0.4 mol dm^{-3} and 3.0 - 6.3 mol dm^{-3}, respectively. However, one should remember that the solubility of BaCd found is higher than the solubility of Ba in Hg (see the Ba-Hg system), which makes the result doubtful. The enthalpy of dissociation of BaCd in its amalgam is +15.6±2.2 kJ mol^{-1}, at the confidence level of 0.95. The compound BaCd is formed in the Ba-Cd binary alloy (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Cd amalgam was prepared by dissolution of the metal in Hg. The Ba amalgam was obtained by an unspecified electrolytic method. Both simple amalgams were mixed and the complex Ba-Cd amalgam formed. It was titrated with Hg in a calorimeter. The heats of dilution (Q) were recorded for various compositions (N) of the amalgam. A break point in the curve of Q vs. N corresponds to the equilibrium concentrations of the metals. All operations were performed in an Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: precision probably ± 10 % (by compilers).

Temperature: stability of ±0.005 K.

REFERENCES:

1. Hansen, M.; Anderdo, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Barium-lead 2:1; Ba_2Pb; [62974-93-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Filippova, L.M.; Zhumakanov, V.Z.;
Zebreva, A.I.; Smurigina, T.V.
Fiz.-Khim. Issled. v Rastvorakh,
Alma-Ata 1982, 40-4.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of Ba_2Pb in Hg at 298 K is 0.20 mol dm^{-3} and the solubility product, K_s = $[Ba]^2[Pb]$, is 3.2×10^{-2} mol^3 dm^{-9} (by compilers). The values are tentative. The heat of dissociation of Ba_2Pb under these conditions is 5.7±0.9 kJ mol^{-1}. Concentrations of Ba and Pb were changed in the ranges 0.15 - 0.40 and 0.90 - 1.10 mol dm^{-3}, respectively. The compound Ba_2Pb is the most stable compound formed in the Ba-Pb binary system (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Pb amalgam was prepared by dissolution of the metal in Hg. The Ba amalgam was obtained by electrolysis. Both amalgams were mixed in various proportions to form the complex heterogeneous amalgam. It was further titrated with Hg. The heats of the titration were recorded and plotted vs. concentrations of the metals. The solubility of Ba_2Pb was determined from a breakpoint on such a plot.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: precision no better than ±10 % (by compilers).

Temperature: nothing specified.

REFERENCES:

1. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Barium-tin 1:3; $BaSn_3$; [72060-61-8]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Filippova, L.M.; Zhumakanov, V.Z.; Zebreva, A.I.; Smurigina, T.V.

Fiz.-Khim. Issled. v Rastvorakh, Alma-Ata 1982, 40-4.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of $BaSn_3$ in Hg at 298 K is 0.25 mol dm^{-3} and the solubility product, K_s = $[Ba][Sn]^3$, is 0.10 mol^4 dm^{-12} (by compilers); the values are tentative. Concentrations of Ba and Sn were changed in the ranges 0.20 - 0.40 and 0.60 - 0.75 mol dm^{-3}, respectively. The heat of formation of $BaSn_3$ under these conditions is -23.2±1.0 kJ mol^{-1}. The compound $BaSn_3$ is also formed in the binary Ba-Sn system (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Sn amalgam was prepared by dissolution of the metal in Hg. The Ba amalgam was obtained by electrolysis. The amalgams were mixed in various ratios to form the complex heterogeneous amalgam. It was further titrated with Hg. Heats of this titration were recorded and plotted vs. concentrations of both metals. The solubility of $BaSn_3$ was determined from a break-point on such a plot.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: precision no better than ± 10 % (by compilers).

Temperature: nothing specified.

REFERENCES:

1. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Barium-zinc 1:1; BaZn; [74018-81-8]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Filippova, L.M.; Zhumakanov, V.Z.; Klyukas, Yu.E.; Zebreva, A.I.

Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 1984, *27*, 1241-2.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product, (K_s = [Ba][Zn]) of BaZn in Hg at 25 °C is 0.18 mol^2 dm^{-6} and the solubility as calculated by the compilers, is 0.42 mol dm^{-3}. Concentrations of Ba and Zn were changed in the ranges 0.2-0.4 mol dm^{-3} and 1.0 - 1.5 mol dm^{-3} respectively. The solubility of BaZn is equal to the solubility of Ba (see Ba-Hg system) so the result obtained may be doubtful and needs an independent confirmation. The enthalpy of formation of BaZn in Hg is -25.3±3.7 kJ mol^{-1} at the confidence level of 0.95. BaZn is a stable compound formed in the Ba-Zn binary system (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Zn amalgam was prepared by dissolution of the metal in Hg. The Ba amalgam was obtained by an unspecified electrolytic method. Both simple amalgams were mixed and the complex Ba-Zn amalgam was titrated with Hg in a calorimeter. The heats of dilution (Q) were recorded for various compositions (N) of the amalgam. A break point on the curve of Q vs. N corresponds to the equilibrium concentrations of the metals. All operations were performed in an Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: precision probably ± 10 % (by compilers).

Temperature: stability of ±0.005 K.

REFERENCES:

1. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Bismuth-cerium 3:4; Bi_3Ce_4; [12048-64-5]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

June 1977

CRITICAL EVALUATION:

Only one potentiometric study on the Bi-Ce-Hg system was performed by Tammann and Jander (1). The authors report an unbelievably high stability constant of Bi_3Ce_4 in Hg, $K = [Bi_3Ce_4]/[Bi]^3[Ce]^4$, assuming that the compound is soluble. The value of K is $(3\pm2)\times10^{120}$ (mol fraction)$^{-6}$ at 291 K. This value is surely not correct due to corrosion of Ce by aqueous solutions in the cell investigated. The potentials measured correspond to undetectable equilibrium amounts of the metals below 10^{-16} mol fraction. Further work on the system is needed and no value is suggested. However, one should notice that '$_3$Ce$_4$ is the most stable compound formed in the binary Bi-Ce system (2).

References

1. Tammann, G.; Jander, W. *Z. Anorg. Chem.* 1922, *124*, 105.
2. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:	EVALUATOR:
(1) Bismuth-lithium 1:1; BiLi; [12048-27-0] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland July 1988

CRITICAL EVALUATION:

Korshunov et al. (1) postulated the formation of moderately stable $BiLi_3$ in Hg. This compound is slightly more soluble in Hg than Li in Hg as concluded from a comparison of the EMF measurements using Li and Bi-Li amalgam electrodes. No numerical value for the stability of $BiLi_3$ in Hg was reported.

Filippova et al. (2) measured heat during dilution of concentrated heterogeneous Bi-Li amalgam with Hg. Formation of BiLi was found, and the solubility product, K_s = [Bi][Li], determined was 0.19 $mol^2 dm^{-6}$ at 298 K. Although similar concentration ranges of the components were covered in (1) and (2), the final conclusions are different. Therefore, the results of (2) are doubtful.

BiLi intermetallic phase is formed in the binary Bi-Li alloys (3) but it is less stable than $BiLi_3$. The doubtful value of the solubility product of BiLi in Hg at 298 K is 0.2 $mol^2 dm^{-6}$ and the solubility is 0.4 mol dm^{-3}.

References

1. Korshunov, V.N.; Khlystova, K.B.; Selevin, V.V. *Elektrokhimiya* 1972, *8*, 1513.
2. Filippova, L.M.; Zhumakanov, V.Z.; Zebreva, A.I. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1980, *23*, 204.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, N.Y., 1958.

COMPONENTS:

(1) Bismuth-potassium 1:3; BiK_3; [12048-26-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Filippova, L.M.; Zhumakanov, V.Z.
Zebreva, A.I.
Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 1978, *21*, 1450-3.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of BiK_3 in Hg, $K_s=[Bi][K]^3$, at 298 K is equal to $4x10^{-2}$ mol^4 dm^{-12} and the solubility concentrations of Bi and K were changed in the ranges up to 0.6 mol dm^{-3} and 0.1 - 0.9 mol dm^{-3}, respectively. The equilibrium concentrations were presented in a small graph in the paper. It was assumed that the Hg activity is constant in these experiments. The heat of dissolution of BiK_3 in its saturated amalgam is 4.4±0.8 kJ mol^{-1}. The BiK_3 solid phase is the most stable one in the Bi-K binary system (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Bi amalgam was obtained by dissolution of Bi in Hg and the K amalgam by electrolysis. The amalgams were mixed in various proportions. Then they were diluted with Hg and heat (Q) was recorded. A bend on the dependence Q vs. concentration of Bi or K corresponds to the equilibrium concentrations of the metals. This allowed the establishment of the stoichiometry of the intermetallic compound being formed and its solubility product. The experiments were performed in an Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

Solubility: no better than ± 20 % (by compilers).

REFERENCES:

1. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Bismuth-lithium 1:1; BiLi; [12048-27-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Filippova, L.M.; Zhumakanov, V.Z.;
Zebreva, A.I.

Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 1980, *23*, 204-6.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of BiLi in Hg, $K_s = [Bi][Li]$, at 298 K equals 0.19 $mol^2\ dm^{-6}$ and the solubility 0.44 mol dm^{-3}. Concentrations of Bi and Li were changed in the ranges 0.30 - 1.60 and 0.15 - 0.80 mol dm^{-3}, respectively. The equilibrium concentrations of both metals are presented in a plot in the paper. The result of the solubility is tentative. The heat of dissolution of BiLi in its saturated amalgam is 6.2±0.4 kJ mol^{-1}. The phase BiLi is formed in the binary Bi-Li alloys, but it is not the most stable (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Li amalgam was prepared by an electrolytic method. The Bi amalgam was obtained by dissolution of the metal in Hg. The amalgams were mixed in various ratios. Then they were diluted with Hg and heat (Q) was measured. A bend on the curve relating Q to concentrations of Bi and Li corresponds to the equilibrium concentrations of the metals. This allowed one to establish the stoichiometry of the compound being formed and its solubility product. The experiments were performed in an Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

Solubility product: precision no better than ± 10 % (by compilers).

REFERENCES:

1. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:	EVALUATOR:
(1) Cadmium-copper 3:4; Cd_3Cu_4; [12050-37-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland, August 1986

CRITICAL EVALUATION:

The formation of a compound between Cd and Cu in Hg was suggested on the basis of various electrochemical experiments (1-5, 14). However, there was a lack of quantitative data on its stoichiometry and stability. On the other hand, other authors did not find any evidence of intermetallic compound formation between these elements in Hg (6-8, 13). More recently, Kublik and coworkers (9, 19) as well as Roston and coworkers (15, 16), after careful electroanalytical experiments, stated that no compound is formed unless the Cu amalgam is unsaturated and homogeneous. If the product of the concentrations of Cd and Cu in Hg exceeds the value of 1.4×10^{-4} mol^2 dm^{-6} (9) and the Cu amalgam is heterogeneous, then codeposition of Cd with solid Cu_7Hg_6 occurs.

Zebreva and coworkers investigated concentrated and heterogeneous Cd-Cu amalgams by potentiometry (10), calorimetric titration (11) and chronoamperometric oxidation (12). The heat of dilution by Hg of the complex, heterogeneous amalgams indicated no interactions between Cd and Cu in the Cd-Cu-Hg system. However, in other work (10, 12) formation of solid Cd_3Cu_4, as the main product, on additions of $CdCu_2$ and Cd_3Cu was established. Kinetics of oxidation of such complex amalgams was investigated (12).

Finally Kairbaeva and coworkers (17) performed manysided studies of the system by roentgenography and chemical analysis. The solubility of Cd_3Cu_4 in Hg was determined and concentrations of the components are reported. The authors concluded that if the complex amalgam is heterogeneous in Cu but homogeneous in Cd, then the solid phase contains Cd_3Cu_4 and Cu_7Hg_6; if the complex amalgam is heterogeneous in both elements, then the solid phase contains a mixture of Cd_8Cu_5, Cd_3Cu_4 and Cu_7Hg_6.

In the binary Cd-Cu system the following compounds exist: Cd_2Cu, Cd_3Cu_4 and Cd_8Cu_5; they are characterized by similar thermal stability (18). Due to a significant spread of results of the determinations in (17) no solubility values are suggested, and a data sheet for this work is included.

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2. Kemula, W.; Galus, Z.; Kublik, Z. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 1958, *6*, 661.
3. Jakuszewski, B.; Grabowski, J.; Kasprzak, J. *Soc. Sci. Lodz Acta Chim.* 1967, *12*, 25.
4. Neyman, E.Ya.; Dolgopolova, G.M.; Trukhacheva, L.N. *Zavod. Lab.* 1969, *35*, 1040.
5. Batley, G.E.; Florence, T.M. *J. Electroanal. Chem.* 1974, *55*, 23.
6. Hartmann, H.; Schölzel, K. *Z. Phys. Chem., N. F.* 1956, *9*, 106.
7. Zebreva, A.I.; Speranskaya, E.F.; Kozlovskii, M.T. *Zh. Fiz. Khim.* 1959, *33*, 2715.
8. Crosum, S.T.; Dean, J.A.; Stokely, J.R. *Anal. Chim. Acta* 1975, *75*, 421.
9. Ostapczuk, P.; Kublik, Z. *J. Electroanal. Chem.* 1977, *83*, 1.

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Cadmium-copper 3:4; Cd_3Cu_4; [12050-37-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland, August 1986

CRITICAL EVALUATION (continued)

10. Matakova, R.N., Zebreva, A.I.; Serikbaeva, L.K. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1973, no. 1, 81.
11. Omarova, N.D.; Filippova, L.M.; Zebreva, A.I. *Sborn. Rabot Khim.*, Alma-Ata 1973, no. 3, 358.
12. Zebreva, A.I.; Matakova, R.N.; Sharipova, N.S. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1979, no. 6, 67.
13. Rodgers, R.S.; Meites, L. *J. Electroanal. Chem.* 1981, *125*, 167.
14. Lihl, F.; Kirnbauer, H. *Z. Metallk.* 1957, *68*, 9, 61.
15. Roston, D.A.; Brooks, E.E.; Heineman, W.R. *Anal. Chem.* 1979, *51*, 1728.
16. Wise, J.A.; Roston, D.A.; Heineman, W.R. *Anal. Chim. Acta* 1983, *154*, 95.
17. Kairbaeva, A.A.; Lange, A.A.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1983, no. 4, 9.
18. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
19. Donten, M.; Kublik, Z. *J. Electroanal. Chem.* 1985, *196*, 275.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cadmium-copper 3:4; Cd_3Cu_4; [12050-37-2] (2) Mercury; Hg; [7439-97-6]	Kairbaeva, A.A.; Lange, A.A.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* <u>1983</u>, no. 4, 9-14.
VARIABLES:	**PREPARED BY:**
Room temperature measurements: 293 K Source of samples	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Content of Cd and Cu in liquid phase of the heterogeneous amalgams containing solid Cd_3Cu_4 + Cu_7Hg_6 under equilibrium conditions at 293 K

$10^2w_{Cd}{}^i$	atom ratio	$10^2w_{Cd}{}^f$	$10^2x_{Cd}{}^f$	$10^2w_{Cu}{}^f$	$10^2x_{Cu}{}^f$	sequence of the metals added
mass fract.	Cd:Cu	mass fract.	at. fract.[a]	mass fract.	at. fract.[a]	
3.5	3:1	1.67	2.94	$3.3x10^{-3}$	$1.04x10^{-2}$	first Cd
3.5	3:1	1.70	2.99	$3.46x10^{-3}$	$1.09x10^{-2}$	first Cd
3.5	4:3	1.03	1.82	$1.40x10^{-3}$	$4.42x10^{-3}$	first Cd
3.5	1:2	1.51	2.66	$4.10x10^{-3}$	$1.29x10^{-2}$	first Cd
3.5	1:3	1.28	2.29	$1.45x10^{-1}$	$4.51x10^{-1}$	first Cu
3.5	1:4	1.42	2.51	$2.11x10^{-2}$	$6.66x10^{-2}$	first Cu
3.5	1:4	1.69	2.97	$5.56x10^{-3}$	$1.76x10^{-2}$	first Cd
5.5	3:1	1.98	3.48	$3.26x10^{-3}$	$1.03x10^{-2}$	first Cd
5.46	2:1	1.39	2.45	$4.80x10^{-2}$	$1.51x10^{-1}$	first Cd
11.17	3:1	4.20	7.26	$1.15x10^{-2}$	$3.63x10^{-2}$	first Cu
11.17	3:4	3.86	6.79	$1.38x10^{-1}$	$4.30x10^{-1}$	first Cu

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The complex amalgams were obtained by electrolysis of $CuSO_4$ and $CdSO_4$ in 0.5 mol dm^{-3} H_2SO_4 at the Hg cathode. The amalgams were conditioned for 500 to 1500 hrs. The solid and liquid phases were separated and chemically analyzed: samples of the amalgam were dissolved in HNO_3, Hg(II) was reduced and the concentrations of Cd and Cu were determined by atomic absorption spectroscopy. In addition the solid phase was investigated by roentgenography. The Cd_3Cu_4 phase (for the last two measurements) was synthesized from the components taken in stoichiometric ratio. The elements were placed in a glass tube filled with Ar and heated at 1273 K. The alloy was homogenized for 72 hrs at 723 K. A roentgenographic test was carried out.

SOURCE AND PURITY OF MATERIALS:

Very pure Cd and Cu were used.

ESTIMATED ERROR:

Solubility: nothing specified; every experiment was repeated three times.

Temperature: ± 2 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cadmium-copper 3:4; Cd_3Cu_4; [12050-37-2] (2) Mercury; Hg; [7439-97-6]	Kairbaeva, A.A.; Lange, A.A.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1983, no. 4, 9-14.

EXPERIMENTAL VALUES (continued)

$10^2 w_{Cd}{}^i$ mass fract.	atom ratio Cd:Cu	$10^2 w_{Cd}{}^f$ mass fract.	$10^2 x_{Cd}{}^f$ at. fract.[a]	$10^2 w_{Cu}{}^f$ mass fract.	$10^2 x_{Cu}{}^f$ at. fract.[a]	sequence of the metals added
5.5	1:2	0.70	1.24	3.43×10^{-3}	1.08×10^{-2}	first Cu
3.5	3:4	0.70	1.24	4.5×10^{-3}	1.42×10^{-2}	alloy Cd_3Cu_4
6.5	3:4	1.02	1.80	5.6×10^{-3}	1.77×10^{-2}	alloy Cd_3Cu_4

[a] at. fract. calculated by compilers.

COMPONENTS:

(1) Cadmium-potassium 1:1; CdK; [98246-92-5]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

March 1980

CRITICAL EVALUATION:

Based on thermometric titrations of the complex Cd-K amalgams with Hg, Filippova and coworkers (1) concluded that solid CdK is formed in Hg. The corresponding solubility product, $K_s = [Cd][K]$, was also determined. However, one should note that the determined solubility value of CdK is higher than the solubility of K in Hg (see the K-Hg system). Moreover, Dzhabarova and coworkers (2) found no compound formation in this complex system. Jänecke (3) investigated the whole Cd-K-Hg phase diagram by thermal analysis and no ternary compound was found; only formation of Cd_3K in the binary Cd-K alloys was observed. These reservations make the value determined in (1) a very doubtful one.

Value of the solubility product of CdK in Hg (doubtful)

The solubility product of CdK in Hg at 298 K is, as in (1):

$$5.4 \text{ mol}^2 \text{ dm}^{-6}$$

and the solubility, as calculated from K_s by evaluators:

$$2.3 \text{ mol dm}^{-3}$$

References

1. Filippova, L.M.; Zebreva, A.I.; Espenbetov, A.A. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1977, *20*, 1468.
2. Dzhabarova, N.K.; Kaplin, A.A.; Anisimova, L.S. *Usp. Polarogr. s Nakopl., Tomsk,* 1973, 39.
3. Jänecke, E. *Z. Metallk.* 1928, *20*, 113.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cadmium-potassium 1:1; CdK; [98246-91-5] (2) Mercury; Hg; [7439-97-6]	Filippova, L.M.; Zebreva, A.I.; Espenbetov, A.A. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1977, *20*, 1468-71.
VARIABLES:	PREPARED BY:
Temperature: 298 K	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of CdK in Hg at 298 K is 5.4 mol^2 dm^{-6}. Input concentrations of Cd and K were changed in the ranges 4.0-7.31 and 0.81-1.72 mol dm^{-3}, respectively. The equilibrium concentrations of the metals were presented in a small plot in the paper. It was assumed that Hg activity is constant in the experiments, which doesn't seem justifiable. The heat of formation of CdK in its saturated amalgam is -42±8 kJ mol^{-1}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The Cd amalgam was obtained by dissolution of Cd in Hg and the K amalgam by electrolysis. The homogeneous Cd and K amalgams were mixed in various proportions. Then they were diluted with Hg and the heat (Q) was measured. A bend on the dependence of Q vs. concentrations of Cd and K corresponds to the equilibrium concentrations of the metals. Then one could establish the stoichiometry of the intermetallic compound being formed and its solubility product. The experiments were performed in an Ar atmosphere.	Nothing specified. ESTIMATED ERROR: Solubility: nothing specified but no better than ± 10 % (by compilers). Temperature: nothing specified.

COMPONENTS:	EVALUATOR:
(1) Cadmium-lithium 2:3; Cd_2Li_3; [56320-82-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland January 1983

CRITICAL EVALUATION:

Based on voltammetric experiments with mercury film electrodes (on Ag or Au base) Kaplin and coworkers (1-4) found the formation of crystalline Cd_2Li_3 in Hg. Temperature of the measurements was not specified and the solubility product, $K_s = [Cd]^2[Li]^3$, determined was reported as 1.0×10^{-5} mol^5 dm^{-15} (1-3) and 1.5×10^{-7} $mol^{5/3}$ cm^{-5} (4). The unit of the second value has no physical sense, but, after recalculation to a consistent unit, the value is 3.4×10^{-6} mol^5 dm^{-15}. It seems that interaction of Li and Cd with the Ag support is negligible in the experiments (1-3), although it is difficult to exclude completely (see the AgCd-Hg system). However, use of the mercury film electrode with Au support, as in (4), may cause significant error due to the Au-Cd interactions in Hg (see the solubility of AuCd or Au_3Cd in Hg). No experimental details of (4) are known to the evaluators. Filippova and coworkers (5) did not find any evidence of Cd-Li compound formation in the complex amalgams by calorimetric titration of concentrated amalgams with Hg when Cd and Li contents were up to 6.8 and 0.8 mol dm^{-3}, respectively. In the light of the latter work the results of previous studies are doubtful. Solid phase Cd_2Li_3 is not known in the binary Cd-Li system (6).

Value of the solubility of Cd_2Li_3 in Hg (doubtful)

The solubility product of Cd_2Li_3 in Hg at 293 K is, as in (1-3),

$$1 \times 10^{-5} \ mol^5 \ dm^{-15}$$

and the solubility, as calculated by evaluators from K_s:

$$4 \times 10^{-2} \ mol \ dm^{-3}$$

References

1. Kaplin, A.A.; Dzhabarova, N.K.; Stromberg, A.G. *Izv. Tomsk. Politekhn. Inst.* 1976, *258*, 52.
2. Dzhabarova, N.K.; Kaplin, A.A.; Stromberg, A.G. *Izv. Tomsk. Politekhn. Inst.* 1976, *302*, 40.
3. Dzhabarova, N.K.; Kaplin, A.A.; Anisimova, L.S. *Usp. Polarogr. s Nakopl., Tomsk*, 1973, 39.
4. Kaplin, A.A.; Dzhabarova, N.K. *Sbor. Tr. Molod. Uchen. Tomsk. Politekhn. Inst.* 1973, no. 1, 60.; cited according to *Ref. Zh. Khim.* 1973, *19 B*, 1174.
5. Filippova, L.M.; Zebreva, A.I.; Zhumakanov, V.Z. *Ukr. Khim. Zh.* 1981, *47*, 473.
6. Van der Marel, C.; Vinke, G.J.B.; Hennephof, J.; Van der Lugt, W. *J. Phys. Chem. Solids* 1982, *43*, 1013.

COMPONENTS:

(1) Cadmium-lithium 2:3; Cd_2Li_3; [56320-82-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Dzhabarova, N.K.; Kaplin, A.A.; Stromberg, A.G.

Izv. Tomsk. Politekhn. Inst. 1976, *302*, 40-2.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of Cd_2Li_3 in Hg at room temperature:

$10^5K_s/mol^5\ dm^{-15}$	Conditions of the experiments:
1.2	$c_{Li(I)} = 8x10^{-4}$ mol dm^{-3}; $1.2x10^{-4} \le c_{Cd(II)} \le 1.2x10^{-3}$ mol dm^{-3}; time of accumulation 3 min; anodic stripping voltammetry of Cd and Li.
1.4	
0.9	
0.2	$c_{Li(I)} = 1x10^{-4}$ mol dm^{-3}; $c_{Cd(II)} = 2.5x10^{-4}$ mol dm^{-3}; time of accumulation changed in the range 3-18 min; anodic stripping voltammetry of Cd and Li.
0.5	
0.1	
1.0±0.5	mean value by the authors
0.7±0.5	mean value and standard deviation by the compilers

The same result is also reported in (1, 2).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Li(I) and Cd(II) were reduced on a mercury film electrode with an Ag base. The solution contained $LiClO_4$, CdI_2 and $2x10^{-2}$ mol dm^{-3} $(C_2H_5)_4NI$ in DMF as supporting electrolyte. The solution was deaerated with Ar. Electrolytic accumulation of the both metals in the film was carried out at -2.2 V vs. potential of mercury pool electrode (the anode). The voltammetric peaks of anodic dissolution of the components were recorded from a linear scan in the positive direction. Analysis of the curves yields the stoichiometry of Cd_2Li_3 and the solubility product of this compound.

SOURCE AND PURITY OF MATERIALS:

$LiClO_4$ chemically pure, CdI_2 analytical grade, doubly distilled DMF and doubly recrystallized $(C_2H_5)_4NI$ were used.

ESTIMATED ERROR:

Solubility product: precision ± 50 %; standard deviation ± 70 % (calculated by compilers). mperature: nothing specified.

REFERENCES:

1. Kaplin, A.A.; Dzhabarova, N.K.; Stromberg, A.G. *Izv. Tomsk. Politekhn. Inst.* 1976, *258*, 52.
2. Dzhabarova, N.K.; Kaplin, A.A.; Anisimova, L.S. *Usp. Polarogr. s Nakopl., Tomsk*, 1973, 39.

COMPONENTS:

(1) Cadmium-manganese 3:1; Cd_3Mn; [12050-4209]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

August 1984

CRITICAL EVALUATION:

According to Russell and coworkers (2) the formation of an intermetallic compound in the Cd-Mn system in Hg is doubtful. Lihl and Kirnbauer (7) reported that the majority of Cd introduced into the complex amalgam was found in a solid phase of undefined composition. Shirinskikh and coworkers (3, 5, 6) found no interaction between Cd and Mn in Hg based on potentiometric measurements, roentgenography and chemical analysis. In the solid phase of the heterogeneous amalgams a mixture of Mn_2Hg_5 and $CdHg_3$ was identified. The Cd and Mn contents in the liquid phase (8.4 at. % and 1.1×10^{-2} at. %, respectively) are similar to the solubilities of these elements in Hg (see Cd-Hg and Mn-Hg systems). However, previously Zebreva and Kozlovskii (1) reported a solubility product of Cd_3Mn in Hg, $K_s = [Cd]^3[Mn]$, equal to $(5.7 \pm 0.5) \times 10^{-11}$ mol^4 dm^{-12} at 293 K; the value was determined by amalgam polarography, but no other details are given. More recently Kaplin and Mamontova (4), using stripping voltammetry, determined the solubility product of 8.3×10^{-10} mol^4 dm^{-12} at room temperature. The solubilities of Cd_3Mn in Hg reported in (1) and (4) do not differ much and they are correctly lower than the solubility of Mn in Hg (see the Mn-Hg system). It is difficult to give a preference to either (1) or (4). The equilibrium in the amalgam polarography technique surely is reached before the oxidation; on the other hand corrosion may be more pronounced under such conditions. The compound Cd_3Mn is known to be formed in the binary Cd-Mn system (8).

Value of the solubility of Cd_3Mn in Hg (doubtful)

The solubility product of Cd_3Mn in Hg at 293 K is, according to (4)

$$8 \times 10^{-10} \text{ mol}^4 \text{ dm}^{-12}$$

and the solubility is, as calculated from K_s by compilers:

$$2 \times 10^{-3} \text{ mol dm}^{-3}$$

References

1. Zebreva, A.I.; Kozlovskii, M.T. *Zavod. Lab.* 1964, *10*, 1193.
2. Russell, A.S.; Kennedy, T.R. Lawrence, R.P. *J. Chem. Soc.* 1934, 1750.
3. Shirinskikh, A.V.; Lange, A.A. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1976, *42*, 16.
4. Kaplin, A.A.; Mamontova, I.P. *Zh. Anal. Khim.* 1978, *33*, 703.
5. Shirinskikh, A.V.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1983, no. 5, 17.
6. Shirinskikh, A.V.; Grigoreva, M.I.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1983, no. 5, 20.
7. Lihl, F.; Kirnbauer, H. *Z. Metallk.* 1957, *48*, 9.
8. Vol, A.E.; Kagan, I.K. *Stroenie i Svoistva Dvoinykh Metallicheskikh Sistem*, vol. IV, Fizmatgiz, Moskva, 1979.

COMPONENTS:

(1) Cadmium-manganese 3:1; Cd_3Mn; [12050-42-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kaplin, A.A.; Mamontova, I.P.

Zh. Anal. Khim. 1978, *33*, 703-9.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubility product of Cd_3Mn in Hg at room temperature is:

$$8.3\times10^{-10}\ \mathrm{mol^4\ dm^{-12}}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixed amalgams were prepared by 3 min electroreduction of Cd(II) and Mn(II) in 1 mol dm^{-3} NaCl at -1.9 V (vs. SCE) on a thin film or a hanging drop mercury electrode on a Pt support. Then voltammetric oxidation of the amalgams was performed. The solubility product was calculated from the heights of the anodic current peaks. The experiments were performed in a N_2 or Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Super pure or chemically pure reagents were used. Water contained no more than 10^{-9}-10^{-10} mol dm^{-3} of other heavy metals.

ESTIMATED ERROR:

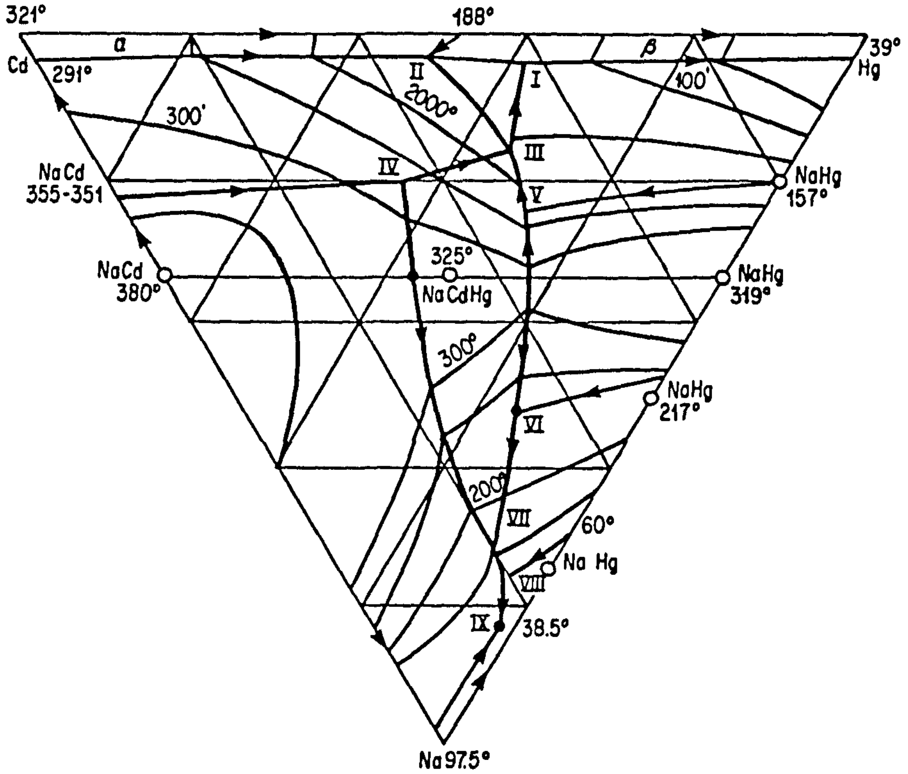
Nothing specified.

Precision of K_s determination should be no better than ± 20 % (compilers).

COMPONENTS:	EVALUATOR:
(1) Cadmium-sodium-mercury 1:1:1; CdNaHg; [98246-93-6] Cadmium-sodium 4:1; Cd_4Na; [98246-94-7] Cadmium-sodium 2:1; Cd_2Na; [12014-25-4] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland March 1981

CRITICAL EVALUATION:

Jänecke (1, 2) found, after detailed investigations, that one ternary CdNaHg compound is formed in the Cd-Na-Hg system. The melting temperature of the compound is 598 K. As one may see from the phase diagram (2) other compounds, Cd_4Na and Cd_2Na, may be formed in this system at high concentrations of these metals in Hg. This is in reasonable agreement with experiments of (3, 4), who observed no precipitation of a solid Cd-Na phase at room temperature when concentrations of Cd and Na were as high as 6.45 and 2.95 mol dm^{-3}, respectively (4).



Value of melting temperature of CdNaHg (tentative)

The melting point of CdNaHg is 598 K.

References

1. Jänecke, E. *Z. Phys. Chem.* 1907, *57*, 507.
2. Jänecke, E. *Z. Metallk.* 1928, *20*, 113.
3. Shvedov, V.P.; Semenyuk, E.Ya *Zh. Prikl. Khim.* 1971, *44*, 80, 282.
4. Filippova, L.M.; Zebreva, A.I.; Espenbetov, A.A. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1977, *20*, 1468.

COMPONENTS:

(1) Cadmium-sodium-mercury 1:1:1; CdNaHg; [98246-93-6]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Jänecke, E.

Z. Metallk. 1928, *20*, 113-7.

VARIABLES:

Composition of the amalgam

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The melting temperature of CdNaHg is 325 °C. Solubilities of Cd_4Na and Cd_2Na in Hg may be estimated roughly after reading the phase diagram given in the Critical Evaluation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Cd-Na alloys were prepared from the parent metals. They were melted under paraffin and then a suitable amount of Hg was added. The liquid alloys were slowly cooled down and temperatures were recorded with the use of a thermometer. The apparatus was made of porcelain.

SOURCE AND PURITY OF MATERIALS:

Pure metals were used.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:	EVALUATOR:
(1) Cadmium-antimony 1:1; CdSb; [12050-27-0] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland March 1982

CRITICAL EVALUATION:

On the basis of potentiometric and anodic oxidation experiments performed by Zebreva (1) the formation of CdSb in Hg was suggested and its solubility reported. However, Stromberg and coworkers (4), with the use of stripping voltammetry, did not find any evidence of an interaction between these metals in Hg, even when total concentrations of Cd and Sb were 1.6×10^{-3} and 7.0×10^{-4} mol dm^{-3}, respectively. The same method was later used by Zakharchuk and coworkers (3). They determined the solubility product of CdSb in Hg, $K_s = [Cd][Sb]$, more precisely than it was done by Zebreva (1). Matakova and Zholdybaeva (6) found that CdSb is more soluble than a Cu-Sb compound in Hg; however the selected values of the solubilities of both compounds (see also the Cu_2Sb-Hg system) are almost equal.

A stable CdSb phase is formed in the binary Cd-Sb system (2).

By potentiometric titration of Cd amalgams with $Sb_2(SO_4)_3$-solution at 293-323 K, some thermodynamic parameters of CdSb-formation in Hg were established by Matakova and coworkers (5); this is an additional proof of CdSb-formation in Hg.

Value of the solubility of CdSb in Hg (tentative)

The solubility product of CdSb in Hg at 293 K is 2×10^{-8} mol^2 dm^{-6}, according to (3), and the solubility is 1.4×10^{-4} mol dm^{-3}, as calculated by evaluators from K_s.

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COMPONENTS: (1) Cadmium-antimony 1:1; CdSb; [12050-27-0] (2) Mercury; Hg; [7439-97-6]	ORIGINAL MEASUREMENTS: Zebreva, A.I. *Zh. Fiz. Khim.* 1962, *36*, 1822-5.
VARIABLES: Temperature: 291 K	PREPARED BY: C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of CdSb in Hg at 18 °C is on the order of 10^{-4} mol dm^{-3}. Precision of the solubility determination is not high, since the solubility of CdSb in Hg is only a little lower than the solubility of Sb itself; see the Sb-Hg system. Compilers calculated the solubility product of CdSb equal to 2×10^{-8} mol^2 dm^{-6}. The typical procedure in the calculations was used.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Potential differences of Cd and Cd-Sb amalgams in a solution of Cd(II) in dil H_2SO_4 were measured. From these differences the solubility of CdSb was estimated by the compilers. Also anodic oxidation of the complex Cd-Sb amalgams with constant current in 0.5 mol dm^{-3} H_2SO_4 solution was carried out allowing extraction of the free Cd from the amalgam. Then the solution was exchanged for 1 mol dm^{-3} NaOH + 0.07 mol dm^{-3} $KNaC_4H_4O_6$, allowing complete extraction of free Sb by further electrooxidation. The amalgam, after the electrolysis, was decomposed with HCl(1:1) and all three solutions were analyzed separately for metal contents: Cd by polarography and Sb by amperometric titration with bromine. These results were used by the authors for the estimation of the solubility of CdSb in Hg.

SOURCE AND PURITY OF

Nothing specified

ESTIMATED ERR

Nothing spec

Experimental

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cadmium-antimony 1:1; CdSb; [12050-27-0] (2) Mercury; Hg; [7439-97-6]	Zakharchuk, N.F.; Zebreva, A.I.; Kozlovskii, M.T. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* <u>1971</u>, *32*, 28-30.
VARIABLES:	PREPARED BY:
Temperature: 193 K	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

CdSb is treated as a sparingly soluble compound in Hg. Its solubility product (K_s) at 20 °C is:

$10^4c_{Sb}{}^{i}$/ mol dm^{-3}	$10^4c_{Cd}{}^{i}$/ mol dm^{-3}	$10^4c_{Sb}{}^{f}$ mol dm^{-3}	$10^4c_{Cd}{}^{f}$/ mol dm^{-3}	10 K_s/ mol^2 dm^{-6}x10^8
1.04	5.58	0.52	4.05	2.1
1.48	3.43	0.96	2.35	2.2
1.22	3.10	0.84	2.75	2.3
1.56	1.94	1.06	1.51	1.6
2.01	2.98	1.03	1.86	1.9
2.14	2.56	1.32	1.57	2.1
2.20	2.56	1.41	1.64	2.2
2.38	3.24	1.25	1.89	2.4
2.26	3.49	1.00	2.26	2.3
	4.39	1.08	2.26	2.5
			mean value	(2.1±0.3)

Sb in Hg equals (1.5±0.3)x10^{-4} mol dm^{-3}.

AUXILIARY INFORMATION

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SOURCE AND PURITY OF MATERIALS:

All reagents were chemically pure. Twice distilled H_2O, deionized on an ion exchanger, with content of heavy metals below 10^{-7} % was used.

COMPONENTS:	EVALUATOR:
(1) Cadmium-tellurium 1:1; CdTe; [1306-2508] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland August 1986

CRITICAL EVALUATION:

There has been much interest recently in the Cd-Hg-Te system. However, only a few papers are devoted directly to solubility measurements of CdTe in Hg. With the use of different techniques the solubility determinations were performed in various temperature ranges: 623-873 K by Vanyukov and coworkers (1, 13, 30), 527-716 K by Herning (24) and 523-664 K by Wong (2). Results of these works are presented in graphical forms, but the major part of them (1, 2, 24) is quite well concordant. The temperature dependence of the solubility may be represented by a linear equation obtained with a least square fit by evaluators (29):

$$pS = -3.68 + 3070\ T^{-1} \qquad r=0.997 \qquad (S/\text{mol}\ \%\ ;\ T/K)$$

The equation seems to be valid between 1000 K and room temperature. The results from papers (30) and (13) are too low (2 times) and too high (2 times), respectively; the authors did not discuss the discrepancies of the measurements performed in the same laboratory. The single numerical value of the solubility of 2.5 mol % at 648 K (28) is reproducibly too high, most probably due to supercooling of the amalgam sample. Kinetics of CdTe dissolution in Hg was investigated in (26).

The solubility of CdTe in Te amalgams (24), as well as the solubilities of various $Cd_xHg_{1-x}Te$ alloys in Hg (1, 13, 24, 28, 30), was investigated also. The data from (1, 13, 28, 30), analyzed as a product of Cd and Te concentrations, show significant spread from the straight line given by the equation; probably the amalgams were not equilibrated properly. Mathematical analysis of the results from (24) by the evaluators (29) points out that the solubility product, $K_s = [Cd][Te]$, is constant at a given temperature. It is very interesting that a similar conclusion may be extracted from the thermal analysis experiments of significantly concentrated amalgams by Szofran and Lehoczky (23), as well as by Meschter and coworkers (25) at high temperature, 1079-1256 K. The Te and Cd+Te contents in the liquid should be not higher than 35 and 50 mol %, respectively. The activity coefficients of the components (Cd, Hg and Te) should be used to test quantitatively the validity of such a rule; unfortunately these coefficients are unknown in the ternary melt.

Several works (3-10, 21, 32, 33) are devoted to the liquidus line of the pseudobinary system Cd-Te. The melting point of the alloys is strongly dependent on pressure (6-8) which partly may explain significant discrepancies between the results of various laboratories. Individual parts and the whole Cd-Hg-Te system have been investigated experimentally by many (1, 9, 11-16, 23-25, 27, 28, 30). The phase diagram was also a subject of fitting calculations using models of the ideal solution (22), the regular associated solution (16-19) and the pair approximation (20). The Cd-Hg-Te phase diagram is taken from (24).

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Cadmium-tellurium 1:1; CdTe; [1306-2508] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland August 1986

CRITICAL EVALUATION (continued)

Sangha and coworkers (31) found that the CdTe solubility in Hg at 518 K is 4.6×10^{-3} mol %; this result is slightly lower than the value calculated from the fitting equation. Brice (34) presented a set of numerical relations describing the Cd-Hg-Te phase diagram in the form of equations and tabulated data.

Values of the solubility of CdTe in Hg

T/K	Soly/mol %	Source	Refer.
500	3.5×10^{-3} [b]	extrapol.	(2, 24) and equation
600	3.5×10^{-2} [a]	interpol.	(2, 24)
700	0.19 [a]	interpol.	(1, 2, 24)
800	0.7 [b]	interpol.	(1)
900	1.9 [b]	extrapol.	(1) and equation

[a] recommended.

[b] tentative.

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14. Harman, T.C. *J. Electron. Mater.* 1980, *9*, 945.
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(continued next page)

COMPONENTS:	EVALUATOR:
(1) Cadmium-tellurium 1:1; CdTe; [1306-2508] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland August 1986

CRITICAL EVALUATION (continued)

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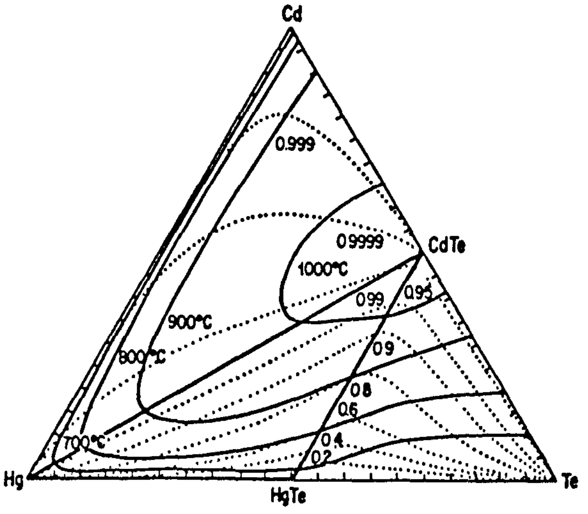

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cadmium-tellurium 1:1; CdTe; [1306-25-8] (2) Mercury; Hg; [7439-97-6]	Vanyukov, A.V.; Pedos, S.I.; Yukhtanov, E.D.; Indenbaum, G.V.; Figelson, Yu.A. *Polumetally i Poluprovodniki s Uzkimi Zapreshchennymi Zonami*, Lvovskii Universytet, Lvov, 1973, 10-15.
VARIABLES:	PREPARED BY:
Temperature: 873 K	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of CdTe in Hg at 600 °C is 0.73 mol %, as read from a graph by compilers. Compared to the subsequent works this value is too low. Solubilities of various $Cd_xHg_{1-x}Te$ alloys in Hg at 400 to 600 °C are also reported. They were determined by the following methods: filtration with chemical analysis, differential thermal analysis and optical observation of crystallization.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Preparation of samples was performed in a pure Ar atmosphere. Plates of CdTe were kept in a closed quartz ampule filled with Hg for 10-12 hours at 873 K. The solution was filtered through a quartz frit and the filtrate was cooled by immersion of the ampule in water. The solidified filtrate was analyzed for Cd and Te content by an unknown method. A correction for Hg condensed dur-ing the experiment was made from the free volume of the ampule, but due to the low solubility value this correction seems to be insignificant.	Nothing specified. The substances used were probably of semiconductor class purity (compilers). ESTIMATED ERROR: Solubility: chemical analysis ± 1 %; Total error of determination ± 5 %; Procedure of reading graph ± 10 %. Temperature: nothing specified.

COMPONENTS:

(1) Cadmium-tellurium 1:1; CdTe; [1306-25-8]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Vanyukov, A.V.; Krotov, I.I.; Ermakov, A.I.

Izv. Akad. Nauk SSSR, Neorg. Mater. 1977, *13*, 815-9.

VARIABLES:

Temperature: 623 - 853 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubilities of CdTe in Hg, as read from the Figures, are:

$t/°C$	T/K [c]	$10^2 w_{CdTe}$/mass fract.	$10^2 x_{CdTe}$/mol fract.
350 [a]	623	0.09	0.075 [c]
395 [a]	668	0.18	0.15 [c]
404 [b]	677	--	0.20
435 [b]	708	--	0.26
450 [a]	723	0.37	0.31 [c]
450 [b]	723	0.42	0.35 [c]
454 [b]	727	--	0.36
495 [a]	768	0.60	0.50 [c]
580 [a]	853	1.34	1.12 [c]

[a] values determined by chemical analysis.

[b] values determined by dew-point method.

[c] values calculated by compilers.

Solubilities of various Cd-Hg-Te alloys in Hg were also determined.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

a) The determinations were performed in a quartz ampule divided partly with a thin wall into two containers. CdTe crystals and liquid Hg were placed in corresponding places, the tube was evacuated and closed. It was heated and kept at a chosen temperature. The crystals were immersed in Hg by turning the ampule. The liquid phase saturated with CdTe crystals was chemically analyzed. The solubility of CdTe in Hg was also calculated from difference of the mass of the crystals before and after the dissolution experiments. b) Samples of CdTe and Hg were placed in an evacuated quartz apparatus. Temperature of the part of the apparatus where the sample is placed was elevated and kept constant while a second part of the apparatus was cooled down allowing observation of the dew-point of Hg. Then the vapor pressure of Hg was measured. The measurements were performed for various compositions of the amalgam. A bend on a plot relating the pressure to composition corresponds to the concentration of the saturated amalgam.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility: precision of weighing was 10^{-4} g for a 20 g sample, but the reading procedure is at the best ± 5 % precise.

Temperature was controlled with ± 1.5 K.

COMPONENTS:

(1) Cadmium-tellurium 1:1; CdTe;
[1306-25-8]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Vanyukov, A.V.; Krotov, I.I.;
Ermakov, A.I.

Izv. Akad. Nauk SSSR, Neorg. Mater. 1978, *14*, 657-61.

VARIABLES:

Temperature: 727 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of CdTe in Hg at 454 °C, as read from the figure in the paper, is 0.8 mass %. The corresponding solubility is 0.6 mol %, as calculated by compilers. This result is too high.

Compositions of liquid amalgam phases in equilibrium with solid $Cd_xHg_{1-x}Te$ alloys (with $x = 0.2; 0.4; 0.6; 0.8$) were also determined.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method used was described in (1). Samples of CdTe and proper amounts of Hg were placed in an evacuated quartz apparatus. The temperature of the part where the sample is placed was elevated and kept constant while a second part of the apparatus was cooled down. The dew-point of Hg was then observed and the vapor pressure measured. The measurements were performed for various compositions of the amalgam. A bend on a plot relating the pressure on the composition corresponds to the concentration of the saturated amalgam.

SOURCE AND PURITY OF MATERIALS:

Nothing specified. The materials are probably of semiconductors class purity (compilers).

ESTIMATED ERROR:

Solubility: precision unspecified, after reading ± 10 %. Temperature: precision and accuracy ± 0.5 K.

REFERENCES:

1. Vanyukov, A.V.; Krotov, I.I.; Ermakov, A.I. *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1977, *13*, 815.

COMPONENTS:

(1) Cadmium-tellurium 1:1; CdTe;
[1306-25-8]
(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Bowers, J.E.; Schmit, J.L.;
Speerschneider, C.J.; Maciolek, R.B.
IEEE Trans. Electron Devices 1980, *Ed-27*,
24-8.

VARIABLES:

Temperature: 748 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of CdTe in Hg at 475 °C and 5 atm is 0.025 mol fraction, which is too low by a factor of 7. Several points on the liquidus of the Cd-Hg-Te system were also determined. Liquid-phase epitaxial growth of $Cd_{0.4}Hg_{0.6}Te$ from Te-, Hg- and HgTe-rich solutions was investigated.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The experiments were performed in a sealed evacuated quartz apparatus. The homogeneous solution of CdTe in Hg was cooled in steps and checked each time for nucleation of a solid phase. Once this appeared, the alloy was quenched and the composition of the solid was determined by electron-beam microprobe analysis.

SOURCE AND PURITY OF MATERIALS:

Nothing specified, but it should be better than for production of semiconductors (compilers).

ESTIMATED ERROR:

Solubility: precision ± 1 % in preparation of the sample. Temperature: accuracy ± 25 K due to probable supercooling (authors); uncertainty even more (compilers).

COMPONENTS: (1) Cadmium-tellurium 1:1; CdTe; [1306-25-8] (2) Mercury; Hg; [7439-97-6]	ORIGINAL MEASUREMENTS: Wong, J.Y. *Rep. Santa Barbara Res. Center*, Santa Barbara, California, 1980.
VARIABLES: Temperature: 523-664 K	PREPARED BY: C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubilities of CdTe in Hg, as read from a figure in (1), are:

T/K	Solubility/mol %
523	0.0083
570	0.0166
607	0.040
625	0.055
631	0.063
635	0.071
639	0.071
643	0.084
655	0.088
653	0.095
664	0.10
664	0.11

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

No details are known to compilers since the values determined were extracted from the work of Su and coworkers (1), who possess the original report not available to compilers.

SOURCE AND PURITY OF MATERIALS:

99.9999 % pure Hg and CdTe of high purity were used.

ESTIMATED ERROR:

Nothing specified, but it is no better than ± 10 % for solubility (by compilers).

REFERENCES:

1. Su, C.-H.; Liao, P.-K.; Tung, T.; Brebrick, R.F. *J. Electron. Mater.* 1982, *11*, 931.

COMPONENTS:

(1) Cadmium-tellurium 1:1; CdTe; [1306-25-8]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Herning, P.E.

J. Electron. Mater. 1984, *13*, 1-14.

VARIABLES:

Temperature: 527-716 K

Excess of unbonded Te.

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of CdTe in Hg and Te amalgams were read from figures:

t/°C	excess of Te/ at.%	solubility of CdTe/mol %	K_s^{CdTe}/(mol %)^2 [a]
254	-	8x10^{-3}	6.4x10^{-5}
297	-	1.5x10^{-2}	2.2x10^{-4}
337	-	4.0x10^{-2}	1.6x10^{-3}
360	-	6.0x10^{-2}	3.6x10^{-3}
369	-	7.1x10^{-2}	5.0x10^{-3}
383	-	8.8x10^{-2}	7.7x10^{-3}
392	-	0.104	1.1x10^{-2}
340	0.01	4.5x10^{-2}	2.5x10^{-3}
360	0.01	6.5x10^{-2}	4.9x10^{-3}
380	0.01	8.5x10^{-2}	8.1x10^{-3}
400	0.01	1.2x10^{-1}	1.6x10^{-2}
322	0.03	2.0x10^{-2}	1.0x10^{-3}
343	0.03	3.5x10^{-2}	2.3x10^{-3}
360	0.03	5.2x10^{-2}	4.3x10^{-3}

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The experiments were performed in a vertical liquid phase epitaxial growth apparatus. The apparatus was partly filled with Hg and the temperature was increased to about 730 K. A carefully weighed piece of bulk CdTe was lowered into the melt on a graphite paddle assembly. The assembly was rotated and the melt stirred for approximately 4 hrs at the desird temperature, which was measured with a thermocouple. After saturating the Hg in this manner, the CdTe piece was again weighed and the difference recorded, allowing calculation of the solubility.

SOURCE AND PURITY OF MATERIALS:

99.99999 % pure Hg was used.

ESTIMATED ERROR:

Solubility: precision of reading graph ± 5 % (by compilers). Temperature: stability ± 0.02 K, accuracy ± 5 K.

COMPONENTS: (1) Cadmium-tellurium 1:1; CdTe; [1306-25-8] (2) Mercury; Hg; [7439-97-6]	ORIGINAL MEASUREMENTS: Herning, P.E. *J. Electron. Mater.* 1984, *13*, 1-14.

EXPERIMENTAL VALUES (continued)

t/°C	excess of Te/ at.%	solubility of CdTe/mol %	K_s^{CdTe}/(mol %)^2 [a]
383	0.03	8.0×10^{-2}	8.8×10^{-3}
400	0.03	1.1×10^{-1}	1.5×10^{-3}
322	0.1	9.5×10^{-3}	1.0×10^{-3}
343	0.1	1.7×10^{-2}	2.0×10^{-3}
360	0.1	3.1×10^{-2}	4.0×10^{-3}
385	0.1	5.8×10^{-2}	9.3×10^{-3}
403	0.1	9.0×10^{-2}	1.7×10^{-2}
322	0.3	2.7×10^{-3}	8.1×10^{-4}
346	0.3	8.5×10^{-3}	2.6×10^{-3}
366	0.3	1.5×10^{-2}	4.6×10^{-3}
383	0.3	4.0×10^{-2}	1.4×10^{-2}
298	1.0	9.0×10^{-4}	9.0×10^{-4}
322	1.0	1.1×10^{-3}	1.1×10^{-3}
343	1.0	2.0×10^{-3}	2.0×10^{-3}
360	1.0	4.2×10^{-3}	4.2×10^{-3}
383	1.0	8.5×10^{-3}	8.6×10^{-3}
403	1.0	1.7×10^{-2}	1.7×10^{-2}
443	1.0	5.0×10^{-2}	5.2×10^{-2}
340	1.8	5.0×10^{-4} [b]	9.0×10^{-4} [b]
360	2.4	5.0×10^{-4} [b]	1.2×10^{-3} [b]
380	3.2	5.0×10^{-4} [b]	1.5×10^{-3} [b]
400	4.0	5.0×10^{-4} [b]	2.0×10^{-3} [b]

[a] The solubility product, $K_s^{CdTe} = [Cd][Te]$, is practically constant as tested by compilers.

[b] The results are low and should be rejected.

The solubilities of various Cd-Hg-Te alloys in Hg were also determined in the temperature range 358-515 °C.

COMPONENTS:

(1) Cadmium-tellurium 1:1; CdTe;
[1306-25-8]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Sangha, S.P.S.; Medland, J.D.; Berry, J.A.; Rinn, L.M.

J. Cryst. Growth 1987, *83*, 127-36.

VARIABLES:

Temperature: 518 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of CdTe in Hg at 245 °C is 0.533 g CdTe in 9.6 kg Hg. The equivalent value calculated by the compilers is 3.13×10^{-3} mol dm^{-3} CdTe, or 4.6×10^{-3} mol %.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

CdTe was received polished. It was further cleaned by a solvent, etched 1 min in 1 % Br_2 solution in CH_3OH and cleaned again. The CdTe sample was weighed and placed in a silica crucible filled with Hg. The crucible was mounted in a stainless steel pressure vessel. The system was operated under a H_2 atmosphere. After equilibration the CdTe sample was weighed again to find the amount of CdTe dissolved in Hg. The sample was examined under an optical microscope.

SOURCE AND PURITY OF MATERIALS:

Hg: 99.9999+ spectrographically pure from Cominco.

CdTe: unspecified purity from Nippon Mining or from Cominco.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:	EVALUATOR:
(1) Cerium-tin 1:2; $CeSn_2$; [93508-87-3] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland September 1981

CRITICAL EVALUATION:

The mercury-rich part of the Ce-Sn-Hg system was investigated by Tammann and Jander (1) by potentiometry. The formation of $CeSn_2$ in Hg with a stability constant, $K = [CeSn_2]/[Ce][Sn]^2$, equal to $(1.1 \pm 0.6) \times 10^{40}$ (mol fraction)$^{-2}$ at 289 K was suggested. This stability constant value is much too high to be determined by potentiometry. Probably the incorrect value is due to corrosion of Ce amalgam by aqueous solution. The compound $CeSn_2$ is one of the less stable formed in the Ce-Sn binary system (2).

Further work on this system is needed and no solubility or other value may be suggested.

References

1. Tammann, G.; Jander, W. *Z. Anorg. Chem.* 1922, *124*, 105.
2. Vogel, R. *Z. Anorg. Chem.* 1911, *72*, 319.

COMPONENTS:	EVALUATOR:
(1) Cobalt-gallium 1:1; CoGa; [12297-62-0] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland May 1985

CRITICAL EVALUATION:

The formation of an intermetallic compound of the formula $Ga_7Co_{10}Hg_x$ in the Co-Ga-Hg system was reported by Lysenko (1). However, Stepanova (2), using the method of stripping voltammetry, found the formation of slightly soluble CoGa in Hg. She determined the solubility product, K_s = [Co][Ga], value equal to 2.6×10^{-10} mol^2 dm^{-6}. The corresponding solubility of this compound is a few orders of magnitude higher than the solubility of Co in Hg (see the Co-Hg system), which makes the result of the solubility product doubtful. It seems that a pseudoequilibrium is attained. Keeling and coworkers (3) showed that Ga reacts with Co particles in Hg, and Ga does not remain in the liquid phase. A CoGa solid phase is formed in the Co-Ga binary system (4).

Value of the solubility of CoGa in Hg (doubtful)

The solubility product value of CoGa in Hg at room temperature is:

2×10^{-10} mol^2 dm^{-6} as reported in (2)

and the solubility, as calculated by evaluators from K_s:

1.5×10^{-5} mol dm^{-3}

References

1. Lysenko, V.I. *Sbor. Tr., Metall. Tsvet. Met. i Metody ikh Anal.* 1962, *7*, 303.
2. Stepanova, O.S. *Izv. Tomsk. Politekh. Inst.* 1966, *151*, 14.
3. Keeling, L.; Charles, S.W.; Popplewell, J. *J. Phys., F* 1984, *14*, 3093.
4. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Cobalt-gallium 1:1; CoGa; [12297-62-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Stepanova, O.S.

Izv. Tomsk. Politekh. Inst. 1966, *151*, 14-20.

VARIABLES:

Room Temperature experiment

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound CoGa is assumed to be sparingly soluble in Hg. The equilibrium is described by the solubility product equal to 2.6×10^{-10} mol^2 dm^{-6}, probably at room temperature. The concentration ratio of Co to Ga was changed in the range 0.1 to 1.05. The solubility of CoGa in Hg is over one hundred times higher than that of Co in Hg (see the Co-Hg system) which makes this value doubtful.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Stripping voltammetry experiments using the hanging mercury drop electrode were performed. Electrolytic codeposition of Co and Ga was carried out for 300 s at -1.4 V vs. SCE. A waiting time of 1 min between the concentration and stripping stages was applied. Acetate buffer (pH = 4.6) was used as a background electrolyte for Ga(III) solution, $(1.0\text{-}2.0) \times 10^{-4}$ mol dm^{-3}. The solubility product was calculated from the oxidation current peaks of the metals. The experiments were performed in a N_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

Solutions contained heavy metal ions at concentrations not higher than 10^{-8} mol dm^{-3}.

ESTIMATED ERROR:

Nothing specified. Error of the solubility product determination is not lower than ± 10 % (compilers).

COMPONENTS:	EVALUATOR:
(1) Cobalt-zinc 1:1; CoZn; [12259-06-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland October 1980

CRITICAL EVALUATION:

In the first study on the Co-Zn-Hg system by Babkin and Kozlovskii (1), it was found that CoZn is formed in Hg as a soluble compound. Its instability constant, $K=[Co][Zn]/[CoZn]$, was estimated to be $(1.28\pm0.6)\mathrm{x}10^{-2}$ and $(6.3\pm3.0)\mathrm{x}10^{-3}$ mol dm^{-3} at room temperature by amalgam polarography and potentiometry respectively. Later Ficker and Meites (2) using controlled potential coulometry suggested the formation of soluble $CoZnHg_x$ in equilibrium with dimers of Co and Zn. The value of the dissociation constant of such a compound, $K'=[Co_2][Zn_2]/[CoZnHg_x]^2$, was calculated to be 25±8 at 298 K. The same conclusions were later reported by Hovsepian and Shain (3), who used different electroanalytical techniques and conditions. Their dissociation constants determined at 298 K were equal: the first one expressed in the same way as that of Ficker and Meites 2.05±0.4 and the second one expressed following Babkin and Kozlovskii $(2.46\pm1.8)\mathrm{x}10^{-2}$ mol dm^{-3}. The agreement of these results with earlier ones is puzzling because the solubility of Co in Hg assumed is much lower, see the Co-Hg system, than that resulting from the cited works. Moreover, Rodgers and Meites (4) showed later that Zn amalgams do not contain measurable amounts of dimers of Zn atoms. It is well known that Co forms semistable amalgams where its content in liquid phase is a million times higher than its solubility. Reexamination of the Co-Zn-Hg system by Scott (5) strongly suggests that CoZn is only slightly soluble in Hg. More recently, Bloom and coworkers (6) confirmed formation of CoZn, which precipitates in Hg, when one increases the Zn concentration in the stripping analysis experiments of the system. No numerical results of solubility are reported in (5, 6). CoZn is formed in the Co-Zn binary alloys (7). Donten (8) found a weak interaction between Co and Zn in stripping voltammetry experiments using a Co electrode covered with Hg film.

Further work on this amalgam is needed and no compilation sheets are prepared.

References

1. Babkin, N.G.; Kozlovskii, M.T. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1958, *1*, 129.
2. Ficker, M.M.; Meites, L. *Anal. Chim. Acta* 1962, *26*, 172.
3. Hovsepian, B.K.; Shain, I. *J. Electroanal. Chem.* 1967, *14*, 1.
4. Rodgers, R.S.; Meites, L. *J. Electroanal. Chem.* 1974, *49*, 401.
5. Scott, F. *B. Sc. Thesis*, Polytechnic Inst. of Brooklyn, 1968; cited after Galus, Z. *Crit. Rev. Anal. Chem.* 1975, 359.
6. Bloom, H.; Noller, B.N.; Richardson, D.E. *Anal. Chim. Acta* 1979, *109*, 157.
7. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
8. Donten, M. *Ph.D. Thesis, University of Warsaw*, 1987.

COMPONENTS:

(1) Copper-gallium 1:1; CuGa; [12191-11-6]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

June 1986

CRITICAL EVALUATION:

Formation of Cu_2Ga in Hg was postulated by Lysenko (1). Such a compound is also formed in the binary Cu-Ga system and shows the highest stability (8). However, Zakharov and coworkers (2-4) reported the formation of poorly soluble CuGa in Hg. Solubility product, K_s=[Cu][Ga], values equal to 2×10^{-6} (2) and 2.9×10^{-7} mol^2 dm^{-6} (4), probably at room temperature, were determined from stripping voltammetry experiments. Using the same method Copeland and coworkers (5) as well as Neiman and coworkers (6) showed correctly that CuGa is less soluble in Hg than CuZn; see the CuZn-Hg system. Abdullah et al. (10) found in stripping voltammetry experiments that $CuGa_2$ formed in Hg is more stable than either NiZn or CuZn. This statement confirms the conclusions of (5, 6) in respect to CuZn (only the stoichiometry of Cu-Ga compounds were differently reported). However, the experimental value of the solubility of NiZn (see the NiZn-Hg system) is only one-fifth that of CuGa. No numerical solubility results are reported in (3, 5, 6).

Experiments of Kozin and coworkers (7), devoted to the distribution coefficient of Cu between Ga and Hg liquid phases, point also to formation of a Cu-Ga compound in Hg, though the authors seem to neglect this in their interpretation. Recently CuGa was discovered in thin films of the binary alloy (9). It is difficult to give a preference to results in (2) or (4), because they originate from the same laboratory and the authors did not discuss the difference. We would suggest the value of (4).

Value of the solubility of CuGa in Hg (tentative)

The solubility product of CuGa in Hg at 293 K is:

3×10^{-7} mol^2 dm^{-6}, as reported in (4)

and the solubility, as calculated by evaluators from K_s:

5.5×10^{-4} mol dm^{-3}

References

1. Lysenko, V.I. *Sbor. Tr., Metall. Tsvet. Met. i Met. ikh Anal.* 1962, *7*, 303.
2. Stepanova, O.S.; Zakharov, M.S.; Trushina, L.F.; Aparaina, V.I. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1964, *7*, 184.
3. Zakharov, M.S.; Stepanova, O.S.; Aparina, V.I. *Izv. Tomsk. Politekh. Inst.* 1965, *128*, 36.
4. Bizina, L.P.; Zakharov, M.S.; Pnev, V.V. *Tr. Tyumen. Ind. Inst., Khim. Khim. Tekhnol.*, Tomsk, 1972, 71.
5. Copeland, T.R.; Osteryoung, R.A.; Skogerbe, R.K. *Anal. Chem.* 1974, *46*, 2093.
6. Neiman, E.Ya.; Dolgopolova, G.M.; Figelson, Yu.A. *VII Vsesoyuznoe Soveshchanie po Polarografii*, Moskva, Nauka, 1978, 175.
7. Kozin, L.F.; Sarmuzina, R.G.; Popova, T.V. *Vestn. Akad. Nauk. Kaz. SSR* 1978, no. 3, 59.
8. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
9. Simic, V.; Marinkovic, Z. *J. Less-Common Met.* 1986, *116*, L7.
10. Abdullah, M.I.; Reusch Berg, B.; Klimek, R. *Anal. Chim. Acta* 1976, *84*, 307.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper-gallium 1:1; CuGa; [12191-11-6] (2) Mercury; Hg; [7439-97-6]	Stepanova, O.S.; Zakharov, M.S.; Trushina, L.F.; Aparina, V.I. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1964, 7, 184-8.
VARIABLES:	PREPARED BY:
Room temperature experiment	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound CuGa is treated as poorly soluble in Hg. Its solubility product is equal to 2×10^{-6} mol^2 dm^{-6}, probably at room temperature. Concentrations of Cu(II) and Ga(III) in the solutions were changed in the ranges 3×10^{-6}-1.6×10^{-4} and $(1.0\text{-}1.6)\times10^{-4}$ mol dm^{-3}, respectively. The concentration ratio of CuGa in the amalgam was changed in the range 0.03 to 1.00.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Anodic stripping voltammetry was used. The bulk solution contained 0.1 mol dm^{-3} KCl and 0.1 mol dm^{-3} sodium salicylate. The electrolytic accumulation lasted 5 minutes at -1.6 V vs. SCE. After 1 minute of waiting the stripping voltammograms were recorded and the solubility product was calculated from the oxidation current peaks. The experiments were carried out in a N_2 atmosphere.	Concentrations of other heavy metal ions in the solution was below 1×10^{-8} mol dm^{-3}.
	ESTIMATED ERROR:
	Nothing specified. Error of the determinations is not lower than ± 10% (by compilers).

COMPONENTS:

(1) Copper-gallium 1:1; CuGa; [12191-11-6]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Bizina, L.P.; Zakharov, M.S.; Pnev, V.V.
Tr. Tyumen. Ind. Inst., Khim. Khim. Tekhnol., Tomsk, <u>1972</u>, 71-3.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubility product, K_s, of CuGa in Hg at room temperature is 2.9x10^{-7} mol^2 dm^{-6}. Concentrations of Cu(II) and Ga(III) in the solution were (1-2)x10^{-4} and 1x10^{-4} mol dm^{-3}, respectively.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Experiments were performed using anodic stripping voltammetry. The bulk solutions contained Cu(II) and Ga(III) in acetate buffer, pH = 4.6. The accumulation electrolysis lasted from 2 to 20 min. Concentrations of the metals introduced into Hg were determined by coulometry. The solubility product was calculated from the anodic peaks of oxidation of both metals from the amalgam.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

Error of the method applied is no less than ± 10 % of K_s (by compilers).

COMPONENTS:	EVALUATOR:
(1) Copper-germanium 3:1; Cu_3Ge; [12158-95-1] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland June 1980

CRITICAL EVALUATION:

Nigmetova and Kozlovskii (1) detected formation of Cu_3Ge in the Cu-Ge-Hg system by amalgam polarography. Stepanova and coworkers (2) found that Cu_3Ge is poorly soluble in Hg and they estimated the solubility product, $K_s = [Cu]^3[Ge]$. However, the solubility of this compound is higher than the solubility of Ge in Hg (see the Ge-Hg system) which makes the K_s value doubtful. Since Ge easily oversaturates its amalgams, pseudoequilibrium in the system is possible. Moreover, in a subsequent work from the same laboratory (5), the formula of the compound formed in Hg was established as CuGe. Neiman and coworkers (3) showed from stripping voltammetry experiments that the Cu-Ge intermetallic is less soluble in Hg than CuZn (see the CuZn-Hg system). This is in agreement with the result reported in paper (2). No numerical data are in (1, 3, 5). A stable phase of Cu_3Ge is formed in the binary Cu-Ge system, whereas existence of CuGe is rather questionable (4).

Value of the solubility of Cu_3Ge in Hg (doubtful)

The solubility product of Cu_3Ge in Hg at 293 K is:

8×10^{-13} mol^4 dm^{-12}, according to work (2)

and the solubility, as calculated by evaluators from K_s:

4×10^{-4} mol dm^{-3}

References

1. Nigmetova, R.M.; Kozlovskii, M.T. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1960, *6*, 144.
2. Stepanova, O.S., Zakharov, M.S., Trushina, L.F.; Aparina, V.I. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1964, *7*, 184.
3. Neiman, E.Ya, Dolgopolova, G.M., Figelson, Yu.A. *VII Vsesoyuznoe Soveshchanie po Polarografii*, Nauka, Moskva, 1978, p. 175.
4. Hultgren, R.; Desai, P.D.; Hawkins, D.T.; Gleiser, M.; Kelley, K.K. *Selected Values of Thermodynamic Properties of Binary Alloys*, ASM, Ohio, 1973.
5. Bizina, L.P.; Zakharov, M.S.; Pnev, V.V. *Tr. Tyumen. Ind. Inst., Khim. Khim. Tekhnol.*, Tomsk, 1972, 71.

COMPONENTS:

(1) Copper-germanium 3:1; Cu_3Ge; [12158-95-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Stepanova, O.S.; Zakharov, M.S.; Trushina, L.F.; Aparina, V.I.

Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 1964, *7*, 184-8.

VARIABLES:

Room temperature experiment

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound Cu_3Ge is treated as insoluble in Hg. It solubility product is, at room temperature,

$$8.4\times10^{-13}\ \mathrm{mol^4\ dm^{-12}}$$

Concentrations of Cu(II) and Ge(IV) in the solution were changed in the ranges: 5.0×10^{-5}-6.4×10^{-4} and 1.0-2.0×10^{-4} mol dm^{-3}, respectively. Concentration ratio of Cu:Ge was changed in the range 0.4-3.2. The solubility of Cu_3Ge in Hg is higher than the solubility of Ge in Hg itself.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Anodic stripping voltammetry was applied. Bulk solutions contained Cu(II) and Ge(IV) in 0.2 mol dm^{-3} Na_2CO_3 and 0.025 mol dm^{-3} EDTA. Electrolytic accumulation of the metals lasted 5 min at -1.8 V vs. SCE and after 1 min the stripping voltammograms were recorded. The solubility product was calculated from the oxidation current maxima of both elements. The experiments were performed in a N_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

Concentration of other heavy metal ions in the solution was below 1×10^{-8} mol dm^{-3}.

ESTIMATED ERROR:

Nothing specified. The determination of the equilibrium concentrations of the metals no better than ± 10 % (by compilers).

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper-manganese; 3:1; Cu_3Mn; [37240-23-6] (2) Mercury; Hg; [7439-97-6]	Kaplin, A.A.; Mamontova, I.P. *Zh. Anal. Khim.*, 1978, *33*, 703-9.
VARIABLES:	PREPARED BY:
Room temperature measurement	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of Cu_3Mn in Hg, $K_s = [Cu]^3[Mn]$, at room temperature is 1.0×10^{-12} $mol^4\ dm^{-12}$; the value is tentative. The compound Cu_3Mn is moderately stable in the Cu-Mn binary system (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixed amalgams were prepared by a 3 min electroreduction of Cu(II) and Mn(II) in 1 mol dm^{-3} NaCl at -1.9 V (vs. SCE) on the thin film or hanging drop mercury electrodes on a Pt support. Then voltammetric oxidation of the amalgams was performed. The solubility product was calculated from the heights of anodic current peaks. The experiments were carried out in a N_2 or Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Super pure or chemically pure reagents were used. Water contained no more than 10^{-9}-10^{-10} mol dm^{-3} of other heavy metals.

ESTIMATED ERROR:

Standard deviation of the oxidation current no worse than ± 5 %.

Temperature: nothing specified.

REFERENCES:

1. Shunk, F.A. *Constitution of Binary Alloys*, II Supplement, McGraw-Hill, New York, 1969.

COMPONENTS:	EVALUATOR:
(1) Copper-platinum 3:1; Cu_3Pt; [12054-22-7] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland May 1982

CRITICAL EVALUATION:

Barlow and Planting (1) investigated amalgamation of Cu_3Pt at higher temperatures. At the beginning the compound was partly decomposed with Hg to form some amount of solid $PtHg_4$. If the Hg phase contains Cu then no such decomposition of the surface occurs and Cu_3Pt is in equilibrium with Cu and Pt atoms in the liquid amalgam. An order of magnitude of the corresponding solubility product, $K_s = [Cu]^3[Pt]$, was estimated.

Earlier Kemula and coworkers (2) did not find evidence of formation of an intermetallic Cu-Pt compound in this amalgam system at room temperature but experimental conditions in (1) and (2) are not comparable. The phase Cu_3Pt is moderately stable in the Cu-Pt binary system (3).

Value of the solubility of Cu_3Pt in Hg (tentative)

The solubility product of Cu_3Pt in Hg at 573 K is of the order:

10^{-6} mol^4 dm^{-12}, as reported in (1)

and the solubility, as calculated by compilers from K_s:

10^{-2} mol dm^{-3}

References

1. Barlow, M.; Planting, P.J. *Z. Metallk.* 1969, *60*, 292.
2. Kemula, W.; Galus, Z.; Kublik, Z. *Bull. Acad. Polon. Sci., Ser. Sci. Chim. Geol. Geogr.* 1959, *7*, 723.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Copper-platinum 3:1; Cu_3Pt; [12054-22-7]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Barlow, M.; Planting, P.J.

Z. Metallk. 1969, *60*, 292-7.

VARIABLES:

One temperature: 573 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of Cu_3Pt in Hg at 300 °C is of the order of 10^{-6} mol^4 dm^{-12}. Kinetics of amalgamation and formation of several intermetallic compounds of Pt were also investigated.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A sample of Cu_3Pt was covered with Cu amalgam and placed in a Pyrex glass capsule. The capsule was filled with H_2, Ar or N_2, sealed and placed in an oven maintained at constant temperature. By determining the equilibrium concentrations of Cu and Pt in the liquid amalgam the solubility product was calculated. Methods of the determination are not described.

SOURCE AND PURITY OF MATERIALS:

The compound Cu_3Pt was obtained from Western Gold and Platinum Co., Belmont. Pt was of purity better than 99.9 % and Cu was reagent or spectrographic grade. Hg was purchased from Mosero Laboratories, Palo Alto and contained total impurities of 1.3×10^{-4} mass %.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:	EVALUATOR:
(1) Copper-antimony 2:1; Cu_2Sb; [12054-21-6] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland January 1980

CRITICAL EVALUATION:

On the basis of the first potentiometric experiments with the Cu-Sb-Hg system done by Zebreva and Kozlovskii (1), it was difficult to determine a stoichiometry of the Cu-Sb compound formed. Later Stromberg and coworkers (2), using stripping voltammetry, suggested the formation of CuSb in Hg.

In the detailed work of Zakharchuk and Zebreva (3), performed also with stripping voltammetry, it was found that under equilibrium conditions Cu_2Sb is precipitated as a solid and its solubility product in Hg, $K_s = [Cu]^2[Sb]$, is 4.4×10^{-12} mol^3 dm^{-9} at 293 K. The CuSb compound was found to be unstable with time. For a concentration ratio of Cu to Sb greater than five, other Cu-Sb intermetallics, richer in Cu, may be formed.

Lange and coworkers (4) investigated further the formation and dissociation of Cu_2Sb in Hg. Based on the polarization curves and chronoamperometric oxidation currents of the Cu-Sb amalgams, values of the solubility products were determined in the temperature range 293-363 K. The solubility product of the compound at 293 K was found to be 5.8×10^{-11} mol^3 dm^{-9}. We do not select this result, because it was calculated incorrectly and is only one-fourth as large as it should be, although this work seems to be more exhaustive than (3). One should also remember that the solubility of Cu_2Sb from (4) is even slightly higher than the solubility of Sb in Hg (see the Sb-Hg system). We do not recommend the data of (4) at higher temperatures for the same reasons. The temperature dependence of the solubility product using results of (4) may be expressed by an equation obtained by the least square method; however the constant 0.33 should be replaced by 0.93 to take into account the values corrected by compilers; see the Data Sheet for (4).

$$pK_s = 0.33 + 2.92 \times 10^3\ T^{-1} \qquad r = 0.997 \qquad (K_s/\text{mol}^3\ \text{dm}^{-9};\ T/\text{K})$$

The equation is doubtful.

Matakova and Zholdybaeva (5) found that the Cu-Sb compound formed in Hg is less soluble than CdSb, though the selected solubilities of both compounds are similar (see also the CdSb-Hg system). No numerical data are reported in (1, 2, 5).

The compounds Cu_2Sb and Cu_4Sb are stable at room temperature in the Cu-Sb binary system, whereas CuSb is not known (6). Solid Cu_2Sb was also separated from the amalgam (4).

Value of the solubility of Cu_2Sb in Hg (tentative)

T/K	K_s/mol^3 dm^{-9}	Soly/mol dm^{-3} [a]	Refer.
293	4×10^{-12}	1×10^{-4}	(3)

[a] calculated by evaluators from K_s.

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Copper-antimony 2:1; Cu_2Sb; [12054-21-6] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland January 1980

CRITICAL EVALUATION (continued)

References

1. Zebreva, A.I.; Kozlovskii, M.T. *Coll. Czech. Chem. Comm.* 1960, *25*, 3188.
2. Stromberg, A.G.; Zakharov, M.S.; Mesyats, N.A.; Zaichko, L.F.; Stepanova, O.S. *Teoria i Praktika Amalgamnykh Protsesov*, Nauka, Alma-Ata, 1966, p. 68.
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4. Lange, A.A.; Kairbaeva, A.A.; Bukhman, S.P. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1976, *42*, 9.
5. Matakova, R.N.; Zholdybaeva, R.B. *VII Vsesoyuznoe Soveshchanie po Polarografii*, Nauka, Moskva, 1978, p. 173.
6. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Copper-antimony 2:1; Cu_2Sb; [12054-21-6]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zakharchuk, N.F.; Zebreva, A.I.

Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR 1971, *32*, 31-4.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound Cu_2Sb is treated as sparingly soluble in Hg, the equilibrium is described by the solubility product, which is $(4.3 \pm 0.4) \times 10^{-12}$ $mol^3\ dm^{-9}$, (probably at 293 K; compilers). The detailed results and concentrations of the metals are as follows:

$10^4c_{Sb}^{i}$/ mol dm^{-3}	$10^4c_{Cu}^{i}$/ mol dm^{-3}	$10^4c_{Sb}^{f}$/ mol dm^{-3}	$10^4c_{Cu}^{f}$/ mol dm^{-3}	stoichiom. coeffic.	formula^a	K_s/ ^{a} $(mol\ dm^{-3})^n$
time of conditioning of the amalgam: 3 min						
2.91	1.39	2.50	1.01	0.92		2.5
2.88	1.94	1.65	0.73	0.97		1.2
2.71	1.22	2.32	0.88	0.87		2.0
2.49	1.05	2.21	0.76	1.06		1.7
2.49	1.36	2.01	1.01	0.73		2.0
2.38	1.88	1.71	1.22	0.99		2.1
2.29	0.88	1.96	0.63	0.76	CuSb	1.2×10^{-8}
2.04	0.70	1.79	0.50	0.90		0.9

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Stripping voltammetry was used. The experiments were performed in solutions containing 1 mol dm^{-3} Na_2CO_3, 0.25 mol dm^{-3} $NaHC_4H_4O_6$, 5×10^{-6} mol dm^{-3} Cu(II) and 5×10^{-6} mol dm^{-3} Sb(III). Accumulation of the metals in the hanging mercury drop electrode lasted 5 min at -1.6 V vs. SCE. Then the metals were conditioned at -0.8 V for various times (3-15 min) and oxidized under voltammetric conditions.

SOURCE AND PURITY OF MATERIALS:

All reagents were chemically pure. Water, twice distilled, deionized on ion exchanger, contained no more than 10^{-7} % of heavy metal ions.

ESTIMATED ERROR:

Solubility product: precision ± 10 % (authors); standard deviation ± 27 % (as calculated by compilers). Temperature: nothing specified, probably ± 0.2 K (compilers).

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper-antimony 2:1; Cu_2Sb; [12054-21-6] (2) Mercury; Hg; [7439-97-6]	Zakharchuk, N.F.; Zebreva, A.I. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* <u>1971</u>, *32*, 31-4.

EXPERIMENTAL VALUES (continued)

$10^4c_{Sb}{}^i$/ mol dm^{-3}	$10^4c_{Cu}{}^i$/ mol dm^{-3}	$10^4c_{Sb}{}^f$/ mol dm^{-3}	$10^4c_{Cu}{}^f$/ mol dm^{-3}	stoichiom. coeffic.	formula[a]	K_s/ [a] (mol dm^{-3})^n
time of conditioning of the amalgam: 3 min						
2.04	1.03	1.79	0.75	1.12		1.3
1.89	1.69	1.32	1.09	0.88		1.4
1.52	2.48	1.27	2.21	1.03		2.8
1.34	2.17	1.02	1.75	1.31		1.8
1.03	2.01	0.73	1.70	1.17		1.2
0.91	1.90	0.72	1.63	0.90		1.2
					mean value	1.7±0.5 [a]
time of conditioning of the amalgam: 10-15 min						
2.48	4.00	1.48	1.96	2.06		5.7
2.48	3.42	1.60	1.70	1.95		4.6
2.27	4.45	1.04	2.10	1.91		4.6
2.06	2.82	1.46	1.70	1.89		4.2
1.70	2.29	1.27	1.39	2.04		2.5
1.52	1.72	1.30	1.30	2.10		2.2
2.24	6.70	0.58	3.20	1.91	Cu_2Sb	5.7×10^{-12}
2.18	5.23	0.91	2.53	2.14		5.8
2.18	5.85	0.67	2.70	2.08		4.9
2.18	6.48	0.42	2.91	2.03		3.6
1.76	4.39	0.84	2.51	2.04		5.2
1.74	4.70	0.66	2.55	1.99		4.3
1.65	3.49	0.93	1.97	2.10		3.6
1.43	4.20	0.70	2.78	1.98		5.4
0.78	3.60	0.38	2.80	2.00		3.0
0.83	4.11	0.22	1.43	4.41	mean value	4.4±1.2 [a]
0.78	4.40	0.18	1.50	4.84		
0.69	2.68	0.30	1.00	4.30	$Cu_{4-5}Sb$	
0.43	2.30	0.22	1.30	4.76		
0.26	1.38	0.18	0.99	4.90		
0.26	1.70	0.15	1.15	5.52		

[a] calculated by compilers.

When conditioning time after the metal deposition is 3 min, CuSb is present, but after 10-15 min of waiting Cu_2Sb is formed in Hg. When the initial concentration of Cu is more than 5 times higher than that of Sb, other compounds with the formula $Cu_{3+x}Sb$ may be formed. If the amounts of Cu and Sb introduced into Hg are lower than those corresponding to the K_s, then all Cu and Sb is stripped out.

COMPONENTS:

(1) Copper-antimony 2:1; Cu_2Sb; [12054-21-6]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Lange, A.A.; Kairbaeva, A.A.; Bukhman, S.P.
Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR 1976, *42*, 9-15.

VARIABLES:

Temperature: 293-363 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound Cu_2Sb is treated as sparingly soluble in Hg. The solubility products of the compound obtained by two methods at temperature 293 to 363 K are reported. Solid Cu_2Sb was separated from the amalgam. The solubility products determined from anodic polarization curves of Cu and Sb from Cu_2Sb in Hg.

t/°C	c_{Cu}^{i}/ mass %	c_{Sb}^{i}/ mass %	c_{Cu}^{f}/ mol dm^{-3}	c_{Sb}^{f}/ mol dm^{-3}	K_s/ [a] mol^3 dm^{-9}	K_s/ [b] mol^3 dm^{-9}
20	$1.43 \cdot 10^{-2}$	$1.39 \cdot 10^{-2}$	$8.08 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$	$5.74 \cdot 10^{-11}$	$2.3 \cdot 10^{-10}$
40	$1.43 \cdot 10^{-2}$	$1.39 \cdot 10^{-2}$	$1.21 \cdot 10^{-3}$	$5.05 \cdot 10^{-4}$	$1.85 \cdot 10^{-10}$	$7.4 \cdot 10^{-10}$
60	$1.43 \cdot 10^{-2}$	$1.39 \cdot 10^{-3}$	$1.81 \cdot 10^{-3}$	$8.85 \cdot 10^{-4}$	$7.26 \cdot 10^{-9}$ [c]	$2.9 \cdot 10^{-9}$

The solubility products determined from chronoamperometric oxidation of Sb from the Cu_2Sb amalgam

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgam with content ratio of Sb:Cu equal to 1/2 was obtained by electrolysis of Cu(II) and Sb(III) sulfate solution in 0.5 mol dm^{-3} H_2SO_4. These heterogeneous amalgams were oxidized under voltammetric and chronoamperometric conditions. The background electrolyte for the electrooxidation contained 1 mol dm^{-3} Na_2CO_3 + 0.2 mol dm^{-3} $NaKC_4H_4O_6$ (pH 12.5-13) and the potential in the chronoamperometric stripping of Sb was -0.15 V vs. SCE. Equilibrium concentrations of Cu and Sb in the method of polarization curves were determined from the limiting currents. The active concentration of Sb was found from the charge due to the first exponential decrease of oxidation current in time. The solubility products were calculated by multiplication of the corresponding concentrations. Composition of the solid phase, separated from the heterogeneous amalgam, was determined with help of complexometry (Cu) and amperometric titration with bromine (Sb) after a sample was dissolved in 5 mol dm^{-3} H_2SO_4.

SOURCE AND PURITY OF MATERIALS:

The reagents were of analytical purity.

ESTIMATED ERROR:

Solubility product: nothing specified; error of currents determinations is not better than ± 5 %; error in K_s calculation was found by compilers.

Temperature: precision ± 0.5 K.

COMPONENTS:

(1) Copper-antimony 2:1; Cu_2Sb; [12054-21-6]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Lange, A.A.; Kairbaeva, A.A.; Bukhman, S.P. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1976, *42*, 9-15.

EXPERIMENTAL VALUES (continued)

t/°C	c_{Cu}^{i}/ mass %	c_{Sb}^{i}/ mass %	c_{Sb}^{f}/ mol dm^{-3}	K_s/ [a] mol^3 dm^{-9}	K_s/ [b] mol^3 dm^{-9}
20	$1.43 \cdot 10^{-2}$	$1.39 \cdot 10^{-2}$	$3.88 \cdot 10^{-4}$	$5.88 \cdot 10^{-11}$	$2.3 \cdot 10^{-10}$
40	$1.43 \cdot 10^{-2}$	$1.39 \cdot 10^{-2}$	$5.47 \cdot 10^{-4}$	$1.66 \cdot 10^{-10}$	$6.6 \cdot 10^{-10}$
60	$1.43 \cdot 10^{-2}$	$1.39 \cdot 10^{-2}$	$9.25 \cdot 10^{-4}$	$7.9 \cdot 10^{-10}$	$3.2 \cdot 10^{-9}$
80	$1.43 \cdot 10^{-2}$	$1.39 \cdot 10^{-2}$	$1.41 \cdot 10^{-3}$	$2.8 \cdot 10^{-9}$	$1.12 \cdot 10^{-8}$
90	$2.4 \cdot 10^{-2}$	$1.86 \cdot 10^{-2}$	$1.76 \cdot 10^{-3}$	$5.5 \cdot 10^{-9}$	$2.2 \cdot 10^{-8}$

[a] $K_s = ([Cu]/2)^2[Sb]$, as calculated incorrectly by authors.

[b] $K_s = [Cu]^2[Sb]$, as calculated by compilers.

[c] A misprint; the value should be 7.26×10^{-10} mol^3 dm^{-9}.

K_s values, presented as a temperature dependence of K_s in the paper, are for the corrected values.

COMPONENTS:	EVALUATOR:
(1) Copper-antimony 1:1; CuSb; [11088-65-6] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland February 1980

CRITICAL EVALUATION:

From potentiometric experiments, Zebreva and Kozlovskii (1) pointed out that several compounds, including CuSb, may be formed in the Hg-rich corner of the Cu-Sb-Hg system. However, Stromberg and coworkers (2) by the stripping voltammetry found only CuSb formed in Hg. According to Zakharchuk and Zebreva (3), who used the same method, CuSb is formed within a few minutes after formation of the complex amalgam. In their opinion CuSb is a heterogeneous mixture of Cu_2Sb and Sb. At longer times CuSb transforms into Cu_2Sb, which is in equilibrium with dissolved Cu and Sb.

This indicates that the formation of CuSb in Hg is not proven conclusively. Moreover, the solubility of this compound, according to (3) and the calculation of evaluators 1.3×10^{-4} mol dm^{-3}, is comparable to the solubility of Cu_2Sb in Hg (see the Data Sheet of work (3) in the Cu_2Sb-Hg system). Even a doubtful value should not be suggested under such circumstances since no true equilibrium is reached in the CuSb-Hg system. No numerical results are reported in (1, 2). No CuSb compound is formed in the binary Cu-Sb alloys (4).

References

1. Zebreva, A.I.; Kozlovskii, M.T. *Coll. Czech. Chem. Comm.* 1960, *25*, 3188.
2. Stromberg, A.G.; Zakharov, M.S.; Mesyats, N.A.; Zaichko, L.F.; Stepanova, O.S. *Teoria i Praktika Amalgamnykh Protsesov*, Nauka, Alma-Ata, 1966, p. 68.
3. Zakharchuk, N.F.; Zebreva, A.I. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1971, *32*, 31.
4. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:	EVALUATOR:
(1) Copper-tin 3:1; Cu_3Sn; [12019-61-3] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland August 1983

CRITICAL EVALUATION:

It was observed by Humphreys (17) as early as in 1896 that although an amalgamation of Cu_3Sn alloy was excellent no parent metals were detected in the Hg phase. When Cu was in excess in the solid, its concentration in the liquid was almost equal to the solubility of Cu in Hg.

The Cu-Sn system in Hg was studied by Kovaleva and Zebreva (1) who reported the formation of Cu_3Sn if the concentration of Cu is considerably larger than that of Sn. This compound was found to be sparingly soluble in Hg and its solubility product, $K_s = [Cu]^3[Sn]$, determined from potentiometric measurements, is 2.8×10^{-12} mol^4 dm^{-12} at 293 K. The compound CuSn was also detected at comparable concentrations of the components. Unfortunately results of the subsequent works are contradictory. Stromberg and coworkers performed new potentiometric experiments (2) as well as recalculated (2, 3, 7) data of (1) and arrived at the conclusion that only one compound, Cu_3Sn, is formed in the system. They claimed it to be soluble in Hg, and its instability constant, $K_d = [Cu]^3[Sn]/[Cu_3Sn]$, was determined to be 2×10^{-8} mol^3 dm^{-9} at room temperature (2, 3, 7). The best fit of the theoretical dependencies to the experimental data of (1) is obtained assuming the formula $Cu_{2.5}Sn$. The evaluated dissociation constants in (2, 3, 7) of Cu_3Sn are 6×10^{-12} mol^3 dm^{-9} (1) and 4×10^{-9} mol^3 dm^{-9} from the unpublished thesis of Zebreva (21). Nazarov and coworkers (8-10, 18) using stripping chronoamperometry reported formation of soluble Cu_3Sn in Hg and investigated its decomposition kinetics. The instability constants obtained are 1×10^{-7} mol^3 dm^{-9} at room temperature (9) and 1.4×10^{-8} mol^3 dm^{-9} at 298 K (18). Igolinskaya and Igolinskii (11) confirmed the result obtained in Stromberg's laboratory by means of stripping chronopotentiometry with a film electrode, but no other details are given. Stripping voltammetry was used by Kaplin and Mamontova (12) who determined the dissociation constant value equal to 2×10^{-8} mol^3 dm^{-9} at room temperature. As one may see, there is no agreement of the K_d values obtained in or recalculated from the works (1, 2, 9, 12, 18). On the other hand, the K_s-values estimated by evaluators from these data are spread in the range 4×10^{-11} - 1×10^{-10} mol^4 dm^{-12}, and it is possible that no true equilibrium was reached under the experimental conditions of these measurements, especially when fast electroanalytical oxidations were applied. To resolve these discrepancies, Zebreva and coworkers (4, 5, 13) again carried out potentiometric and chronoamperometric experiments, which led to the conclusion that in the Cu-Sn-Hg system, depending on the concentration of the components, the following solid phases are formed: CuSn, Cu_3Sn and Cu_7Hg_6 (at significant excess of Cu). The solubility product of Cu_3Sn using very different concentrations of components was determined to be precisely 4.2×10^{-12} mol^4 dm^{-12} at 298 K (4) and was characterized by perfect constancy. This solid phase was analyzed chemically and by X-ray radiography after separation from the amalgam. According to exhaustive study of Aldinger and Kraft (6) performed at 310 K on this system there is observed formation of Cu_3Sn as well as Cu_6Sn_5 (previously recognized as CuSn). An excess of Cu or Sn with Hg forms Cu_7Hg_6 and $Sn_{7-8}Hg$, respectively. Thus this paper confirms works of Zebreva and coworkers (1, 4, 5,

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Copper-tin 3:1; Cu_3Sn; [12019-61-3] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland August 1983

CRITICAL EVALUATION (continued)

13). The formation of solid Cu_3Sn in Hg proceeds also in the presence of Ag (6, 19), Ni (14) or Pt (15). Therefore it is difficult to explain why Kairbaeva and coworkers (16), who carried out similar experiments as in (6), did not find Cu_3Sn precipitation in Hg but only solids CuSn (relatively soluble in Hg) and Cu_7Hg_6. Under such circumstances one may conclude after all that the Cu_3Sn crystals dissolve in Hg to form Cu_3Sn molecules, and they dissociate further partly to Cu and Sn atoms. However, such a compromise concept was not proven experimentally in any paper. The papers (1, 2, 4, 9, 12 18) are compiled, since only they contain original numerical results; work (16) is on the CuSn-Hg system. The Cu-Sn-Hg phase diagram at 310 K is from (6). The phase Cu_3Sn is the most stable formed in the Cu-Sn binary system (20).

Value of the solubility of Cu_3Sn in Hg (tentative)

The solubility product of Cu_3Sn in Hg at 298 K is, according to (4) as the most convincing source to evaluators:

$$4\times10^{-12}\ mol^4\ dm^{-12}$$

and the solubility, as calculated by evaluators from K_s,

$$6\times10^{-4}\ mol\ dm^{-3}$$

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2. Stromberg, A.G.; Mesyats, N.A.; Mikheeva, N.P. *Zh. Fiz. Khim.* 1972, *46*, 941.
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COMPONENTS:	EVALUATOR:
(1) Copper-tin 3:1; Cu_3Sn; [12019-61-3] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland August 1983

CRITICAL EVALUATION (continued)

13. Zebreva, A.I.; Serikbaeva, L.K.; Matakova, R.N. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1976, *19*, 1299.
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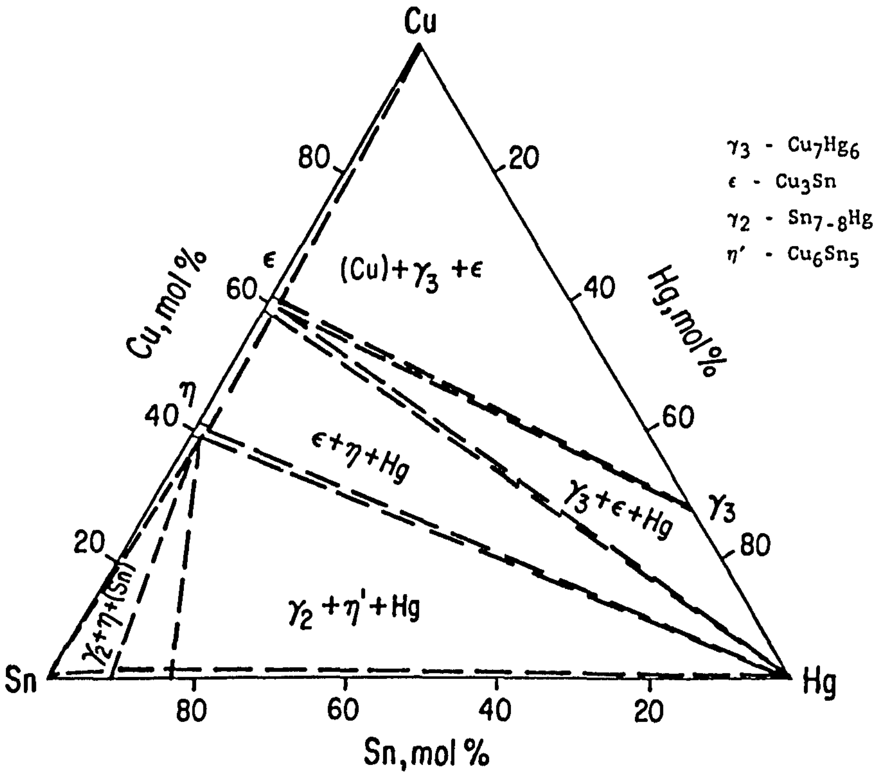
19. Kraft, W.; Petzow, G.; Aldinger, F. *Z. Metallk.* 1980, *71*, 699.
20. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
21. Zebreva, A.J. *Ph.D. Thesis*, University of Alma-Ata, Alma-Ata, 1968; as reported in 7.



COMPONENTS:

(1) Copper-tin 3:1; Cu_3Sn; [12019-61-3]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kovaleva, L.M.; Zebreva, A.I.

Zh. Fiz. Khim. 1964, *38*, 1162-5.

VARIABLES:

Temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound Cu_3Sn is considered as sparingly soluble in Hg. The equilibrium of its formation is described by the solubility product with values determined:

Potentiometric results at 20 °C

$10^3 c_{Cu}{}^{i}$/ mol dm^{-3}	$10^3 c_{Sn}{}^{i}$/ mol dm^{-3}	$10^3 c_{Cu}{}^{f}$/ mol dm^{-3}	$10^3 c_{Sn}{}^{f}$/ mol dm^{-3}	$10^{12} K_s$/ mol^4 dm^{-12}
3.02	0.16	2.78	0.074	1.58
3.02	0.37	2.20	0.1	1.07
5.09	1.21	2.59	0.374	2.51
5.09	2.67	2.67	0.157	2.95
7.91	0.66	5.96	0.012	2.45
7.91	0.84	5.48	0.025	4.15
7.91	1.32	4.11	0.056	3.95
7.91	2.32	2.10	0.383	3.56
			mean value	2.8±1.3

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AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The complex amalgams were prepared by electrolytic deposition of the metals on a Hg cathode. Amalgam polarography and potentiometric methods were used in the studies. In the potentiometry the EMF of the cell: Cu-Sn-Hg $SnCl_2$, 2 mol dm^{-3} KCl+HCl Sn-Hg was measured; pH of the solution was ~1. In the polarography, oxidation currents of Cu and Sn from the complex and simple amalgams in solution of 0.5 mol dm^{-3} NaF were recorded and compared. The solubility product was calculated from the potential differences and the current differences respectively. The experiments were performed in atmosphere of an inert gas.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: standard deviation ± 45 % (potentiom.); ± 22 % (polarography) as calcuated by compilers.

Temperature: nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper-tin 3:1; Cu_3Sn; [12019-61-3] (2) Mercury; Hg; [7439-97-6]	Kovaleva, L.M.; Zebreva, A.I. *Zh. Fiz. Khim.* 1964, *38*, 1162-5.

EXPERIMENTAL VALUES (continued)

$10^3 c_{Cu}{}^i$/ mol dm^{-3}	$10^3 c_{Sn}{}^i$/ mol dm^{-3}	$10^3 c_{Cu}{}^f$/ mol dm^{-3}	$10^3 c_{Sn}{}^f$/ mol dm^{-3}	$10^{12} K_s$/ mol^4 dm^{-12}
Polarographic results				
2.0	1.0	2.1	1.0	-- [a]
3.0	1.0	3.0	1.0	-- [a]
4.2	1.1	2.4	0.5	6.9
6.0	1.0	3.7	0.2	10.2
5.1	2.1	2.4	0.9	12.6
6.0	2.0	2.5	0.6	9.4
7.0	2.0	2.6	0.6	11.3
9.0	2.0	3.0	0.5	13.1
			mean value	1.06±0.23

[a] no precipitation occurred.

The larger results of the solubility product found by the polarographic method is explained by partial dissolution of the compound during the time of the anodic oxidation.

COMPONENTS:

(1) Copper-tin 3:1; Cu_3Sn; [12019-61-3]
(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENT:

Stromberg, A.G.; Mesyats, N.A.;
Mikheeva, N.P.
Zh. Fiz. Khim. 1972, *46*, 941-3.

VARIABLES:

Temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

It was found that in the Cu-Sn-Hg system only Cu_3Sn is formed in Hg. This compound is found to be soluble in Hg. Its instability constant, K_d, at 20 °C is equal to 2×10^{-8} $mol^3\ dm^{-9}$. The concentration of Cu was 7.0×10^{-3} mol dm^{-3} and of Sn was changed in the range 1.8×10^{-4} - 3.8×10^{-3} mol dm^{-3}. The estimated K_s value (by compilers based on graphical results) ranges from 4×10^{-12} to 1.4×10^{-10} $mol^4\ dm^{-12}$, whereas K_d changes from 1.9×10^{-8} to 1.2×10^{-7} $mol^3\ dm^{-9}$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Both simple amalgams were prepared by dissolution of the metals in Hg. Portions of the Sn amalgam were subsequently added to the complex Cu-Sn amalgam. The potentials of the electrodes constructed from the complex Cu-Sn and Sn amalgams were measured for 1 hour with respect to a reference electrode. The solution in contact with the amalgam had the composition: 0.5 mol dm^{-3} $SnCl_2$, 2 mol dm^{-3} HCl, 2 mol dm^{-3} KCl. On basis of the measured potentials the composition and the stability constant were calculated. The experiments were performed in an Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

K_d: standard deviation, as calculated by compilers, ± 25 %.

COMPONENTS:

(1) Copper-tin 3:1; Cu_3Sn; [12019-61-3]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Mikheeva, N.P.; Nazarov, B.F.;
Stromberg, A.G.

Sbor. Tr. Molod. Uchen. Tomsk. Poltiekhn. Inst. 1973, no. 1, 31-3.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound Cu_3Sn is assumed to be soluble in Hg with dissociation constant equal to 1×10^{-7} mol^3 dm^{-9} at room temperature. Kinetic formation and dissociation constants of Cu_3Sn in Hg were evaluated treating the reactions as pure electrode processes.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Stripping chronoamperometry experiments were performed on hanging mercury drop electrodes. The electrodes with Hg and Cu amalgam were prepared by unspecified electrolyses on Pt wire. They were introduced into 3 mol dm^{-3} HCl solution which contained 1×10^{-4} mol dm^{-3} Sn(II). The Sn(II) was reduced at -0.96 V vs. SCE for 180 s. Then Sn was oxidized from both electrodes at -0.30 V and the corresponding constant calculated from the oxidation currents. The concentrations of both metals were determined by coulometry.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:

(1) Copper-tin 3:1; Cu_3Sn; [12019-61-3]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kaplin, A.A.; Mamontova, I.P.

Zh. Anal. Khim. 1978, *33*, 703-9.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound Cu_3Sn is assumed to be soluble in Hg, with a dissociation constant of $2x10^{-8}$ mol^3 dm^{-9} at room temperature. The concentration of Sn(IV) was $6x10^{-6}$ g cm^{-3}. The concentration of Cu(II) ranged from $5x10^{-7}$ to $1.6x10^{-5}$ g cm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Thin film and hanging drop mercury electrodes were used. The complex amalgams were prepared by electroreduction of Cu(II) and Sn(IV) in 3 mol dm^{-3} HCl at -1.2 V vs. SCE for 3 min. Voltammetric oxidation of the amalgams was performed and the corresponding concentrations calculated from peak currents. The experiments were performed in an Ar or N_2 atmosphere with O_2 content lower than $1x10^{-2}$ %.

SOURCE AND PURITY OF MATERIALS:

Super pure or chemically pure reagents were used. The solutions contained no more than 0^{-9}-10^{-10} mol dm^{-3} of other heavy metal ions.

ESTIMATED ERROR:

Standard deviation of oxidation currents no worse than 5 %.

Temperature: nothing specified.

COMPONENTS:

(1) Copper-tin 3:1; Cu_3Sn; [12019-61-3]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zakharova, Z.A.; Ignateva, L.A.;
Nazarov, B.F.

Dep. ONIITEKhim, 1730-78, 1978.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound Cu_3Sn is considered soluble in Hg and its instability constant, K_d, at 25.0 °C is $(1.4 \pm 0.8) \times 10^{-8}$ $mol^3\ dm^{-9}$ (standard deviation calculated by compilers). The concentrations of Cu and Sn in the experiments were changed in the ranges $(6.6 - 28) \times 10^{-3}$ $mol\ dm^{-3}$ and $(1.0 - 3.1) \times 10^{-3}$ $mol\ dm^{-3}$, respectively.

Results reported in the paper are:

time of conditioning/min	$10^{17} K_d/mol^3\ cm^{-9}$
2	2.64
2	0.68
2	1.85
15	0.96
30	1.10
mean value	1.4±1.0

Using the chronoamperometric dependence $it^{1/2}$ vs. $t^{1/2}$ the solubility product, K_s, and K_d values were calculated by the compilers. The free Sn concentration was found from

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The stripping chronoamperometry experiments were performed at a semi-spherical mercury electrode with an Ag base. At first Cu(II) was reduced for 3-5 min from 0.1 $mol\ dm^{-3}$ $(NH_4)_2C_4H_4O_6$ solutions at -0.7 V vs. SCE. Then Sn(IV) was reduced for 3-5 min from 3 $mol\ dm^{-3}$ HCl solutions at the same potential. The mixed amalgam electrode was conditioned for 2-30 min at potentials -0.7 V and subsequently Sn was oxidized at -0.35 V. The instability constant was calculated from the oxidation currents of Sn and mass balance.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Constant precision: ± 70 %.

Temperature: ± 0.2 K.

COMPONENTS:

(1) Copper-tin 3:1; Cu_3Sn; [12019-61-3]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zakharova, Z.A.; Ignateva, L.A.;
Nazarov, B.F.

Dep. ONIITEKhim, 1730-78, 1978.

EXPERIMENTAL VALUES (continued)

Cottrell's equation: $it^{1/2} = \pi^{-1/2} nFAD_{Sn}^{1/2} c_{Sn}^{f}$. The value of $it^{1/2}$ at $t=0$ was read from the figure, $n=4$, $F=96500$ C, $A=2\pi r^2=6.28\times(4.75\times10^{-2}\ cm)^2$, $D_{Sn}=1.48\times10^{-5}\ cm^2\ s^{-1}$; the equation is valid for $t\to0$.

t'/[a] s	$it^{1/2}$/ $\mu A\ s^{1/2}$	c_{Cu}^{i}/ $mol\ dm^{-3}$	c_{Sn}^{i}/ $mol\ dm^{-3}$	c_{Sn}^{f}/ $mol\ dm^{-3}$	c_{Cu}^{f}/ $mol\ dm^{-3}$	K_d/ $mol^3\ dm^{-9}$	K_s/ $mol^4\ dm^{-12}$
15	1.20	6.6×10^{-3}	1.0×10^{-3}	3.2×10^{-4}	4.6×10^{-3}	4.5×10^{-8}	3.1×10^{-11}
30	1.36	6.6×10^{-3}	1.0×10^{-3}	3.6×10^{-4}	4.7×10^{-3}	5.8×10^{-8}	3.7×10^{-11}
2	1.58	6.6×10^{-3}	1.0×10^{-3}	4.2×10^{-4}	4.9×10^{-3}	8.4×10^{-8}	4.9×10^{-11}

[a] t' is the conditioning time.

One may see that K_s values are more reproducible than K_d values.

COMPONENTS:

(1) Copper-tin 3:1; Cu_3Sn; [12019-61-3]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zebreva, A.I.; Matakova, R.N.;
Sharipova, N.S.
Dep. VINITI, 1934-78, <u>1978</u>.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of Cu_3Sn in Hg at 25 °C is $(4.21 \pm 0.12) \times 10^{-12}$ mol^4 dm^{-12} (the mean value and standard deviation by compilers).

$x_{Cu}{}^{i}$/ at. %	$x_{Sn}{}^{i}$/ at. %	$10^4 c_{Cu}{}^{f}$/ mol dm^{-3}	$10^3 c_{Sn}{}^{f}$/ mol dm^{-3}	K_s/mol^4 dm^{-12} [a]	K_s/mol^4 dm^{-12} [b]
2.2	1.2	3.78	3.03	4.40×10^{-12}	1.6×10^{-13}
3.6	1.2	4.16	2.10	4.10×10^{-12}	1.5×10^{-13}
4.0	1.2	4.00	2.41	4.15×10^{-12}	1.5×10^{-13}

[a] authors.

[b] as calculated by compilers. The authors used formula $K_s = (3c_{Cu}{}^{f})^3 c_{Sn}{}^{f}$ while compilers used $K_s = (c_{Cu}{}^{f})^3 c_{Sn}{}^{f}$.

The Cu_3Sn solid phase was analyzed by x-ray analysis after separation from the heterogeneous amalgam.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Sn amalgam was prepared by dissolution of weighed amounts of Sn in Hg. The Cu was introduced into the Sn amalgam by electrolysis. Then liquation of the complex amalgams, in respect to relative specific gravity, was performed in glass capillaries for 60 days. The upper, middle and lower parts of the amalgams in the capillaries were analyzed after dissolution: Cu by polarography and Sn by colorimetry. Taking into account the concentrations of the metals in the homogeneous (lower) fraction of the amalgams the solubility product was calculated.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: standard deviation of 3 % (by compilers).

Temperature: ± 0.5 K.

COMPONENTS:	EVALUATOR:
(1) Copper-tin 1:1; CuSn; [29888-30-0] or Copper-tin 6:5; Cu_6Sn_5; [12019-69-1] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland August 1982

CRITICAL EVALUATION:

The formation of a solid compound with the Cu: Sn stoichiometry close to 6:5 in Hg was reported by Lihl and Kirnbauer (1). Later Kovaleva and Zebreva (2), using potentiometry and amalgam polarography, confirmed the existence of CuSn in the complex Cu-Sn amalgam. To observe the formation of the compound the concentration of Sn in the amalgam should be larger than that of Cu. The solubility product, K_s = [Cu][Sn], was determined to be 4.6×10^{-6} mol^2 dm^{-6} at 293 K. It should be mentioned that Stromberg and coworkers (3, 4) postulated only formation of Cu_3Sn which is soluble in Hg but poorly dissociated.

Zebreva and coworkers (5, 7, 8) repeated the potentiometric measurements and performed additional experiments; chronoamperometric oxidation, segregation and x-ray analysis of the amalgam and its components. They confirmed (5) their previous result (2) of the solubility product of CuSn in Hg, precisely 1.9×10^{-6} mol^2 dm^{-6} at 298 K. They also found that in the Cu-Sn-Hg system CuSn, Cu_3Sn and a mixture of Cu_3Sn and Cu_7Hg_6 are formed depending on the composition of the amalgam. These statements are in concordance with observations of Aldinger and Kraft (6) that in the system investigated the following intermetallics: Cu_6Sn_5 (formerly assumed to be CuSn), Cu_3Sn and Cu_7Hg_6 or $Sn_{7-8}Hg$ for excesses of Cu or Sn, respectively, are formed.

However, Kairbaeva and coworkers (9) found that solid CuSn dissociates in Hg to produce a concentration of Cu close to its solubility in Hg and of Sn, almost one-fifth of its solubility (see the Cu-Hg and Sn-Hg systems) at 293 K. There is significant scatter of these data and some results in this work suggest considerably a lower value of the solubility; therefore we treat these results as too high. The numerical results concerning the solubility of CuSn in Hg are reported only in (2, 5, 9). Only a doubtful value of the solubility may be suggested; however, the results of (2, 5) are more persuasive to evaluators than of (9). The Cu-Sn-Hg phase diagram from (6) is given in the figure in the Critical Evaluation of the Cu_3Sn-Hg system. The compound Cu_6Sn_5 is moderately stable in the Cu-Sn binary system (10).

Value of the solubility of CuSn in Hg (doubtful)

The solubility product of CuSn in Hg at 298 K is, according to (5):

$$2\times10^{-6}\ mol^2\ dm^{-6}$$

and the solubility, as calculated by evaluators from K_s:

$$1.4\times10^{-3}\ mol\ dm^{-3}$$

References

1. Lihl, F.; Kirnbauer, H. *Z. Metallk.* 1957, *48*, 17.
2. Kovaleva, L.M.; Zebreva, A.I. *Zh. Fiz. Khim.* 1964, *38*, 1162.

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Copper-tin 1:1; CuSn; [29888-30-0] or Copper-tin 6:5; Cu_6Sn_5; [12019-69-1] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland August 1982

CRITICAL EVALUATION (continued)

3. Stromberg, A.G.; Mesyats, N.A.; Mikheeva, N.P. *Zh. Fiz. Khim.* 1972, *46*, 941.
4. Stromberg, A.G.; Mikheeva, N.P. *Elektrokhimia* 1971, *7*, 1728.
5. Zebreva, A.I.; Matakova, R.N.; Sharipova, N.S. *Dep. VINITI*, 1934-78, 1978; abstracted in *Elektrokhimia* 1978, *14*, 1613.
6. Aldinger, F.; Kraft, W. *Z. Metallk.* 1977, *68*, 523.
7. Zebreva, A.I.; Serikbaeva, L.K.; Matakova, R.N. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1976, *19*, 1299.
8. Zebreva, A.I.; Matakova, R.N.; Sharipova, N.S. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1976, no. 1, 60.
9. Kairbaeva, A.A.; Lange, A.A.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1980, no. 4, 20.
10. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Copper-tin 1:1; CuSn; [29888-30-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kovaleva, L.M.; Zebreva, A.I.

Zh. Fiz. Khim. 1964, *38*, 1162-5.

VARIABLES:

One temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

CuSn was found to be insoluble in Hg. The equilibrium of its dissolution is described by the solubility product with the values:

Polarographic results

$10^3c_{Cu}^i$/ mol dm^{-3} 10^3	$10^3c_{Sn}^i$/ mol dm^{-3} 10^3	$10^3c_{Cu}^f$/ mol dm^{-3} 10^3	$10^3c_{Sn}^f$/ mol dm^{-3} 10^3	10^6K_s/ mol^2 dm^{-6} 10^6
0.5	1.0	0.4	1.0	-- [a]
1.0	1.0	1.0	0.95	-- [a]
2.0	3.0	1.4	2.4	3.3
3.0	3.0	1.9	1.9	3.6
4.0	3.0	2.4	1.6	3.9
0.5	4.0	0.5	3.9	-- [a]
4.0	4.0	2.7	2.7	7.3
5.2	4.2	3.3	2.3	7.6
3.0	6.0	2.4	4.4	6.1

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Cu and Sn amalgams were prepared by an electroreduction of the corresponding ions at the Hg pool cathode. Then polarographic oxidation of the mixed and simple amalgams in solution of 0.5 mol dm^{-3} NaF was performed. Also potentials of the cell: Cu-Sn-Hg|SnCl$_2$, 2 mol dm^{-3} KCl + HCl (pH≈1) Sn-Hg were measured. The solubility product was calculated from the potentials as well as from the oxidation currents, with the help of the mass balance equation. The experiments were performed in an inert gas atmosphere.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: standard deviation ± 18 % (potentiom); ± 33 % (polarogr.) calculated by compilers.

Temperature: nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper-tin 1:1; CuSn; [29888-30-0] (2) Mercury; Hg; [7439-97-6]	Kovaleva, L.M.; Zebreva, A.I. *Zh. Fiz. Khim.* 1964, *38*, 1162-5.

EXPERIMENTAL VALUES (continued)

$10^3 c_{Cu}^{i}$/ mol dm^{-3} 10^3	$10^3 c_{Sn}^{i}$/ mol dm^{-3} 10^3	$10^3 c_{Cu}^{f}$/ mol dm^{-3} 10^3	$10^3 c_{Sn}^{f}$/ mol dm^{-3} 10^3	$10^6 K_s$/ mol^2 dm^{-6} 10^6
4.0	6.0	1.5	3.5	5.2
6.0	6.0	2.8	2.8	7.8
			mean value	5.6±1.9

[a] no precipitation occurred.

Potentiometric results at 20 °C

3.10	1.90	2.54	1.34	3.40
3.10	2.27	2.55	1.72	4.36
3.10	2.22	2.57	1.78	4.57
4.05	2.17	3.29	1.42	4.75
4.07	2.65	2.86	1.44	4.12
4.07	2.96	3.00	1.90	5.70
5.09	1.69	4.29	0.89	3.84
5.76	2.62	4.40	1.25	5.50
6.64	2.45	5.08	0.89	4.51
6.81	3.53	4.40	1.12	4.92
7.91	2.83	5.91	0.83	4.93
			mean value	4.6±0.8

The value found by potentiometry is preferred since the amalgam equilibrium in the polarographic experiments may be disturbed due to oxidation of the metals during the electrolysis.

COMPONENTS:

(1) Copper-tin 1:1; CuSn; [29888-30-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zebreva, A.I.; Matakova, R.N.;
Sharipova, N.S.

Dep. VINITI, 1934-78, 1978.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of CuSn in Hg at 25 °C is (1.93±0.10)x10^{-6} mol^2 dm^{-6} (as calculated by compilers).

$c_{Cu}{}^i$/mol dm^{-3}	$c_{Sn}{}^i$/mol dm^{-3}	$10^3c_{Cu}{}^f$/mol dm^{-3}	$10^3c_{Sn}{}^f$/mol dm^{-3}	K_s/mol^{2}dm^{-6}
10^{-3}	10^{-2}	3.81	4.80	1.82x10^{-6}
10^{-2}	10^{-2}	2.86	6.25	1.85x10^{-6}
1.2	1.2	2.99	7.10	2.12x10^{-6}

The CuSn solid phase was analyzed by roentgenography after separation from the heterogeneous amalgam.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgams of Sn were prepared by dissolution of weighed amounts of Sn in Hg. The Cu was introduced to the Sn amalgam by electrolysis. Then liquation of the complex amalgams was performed in glass capillaries for 60 days. The upper, middle and lower fractions of the amalgams in the capillaries were analyzed after a dissolution: Cu by polarography and Sn by colorimetry. The solubility product was calculated from the concentrations of the metals in the lower, homogeneous part of the amalgam.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: standard deviation of 5 % (by compilers). Temperature: ± 0.5 K.

COMPONENTS:

(1) Copper-tin 1:1; CuSn; [29888-30-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kairbaeva, A.A.; Lange, A.A.; Bukhman, S.P.
Izv. Akad. Nauk Kaz. SSR, Ser. Khim. 1980, no. 4, 20-6.

VARIABLES:

Temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Distribution of the metals in Cu-Sn amalgam at equilibrium segregation at 20±2 °C

c_{Cu}^{i}/mol dm^{-3}	c_{Sn}^{i}/mol dm^{-3}	time of sectioning/h	10^3c_{Cu}/mol dm^{-3} ^{a}
0.102	0.101	72	-, 1.4, 2.8, 2.3, -
0.340	0.340	264	3.7, 1.2, 2.8, 2.7, 3.1
0.750	0.740	268	2.4, 2.8, 3.9, -, -
0.370	0.668	144	21.2, 16.8, 17.6, -, -
0.159	0.627	168	130, 143, 157, 103, 95
0.160	0.674	312	173, 137, 135, 108, -
0.373	0.187	274	2.3, -, 3.3, 2.2, 80.4
0.687	0.241	264	2.1, 2.7, 3.2, 2.5, 10.7
0.343	0.560	312	362, 382, 387, 3.1, 455
0.456	1.37	504	2.2, 1.7, 2.5, 2.0, 2.0
2.56	1.37	696	2.1, 2.0, 2.0, 1.5, 2.0
solid CuSn		528	-, 1.81, 1.40, -, 3.35, 1.38
solid CuSn		523	-, 1.35, 1.29, -, 1.94, 4.26

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Cu-Sn heterogeneous amalgams were prepared by dissolution of Sn in Hg and introduction of Cu by electrolysis from $CuSO_4$ solution. The amalgams were placed in narrow tubes and were cathodically polarized for 100-600 h in 0.5 mol dm^{-3} H_2SO_4. Then the tubes with amalgams were divided into 5 or 6 consecutive fractions. The solid phase in each fraction was separated from the liquid amalgam by filtration with filter paper in a special press (1). The liquid phase was polarized anodically in H_2SO_4 solution at -0.2 V vs. SCE for Sn and at +0.2 V for Cu. The solution obtained, after the extraction was complete, was analyzed for Cu by EDTA titration, polarography and AAS and for Sn by iodometric titration and AAS. The solid residue was analyzed by chem analysis. The solubility of solid CuSn dipped in Hg was also determined in a similar way. The CuSn alloy was synthesized from the elements in a glass ampule at 1473 K in an Ar atmosphere; the homogenization of the sample was carried out for 24 h at 653 K and tested by X-ray analysis.

SOURCE AND PURITY OF MATERIALS:

Very pure Sn and $CuSO_4$ were used.

ESTIMATED ERROR:

Solubilities: According to the authors the Cu contents in the range (1-4)x10^{-3} mol dm^{-3} could be too low, because the amalgam samples were small and the determinations were performed in the vicinity of the AAS detection limit. We do not understand this statement. Precision of other results seems to be ± 5 % (compilers).

Temperature: stability ± 2 K.

REFERENCES:

1. Shirinskikh, A.V.; Lange, A.A.; Bukhman, S.P. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1973, *35*, 54.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper-tin 1:1; CuSn; [29888-30-0] (2) Mercury; Hg; [7439-97-6]	Kairbaeva, A.A.; Lange, A.A.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1980, no. 4, 20-6.

EXPERIMENTAL VALUES (continued)

$10^1 c_{Sn}$/mol dm^{-3} [a]	equilibrium solid phases
0.8, 0.6, 0.7, 0.9, -	Cu_7Hg_6
3.3, 3.2, 3.2, 3.4, 3.5	Cu_7Hg_6
7.3, 7.1, 6.9, -, -	-
5.9, 6.2, 6.4, -, -	Cu_7Hg_6
4.9, 5.5, 5.7, 6.1, 6.0	Cu_7Hg_6
5.8, 7.0, 6.9, 6.3, -	-
1.7, 1.6, 1.7, 1.8, 1.9	Cu_7Hg_6
2.4, 2.4, 2.4, 2.5, 2.3	Cu_7Hg_6
6.1, 5.7, 6.0, 5.8, 5.7	-
1.6, 1.5, 1.7, 1.5, 1.7	Cu_7Hg_6 + CuSn
1.3, 1.5, 1.4, 1.5, 1.4	Cu_7Hg_6 + CuSn
1.97, 1.85, 2.68, 2.31, 2.34, 5.85	Cu_7Hg_6 + CuSn
3.44, 2.24, 3.04, 3.40, 2.06, 2.36	Cu_7Hg_6 + CuSn

[a] All numbers are correct. The concentrations of Cu and Sn are equilibrium concentrations of these metals in consecutive fractions from the tube.

It is interesting and unexplained why c_{Cu} is commonly a hundred times lower than c_{Sn} and sometimes no precipitation is observed.

COMPONENTS:	EVALUATOR:
(1) Copper-thallium-mercury 3:1:10; Cu_3Hg_4-$TlHg_6$; [104299-24-3] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland July 1988

CRITICAL EVALUATION:

Using anodic stripping with a hanging mercury electrode Zhang et al. (1) determined the stability constant of the intermetallic compound "Cu_3Hg_4:$TlHg_6$=1:1" equal to 4.0×10^4 mol^{-1} dm^3 at room temperature. This would mean that the compound is very soluble in Hg. There are, however, several reservations about the result obtained in (1). The determination of the overall stoichiometry Cu_3TlHg_{10} is not properly documented. The initially proposed formula of the solid phase formed in the Cu-Hg simple system is Cu_3Hg_4, but it should be Cu_7Hg_6. The only compound known in the Tl-Hg system is Tl_2Hg_5 (5). Disrolved Cu and Fl exist in liquid amalgams in the form of separated atoms being effectively solvated by 1-2 atoms of Hg as determined by examination of diffusion coefficients (6). Therefore the stoichiometry proposed above is seriously questionable. Further, Russel et al. (2) performed fractional oxidation with $KMnO_4$ solution of amalgams more concentrated than in (1), and they did not observe any interaction between Cu and Tl. Donten and Kublik (3) carried out Tl anodic stripping experiments on the mercury film electrode with a Cu base and also did not observe either formation of Cu-Tl intermetallic in Hg or at the Cu base. These facts show that, as in the Cu-Tl binary system (4), no intermetallics are formed in the Cu-Tl amalgams. Use of KCl background electrolyte may complicate reduction of Cu(II) and Tl(I).

No value could be selected for recommendation without further investigation.

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COMPONENTS:

(1) Copper-thallium-mercury 3:1:10; Cu_3Hg_4:$TlHg_6$; [104299-24-3]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zhang, Z.X.; Pu, D.B.; Zhu, Q.W.

Acta Chim. Sinica 1986, 44, 460-5.

VARIABLES:

Room temperature measurement

PREPARED BY:

J. Fu; C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The equilibrium constant of the reaction $Cu_3Hg_4 + TlHg_6 = Cu_3Hg_4{:}TlHg_6$ in Hg at 293 K (probably; compilers) was found to be $10^{6.43\pm0.30}$. The value recalculated by the compilers is 4.0×10^{4} mol^{-1} dm^{3}. This suggests that the solubility limit of Cu_3Hg_4:$TlHg_6$ was not reached under the experimental conditions. Note the several objections about the correctness of this work which are described in the Critical Evaluation of this system.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions of Tl(I) and Cu(II) were prepared by dissolution of Tl_2SO_4 and $CuSO_4\cdot5H_2O$, respectively, in H_2O. The electrolytes for the investigation were composed of (1.86-4.10) x 10^{-4} mol dm^{-3} Cu(II) and (0.73-9.5)x10^{-4} mol dm^{-3} Tl(I) in 0.1 mol dm^{-3} KCl. The hanging Hg electrode was introduced into the solution which was freed from O_2 by passing through N_2. Preconcentration electrolysis was carried out at -0.80 V vs. Ag/AgCl/Cl^- for 2 min in the stirred solution. Anodic stripping of Tl from the mixed Cu-Tl amalgam was performed after 30 s of equilibration. The equilibrium constant was calculated from the stripping current.

SOURCE AND PURITY OF MATERIALS:

H_2O: distilled and redistilled from a quartz still. $CuSO_4\cdot5H_2O$, Tl_2SO_4, KCl: all analytically pure reagents.

ESTIMATED ERROR:

Constant: precision ± 50 %.

Temperature: nothing specified.

COMPONENTS:	EVALUATOR:
(1) Copper-zinc 6:1; Cu_6Zn; [56729-83-0] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland December 1983

CRITICAL EVALUATION:

On the basis of careful analysis of potentiometric experiments Stromberg and Belousov (1) found formation of Cu_6Zn in Hg when over ten fold excess of Cu in relation to Zn is present in the amalgam; the solubility product was determined. Also the results of Kozin and coworkers (2) confirm this statement, but no quantitative data are reported. The compound Cu_6Zn is sparingly soluble in Hg and it is not stable above 323 K.

One should remember that the solubility of Cu in Hg is not much higher than the concentration of Cu in equilibrium with solid Cu_6Zn (see the Cu-Hg system). No Cu_6Zn is formed in the binary Cu-Zn alloys (3), so it may be that the compound precipitated in Hg contains Hg as the third component.

Value of the solubility of Cu_6Zn in Hg (tentative)

The solubility product of Cu_6Zn in Hg ($K_s = [Cu]^6[Zn]$) at 293 K is, according to (1):

$$6 \times 10^{-18} \text{ mol}^7 \text{ dm}^{-21}$$

and the solubility, as calculated by evaluators from K_s:

$$7.5 \times 10^{-4} \text{ mol dm}^{-3}$$

References

1. Stromberg, A.G.; Belousov, Yu.P. *Zh. Anal. Khim.* 1975, *30*, 859.
2. Kozin, L.F.; Dergacheva, M.B.; Abramova, N.S. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1970, no. 3, 19.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958; Elliott, R. P. First Supplement, 1965; Shunk, F. A. Second Supplement, 1969.

COMPONENTS:

(1) Copper-zinc 6:1; Cu_6Zn; [56729-83-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Stromberg, A.G.; Belousov, Yu.P.

Zh. Anal. Khim. 1975, *30*, 859-64.

VARIABLES:

Temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of Cu_6Zn (written originally as Cu_3Zn by a misprint) in Hg equals 6.2×10^{-18} mol^7 dm^{-21} at 20 °C. Concentration of Cu was 6.8×10^{-3} mol dm^{-3} and the concentration of Zn was changed in the range 2.4×10^{-4}-5.0×10^{-4} mol dm^{-3}. In the range of higher Zn concentrations Cu_3Zn and CuZn compounds are formed in the system.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgams of Cu and Zn were obtained by constant current electrolysis on the hanging mercury drop electrode with a Pt base. Potentials of the simple Zn amalgam and the complex Cu-Zn amalgam electrodes vs. SCE were measured. After about 700 s from the end of the electrolysis, when the equilibrium in the system was reached, anodic currents of Zn dissolution under stationary voltammetric conditions were recorded. The solubility product was calculated from the potential differences and the oxidation currents. The experiments were performed in an Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Analytically pure reagents were used. Hg was obtained by electrolysis of $Hg_2(NO_3)_2$. Triply distilled H_2O was used.

ESTIMATED ERROR:

Nothing specified. Solubility product: due to high power of the value precision may be ± 50-100 % (compilers).

COMPONENTS:	EVALUATOR:
(1) Copper-zinc 3:1; Cu_3Zn; [12444-36-9] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland December 1982

CRITICAL EVALUATION:

According to Stromberg and Belousov (1) insoluble Cu_3Zn may be formed when over three fold excess of Cu in relation to Zn is present in the amalgam. The authors determined its solubility product, $K_s = [Cu]^3[Zn]$. The potentiometric results of Kozin and coworkers (2) qualitatively confirm this statement.

Russell and coworkers (3) performed chemical analyses on the solid phases precipitated in the Cu-Zn-Hg system and found two compounds present: Cu_3ZnHg_2 and $Cu_3ZnHg_{0.5}$. Transformation of the first form into the second one occurs at 373 K.

Cu_3Zn is formed in the binary Cu-Zn alloys (4).

Value of the solubility of Cu_3Zn in Hg (tentative)

The solubility product of Cu_3Zn in Hg at 293 K is, according to (1):

$$3\times10^{-11}\ mol^4\ dm^{-12}$$

and the solubility, as calculated by evaluators from K_s:

$$1\times10^{-3}\ mol\ dm^{-3}$$

References

1. Stromberg, A.G.; Belousov, Yu.P. *Zh. Anal. Khim.* 1975, *30*, 859.
2. Kozin, L.F.; Dergacheva, M.B.; Abramova, N.S. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1970, no. 3, 19.
3. Russell, A.S.; Cazalet, P.V.F.; Irvin, N.M. *J. Chem. Soc.* 1932, 852.
4. Elliott, R.P. *Constitution of Binary Alloys*, First Supplement, McGraw-Hill, New York, 1965.

COMPONENTS:

(1) Copper-zinc 3:1; Cu_3Zn; [12444-36-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Stromberg, A.G.; Belousov, Yu.P.

Zh. Anal. Khim. 1975, *30*, 859-64.

VARIABLES:

Temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of Cu_3Zn in Hg at 293 K is 3.1×10^{-11} mol^4 dm^{-12}. The concentration of Cu was 6.8×10^{-3} mol dm^{-3} and the concentration of Zn was changed in the range 5.0×10^{-4}-2.5×10^{-3} mol dm^{-3}.

In the range of higher Zn concentrations CuZn is formed, while at lower Zn concentrations Cu_6Zn is found.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgams of Cu and Zn were obtained by constant current electrolysis on hanging mercury drop electrodes with a Pt base. Potentials of Zn and Cu-Zn amalgam electrodes vs. SCE were measured after the end of the electrolysis. After equilibrium in the system was reached (after 700 s of waiting), anodic currents of Zn dissolution under stationary voltammetric conditions were recorded. The solubility product was calculated from the potential differences and oxidation currents. The experiments were performed in an Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Analytically pure reagents were used. Hg was obtained by electrolysis of $Hg_2(NO_3)_2$. Triply distilled H_2O was used.

ESTIMATED ERROR:

Nothing specified. Solubility product: precision ± 50 % (by compilers).

COMPONENTS:	EVALUATOR:
(1) Copper-zinc 1:1; CuZn; [12019-27-1] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland December 1984

CRITICAL EVALUATION:

Almost 90 years ago Humphreys (26) noticed that the alloy $Cu_{54}Zn_{46}$ does not dissolve in measurable amounts in Hg. In the first potentiometric experiments (1, 2) on the Cu-Zn-Hg system no significant interaction between Cu and Zn was found. However, subsequent work performed with the use of the same technique (3-9) supplied proof that CuZn is formed in Hg as a solid. Numerical data of the solubility product, $K_s = [Cu][Zn]$; expressed in $mol^2\ dm^{-6}$ are reported in the following work: Zebreva (5), 4.4×10^{-6} at 298 K; Dergacheva in an unpublished thesis (6), 2.5×10^{-6} and 1.2×10^{-5} at 298 and 323 K respectively; Kozin and coworkers (7), 4.0×10^{-6} at 298 K; Stromberg and Belousov (8), 3.0×10^{-6} at 293 K; Ostapczuk and Kublik (9), 5.1×10^{-6} at 298 K. Stromberg and coworkers (24) elaborated the data of (7) with their own method and obtained the result of K_s equal to $2.6 \times 10^{-6}\ mol^2\ dm^{-6}$ at 298 K. These values agree quite well except that of Kozin (4); his original K_s values changed in the range 7.1×10^{-8} - $2.8 \times 10^{-5}\ mol^2\ dm^{-6}$ and the proposed dissociation constant, $K_d = [Cu][Zn]/[CuZn]$, also changed from 1×10^{-3} to $4.2 \times 10^{-3}\ mol\ dm^{-3}$. Such discrepancies are due to neglecting the poor solubility of Cu in Hg, corrosion of Zn at low concentration, and formation of other compounds in the Cu-Zn-Hg system under these experimental conditions. Giving no details, Kozin (4) calculated $K_s = 1.21 \times 10^{-6}\ mol^2\ dm^{-6}$ at room temperature based on the amalgam polarography experiments of Zebreva and Kozlovskii (18). Less consistent are results obtained from anodic stripping voltammetry. Stromberg and Gorodovykh (10) determined the solubility product of CuZn in Hg to be as low as $5 \times 10^{-8}\ mol^2\ dm^{-6}$ at room temperature. This value was afterwards corrected by Stromberg and coworkers (11-13) subsequently to 2×10^{-6} and then to 1×10^{-6}. Bradford (14) used the thin film mercury electrode in his experiments; he concluded that the intermetallic compound has dissociation constant equal to $1 \times 10^{-5}\ mol\ dm^{-3}$ at room temperature. Using the hanging mercury drop as well as film mercury electrodes Shuman and Woodward (15) determined the instability constant, $1.9 \times 10^{-3}\ mol\ dm^{-3}$, and the solubility product, $3.7 \times 10^{-6}\ mol^2\ dm^{-6}$, at room temperature. Nevertheless, the last authors suggested that CuZn is soluble in Hg but poorly dissociated. Ostapczuk and Kublik (9) observed an increase of the solubility product from 5.4×10^{-6} to $7.2 \times 10^{-6}\ mol^2\ dm^{-6}$ when the scan rate decreased from 25 to 2.1 $mV\ s^{-1}$; this fact may explain partly why in (15) the solubility constant is more nearly constant than the instability constant. Nazarov (23) found formation of insoluble CuZn using stripping chronoamperometry; no quantitative data were generated. Igolinskaya and Igolinskii (25) reported that they confirmed the value of work (13) by stripping chronopotentiometry on the thin film mercury electrode, but no numerical results are given. Rudolph (16), using voltammetry on the stationary mercury electrode, found CuZn to be formed. Assuming that it is sparingly soluble in Hg he calculated the solubility product equal to $6.6 \times 10^{-6}\ mol^2\ dm^{-6}$ at room temperature. Other electroanalytical investigations of Rodgers and Meites (21), Ma and coworkers (29), Ben-Bassatt and coworkers (27) as well as Lazar and coworkers (22) confirm formation of solid CuZn, but they point out the complexity of the system. Some of these authors suggest occurrence of other compounds in addition to with excess of Zn or Cu. The solubility product values of CuZn in Hg at 298 K were confirmed to be 3.8×10^{-6} (21) and $2.9 \times 10^{-6}\ mol^2\ dm^{-6}$ (29).

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Copper-zinc 1:1; CuZn; [12019-27-1] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland December 1984

CRITICAL EVALUATION (continued)

In conclusion, the solubility product data found in the referred works are in much better agreement than the dissociation constants. No data sheets of papers (1-3, 5, 6, 10, 11, 14, 16-20, 22, 23, 26-28, 30, 32) are prepared since they do not contain original numerical data and experimental details or are unavailable to the compilers. To clarify the nature of CuZn in Hg we should mention that the potentiometric method is more exact in such studies than the electroanalytical techniques, since the methods based on an electrolysis may disturb the equilibrium conditions to a significant degree. Moreover, other compounds such as Cu_6Zn (8), Cu_3Zn (8), Cu_5Zn_2 (22), Cu_3ZnHg_2 (32), $Cu_3ZnHg_{0.5}$ (32), Cu_5Zn_8 (4), $CuZn_2$ (15), $CuZn_3$ (4, 15), $CuZn_4$ (4), $CuZn_6$ (28), $Cu_xZn_{0-6}Hg_z$ (27) may be formed in the amalgams. An interference of these forms may give the impression of the existence of soluble CuZn in Hg. On the basis of chemical analysis (3, 7) and calorimetry (19, 20) it was stated that this compound exists as a solid in Hg, and the majority of electrochemical works cited above are in agreement with this statement. According to Kozin and Dergacheva (17) CuZn exists in soluble as well as solid forms being in the mutual equilibrium. $Cu + Zn \overset{Hg}{\rightleftharpoons} CuZn \overset{Hg}{\rightleftharpoons} CuZn \downarrow$. Kozin and coworkers (7) determined the K_s values in the temperature range 298 - 363 K. Compilers constructed an equation relating pK_s vs. $1/T$, with the use of data in (5-9, 12, 15, 21, 24, 29), based on the least square method:

$$pK_s = -5.08 + 3.15 \times 10^3\ T^{-1} \qquad r = 0.98 \qquad (T/K;\ K_s/mol^2\ dm^{-6})$$

Kinetics of formation (7) and dissociation (17, 30) of CuZn in Hg were also investigated. The phase CuZn, with small excess of Cu, is stable in the Cu-Zn binary system (31).

Zhang et al. (33) performed stripping analysis of mixed Cu-Zn amalgams and found an equilibrium constant of CuZn in Hg equal to 2.7×10^6 $mol^{-1}\ dm^3$. This value is significantly higher than the values estimated in (4, 14, 15). It seems that the equilibration time was not long enough to reach true equilibrium in the system, which may explain this high result (33).

Piccardi and Udisti (34) also carried out stripping voltammetry experiments and found a K_s-value of CuZn in Hg as high as 5×10^{-4} $mol^2\ dm^{-6}$ at 298 K. This value is obviously too high in spite of the fact that the experimental conditions were quite similar to those of the numerous measurements performed in other laboratories. The paper is rejected and not compiled (the experimental procedure is the same as in the Data Sheet of $CuZn_2$ in Hg by the same authors).

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Copper-zinc 1:1; CuZn; [12019-27-1] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland December 1984

CRITICAL EVALUATION (continued)

Values of the solubility of CuZn in Hg

T/K	$K_s/\text{mol}^2\ \text{dm}^{-6}$	soly/mol dm^{-1} [c]	Refer.
293	2.2×10^{-6}	1.5×10^{-3}	from the fitting equation
298	3.3×10^{-6}	1.8×10^{-3}	(5-9, 12, 15, 21, 24, 29) mean value as well as the fitting equation
323	2.2×10^{-5} [b]	4.7×10^{-3}	(7, 8) mean value as well as the fitting equation
348	1.2×10^{-4} [b]	1.1×10^{-2}	(7) also the fitting equation
363	2.8×10^{-4} [b]	1.7×10^{-2}	(7)

[a] recommended.

[b] tentative.

[c] calculated by evaluators from K_s.

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5. Zebreva, A.I. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1967, *15*, 54.
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17. Kozin, L.F.; Dergacheva, M.B. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1972, *3*, 31.

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COMPONENTS:	EVALUATOR:
(1) Copper-zinc 1:1; CuZn; [12019-27-1] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland December 1984

CRITICAL EVALUATION (continued)

18. Zebreva, A.I.; Kozlovskii, M.T. *Zh. Fiz. Khim.* 1956, *30*, 1553.
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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper-zinc 1:1; CuZn; [12019-27-1] (2) Mercury; Hg; [7439-97-6]	Kozin, L.F. *Fiziko-Khimicheskie Osnovy Amalgamnoi Metallurgii, Nauka, Alma-Ata,* 1964, p. 182-7.
VARIABLES:	**PREPARED BY:**
Temperature: 298 K	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound CuZn is treated as soluble in Hg because the dissociation constant (K_d) has a more immutable value than that of the solubility product (K_s). The value of K_d changes from $3x10^{-4}$ to $8x10^{-3}$ mol dm^{-3}, whereas the value of K_s changes from $7.1x10^{-8}$ to $2.8x10^{-5}$ mol^2 dm^{-6}. The proposed mean value of K_d at 25 °C is $2.5x10^{-3}$ mol dm^{-3}.

$c_{Cu}{}^i$/ mol dm^{-3}	$10^4 c_{Zn}{}^i$/ mol dm^{-3}	$10^4 c_{Zn}{}^f$/ mol dm^{-3}	K_s/ mol^2 dm^{-6}	K_d/ mol dm^{-3}
$3.3x10^{-2}$	0.77	0.0216	$7.1 \cdot 10^{-8}$	$0.94 \cdot 10^{-3}$
	2.18	0.108	$3.54 \cdot 10^{-7}$	$1.72 \cdot 10^{-3}$
	2.97	0.121	$3.95 \cdot 10^{-7}$	$1.30 \cdot 10^{-3}$
	3.75	0.128	$4.17 \cdot 10^{-7}$	$1.15 \cdot 10^{-3}$
	4.55	0.120	$3.90 \cdot 10^{-7}$	$0.88 \cdot 10^{-3}$
	7.70	0.155	$4.99 \cdot 10^{-7}$	$0.66 \cdot 10^{-3}$
	10.90	0.810	$2.59 \cdot 10^{-6}$	$2.56 \cdot 10^{-3}$
	16.5	4.45	$1.42 \cdot 10^{-5}$	$1.17 \cdot 10^{-3}$
	35.9	6.75	$2.03 \cdot 10^{-5}$	$7.00 \cdot 10^{-3}$

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Differences of potentials between simple Zn and complex Cu-Zn amalgams in half saturated solutions of $ZnSO_4$ were measured. The Zn content in both electrodes was always equal. The values of K_s and K_d were calculated from the potential differences and mass balance.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Zebreva, A.I. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1967, *15*, 54.
2. Stromberg, A.G.; Belousov, Yu.P. *Zh. Anal. Khim.* 1975, *30*, 859.
3. Zebreva, A.J.; Kozlovskii, M.T. *Zh. Fiz. Khim.* 1956, *30*, 1553.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper-zinc 1:1; CuZn; [12019-27-1] (2) Mercury; Hg; [7439-97-6]	Kozin, L.F. *Fiziko-Khimicheskie Osnovy Amalgamnoi Metallurgii*, *Nauka*, *Alma-Ata*, 1964, p. 182-7.

EXPERIMENTAL VALUES (continued)

$c_{Cu}{}^{i}$/ mol dm^{-3}	$10^4 c_{Zn}{}^{i}$/ mol dm^{-3}	$10^4 c_{Zn}{}^{f}$/ mol dm^{-3}	K_s/ mol^2 dm^{-6}	K_d/ mol dm^{-3}
	45.0	6.28	$1.82 \cdot 10^{-5}$	$4.70 \cdot 10^{-3}$
	64.0	6.00	$1.63 \cdot 10^{-5}$	$2.80 \cdot 10^{-3}$
	93.0	6.00	$1.45 \cdot 10^{-5}$	$1.67 \cdot 10^{-3}$
	185.0	6.00	$0.90 \cdot 10^{-5}$	$0.50 \cdot 10^{-3}$
	340.0	49.9	$1.99 \cdot 10^{-5}$	$0.68 \cdot 10^{-3}$
	640.0	365.0	$2.00 \cdot 10^{-4}$	$7.00 \cdot 10^{-3}$
	870.0	564.0	$1.35 \cdot 10^{-4}$	$4.40 \cdot 10^{-3}$
		mean values (authors)	2.82×10^{-5}	2.4×10^{-3}
7.4×10^{-3}	0.80	0.236	$17.5 \cdot 10^{-8}$	$2.8 \cdot 10^{-3}$
	3.12	1.28	$9.2 \cdot 10^{-7}$	$5.1 \cdot 10^{-3}$
	3.91	1.21	$8.6 \cdot 10^{-7}$	$3.1 \cdot 10^{-3}$
	5.45	2.02	$1.4 \cdot 10^{-6}$	$4.1 \cdot 10^{-3}$
	7.10	3.10	$2.2 \cdot 10^{-6}$	$5.6 \cdot 10^{-3}$
	14.8	8.10	$5.4 \cdot 10^{-6}$	$7.9 \cdot 10^{-3}$
	22.1	8.7	$5.3 \cdot 10^{-6}$	$3.9 \cdot 10^{-3}$
	32.8	8.7	$4.3 \cdot 10^{-6}$	$1.8 \cdot 10^{-3}$
	50.1	8.1	$2.5 \cdot 10^{-6}$	$0.6 \cdot 10^{-3}$
	65.0	10.1	$1.9 \cdot 10^{-6}$	$0.4 \cdot 10^{-3}$
	70.3	20.5	$4.9 \cdot 10^{-6}$	$1.0 \cdot 10^{-3}$
	120	58	$7.0 \cdot 10^{-6}$	$1.1 \cdot 10^{-3}$
	170	108	$1.3 \cdot 10^{-5}$	$2.1 \cdot 10^{-3}$
	190	121	$0.6 \cdot 10^{-5}$	$0.9 \cdot 10^{-3}$
	280	202	$-0.8 \cdot 10^{-5}$ [a]	$0.2 \cdot 10^{-3}$
	450	290	$-24.9 \cdot 10^{-5}$ [a]	$1.6 \cdot 10^{-3}$
	537	405	$-23.5 \cdot 10^{-5}$ [a]	$1.8 \cdot 10^{-3}$
		mean values (authors)	3.98×10^{-6}	2.6×10^{-3}

[a] rejected

Elaborating on their own results, the authors did not consider the influence of the rather poor solubility of Cu in Hg; for example the 3.8×10^{-2} mol dm^{-3} Cu amalgam used was heterogeneous. For 1.4×10^{-3} mol dm^{-3} Cu amalgam, no difference of potentials between the Cu-Zn and Zn amalgam electrodes occurred. This may indicate that there is no precipitation of solid CuZn, but, on the other hand, formation of soluble CuZn should cause some difference of potentials. For higher concentrations of Cu in the amalgam the

(continued next page)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper-zinc 1:1; CuZn; [12019-27-1] (2) Mercury; Hg; [7439-97-6]	Kozin, L.F. *Fiziko-Khimicheskie Osnovy Amalgamnoi Metallurgii, Nauka, Alma-Ata*, 1964, p. 182-7.

EXPERIMENTAL VALUES (continued)

potentiometric curves show 2 humps connected with formation of CuZn and a compound richer in Cu. On the basis of these experimental results the solubility product, which seems to be the correct thermodynamic value for the system, was calculated by other authors. Recalculations of Zebreva (1) give $(4.4\pm0.5)\times10^{-6}$ and $(3.8\pm1.5)\times10^{-6}$ mol^2 dm^{-6} for 3.3×10^{-2} and 7.4×10^{-3} mol dm^{-3} Cu amalgam, respectively. Recalculations of Stromberg and Belousov (2) resulted in the value 3.1×10^{-6} mol^2 dm^{-6}. They suggested also that for low Zn concentrations some corrosive oxidation of the amalgam is quite possible. It may simulate the formation of other Cu-Zn compounds and makes K_s values much lower. The solubility product calculated by the author from experiments of Zebreva and Kozlovskii (3) is reported as 1.21×10^{-6} mol^2 dm^{-6} at room temperature.

COMPONENTS:

(1) Copper-zinc 1:1; CuZn; [12019-27-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Mesyats, N.A.; Stromberg, A.G.;
Zakharov, M.S.
Elektrokhimia 1968, 4, 987-90.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of CuZn in Hg was determined under different conditions.

$c_{Zn(II)}$/mol dm^{-3}	$c_{Cu(II)}$/mol dm^{-3}	time of preelectrolysis/min	K_s/mol^2 dm^{-6}
5x10^{-5}	5x10^{-5}	3-21	2x10^{-6}
5x10^{-5}	1.0x10^{-4}		
5x10^{-5}	(5-9)x10^{-5}	3-18	1x10^{-6}

The same results are reported in (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Anodic stripping voltammetry was used. The supporting electrolyte contained 0.05 mol dm^{-3} ammonium tartrate and 0.25 mol dm^{-3} acetate ion. Time of accumulative preelectrolysis was changed from 180 to 1260 s. Anodic oxidation of the complex Cu-Zn amalgams was performed using various scan rates between 1 and 0.014 V s^{-1}. The solubility product was calculated from the oxidation current peaks of the metals.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified. Solubility product: precision no better than ± 50 % (by compilers).

REFERENCES:

1. Mesyats, N.A.; Zakharov, M.S. *Izv. Tomsk. Politekhn. Just.* 1971, *174*, 69.

COMPONENTS:

(1) Copper-zinc 1:1; CuZn; [12019-27-1]
(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kozin, L.F.; Dergacheva, M.B.; Abramova, N.S.
Izv. Akad. Nauk Kaz. SSR, Ser. Khim. 1970, no. 3, 19-24.

VARIABLES:

Temperature: 297-363 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound CuZn is treated as sparingly soluble in Hg and its equilibrium is described by the solubility product. Initial Zn concentration is changed from 2.5x10^{-5} to 1.85x10^{-2} mol dm^{-3}

t/°C	c_{Cu}^{1}/mol dm^{-3}	K_s/mol^2 dm^{-6}
25	3.4x10^{-3}	(2.5±0.3)x10^{-6}
	6.8x10^{-3}	(4.3±0.5)x10^{-6}
	3.4x10^{-2} [a]	(5.3±0.1)x10^{-6}
50	6.8x10^{-3}	(9.4±0.3)x10^{-6}
	3.4x10^{-2}	(4.6±0.9)x10^{-5}
75	6.8x10^{-3}	(2.4±0.4)x10^{-6} [b]
	3.4x10^{-2}	(1.2±0.4)x10^{-4}
90	3.4x10^{-2}	(2.8±0.6)x10^{-4}

[a] amalgam is heterogeneous (compilers).

[b] erroneous, a misprint (?).

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Differences of potential between simple Zn and complex Cu-Zn amalgams in a solution of $ZnSO_4$ were measured. The solubility products were calculated from these differences. Moreover, various fractions of the complex heterogeneous amalgam placed in a capillary for a longer time of 1-2 months were analyzed by polarography after decomposition of the amalgam.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility product: precision no better than ± 2 % but typically ± 10 %.
Reproducibility of potentials ± 1 mV.

REFERENCES:

1. Stromberg, A.G.; Belousov, Yu.P. *Zh. Anal. Khim.* 1975, *30*, 859.
2. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1974, *7*, 42.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper-zinc 1:1; CuZn; [12019-27-1] (2) Mercury; Hg; [7439-97-6]	Kozin, L.F.; Dergacheva, M.B.; Abramova, N.S. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1970, no. 3, 19-24.

EXPERIMENTAL VALUES (continued)

Dependence of pK_s on $1/T$ based on the method of weighted least squares linear regression, as calculated by compilers, is expressed by the following equation:

$$pK_s = -(4.21 \pm 0.75) + (2.83 \pm 0.23) \times 10^3 T^{-1} \qquad (K_s/\mathrm{mol}^2\mathrm{dm}^{-6};\ T/\mathrm{K})$$

The value of the solubility product of CuZn in Hg, 2.0 ± 10^{-6} mol^2 dm^{-6} at 24 °C, obtained on the basis of phase separation analysis, is similar but not as precise as the one obtained with the use of potentiometry. It is evident on the potentiometric curves that other compounds in the Cu-rich amalgams should be present. According to the elaboration of Stromberg and Belousov (1), sparingly soluble compounds Cu_3Zn and Cu_6Zn are then formed; the latter is unstable at higher temperature. Stromberg and coworkers (2) calculated the solubility product with their own procedure using the data from this work. They obtained 2.6×10^{-6} and 1.15×10^{-5} mol^2 dm^{-6} at 298 and 323 K, respectively.

COMPONENTS:

(1) Copper-zinc 1:1; CuZn; [12019-27-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Stromberg, A.G.; Belousov, Yu.P.

Zh. Anal. Khim. 1975, *30*, 859-64.

VARIABLES:

Temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of CuZn in Hg at 293 K is 2.6×10^{-6} and 3.4×10^{-6} mol^2 dm^{-6} for concentrations of Cu 3.4×10^{-3} and 6.8×10^{-3} mol dm^{-3}, respectively with the concentration of Zn changed from 2.4×10^{-4} to 1.7×10^{-2} mol dm^{-3}.

In the range of low Zn concentrations Cu_3Zn and Cu_6Zn intermetallics are formed.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgams of Cu and Zn were obtained by electrolysis. Potentials of Zn and Cu-Zn amalgam electrodes vs. SCE were measured. When the equilibrium potentials were reached, 700 s after stopping the electrolysis, anodic currents of Zn dissolution under voltammetric conditions were recorded. The solubility product was calculated from the potential differences and additionally confirmed by voltammetric oxidation. The experiments were performed in an Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Analytically pure reagents were used. Hg was obtained by electrolysis of $Hg_2(NO_3)_2$. Triply distilled H_2O was used.

ESTIMATED ERROR:

Solubility product: precision no better than ± 10 % (compilers). Temperature: nothing specified.

COMPONENTS: (1) Copper-zinc 1:1; CuZn; [12019-27-1] (2) Mercury; Hg; [7439-97-6]	ORIGINAL MEASUREMENTS: Shuman, M.S.; Woodward, G.P. *Anal. Chem.* 1976, *48*, 1979-83.
VARIABLES: Room temperature measurement	PREPARED BY: C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound CuZn in Hg is treated as soluble but poorly dissociated. The instability constant is $(1.9\pm0.2)\times10^{-3}$ mol dm^{-3} at room temperature. Moreover, the solubility product value is reported to be $(3.7\pm1.1)\times10^{-6}$ mol^{2} dm^{-6}.

Formation of other compounds is proposed: soluble $CuZn_2$ and insoluble $CuZn_3$; but their existence in Hg is not documented sufficiently. It is not evident whether an equilibrium state was reached before the stripping step. It seems erroneous to fit these cyclic voltammetry curves to the theory for higher order electrode processes (1) when the reaction between Cu and Zn is rate-limited in the crystallization step and follows the electroreduction of Zn(II) on Cu amalgam.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Anodic stripping voltammetry was used. The thin mercury film on glassy carbon and hanging mercury drop (Metrohm) electrodes were used. The preelectrolysis was carried out at -1.25 V vs. SCE for 1-10 minutes. After that, the electrodes were linearly polarized to +0.15 V. Supporting electrolytes used were 0.05 mol dm^{-3} acetate buffer pH = 4.5 in the thin film and 0.1 mol dm^{-3} KBr in the hanging drop electrode experiments. The K_d and K_s were calculated from the oxidation currents and mass balance equations.	SOURCE AND PURITY OF MATERIALS: Solutions of Cu(II) and Zn(II) were prepared from the metals. Glassy carbon was from Chemitrix Corp. No more specified. ESTIMATED ERROR: Solubility product: precision no better than ± 30 %. REFERENCES: 1. Shuman, M.S. *Anal. Chem.* 1969, *41*, 142.

COMPONENTS:

(1) Copper-zinc 1:1; CuZn; [12019-27-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Ostapczuk, P.; Kublik, Z.

J. Electroanal. Chem. 1977, *83*, 1-17.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

On the basis of potentiometric measurements the solubility product of CuZn in Hg was determined to be $(5.1\pm0.8)\times10^{-6}$ mol^2 dm^{-6} at 298 K. The concentration of Cu in the amalgam was 7.3×10^{-3} mol dm^{-3} (saturated). The concentration of Zn was changed from 1.4×10^{-4} to 2.8×10^{-2} mol dm^{-3}.

On the basis of stripping voltammetry experiments, the solubility product value decreased on decreasing the scan rate from 2.1 to 5.4 mV s^{-1}. The proposed value is 5.4×10^{-6} mol^2 dm^{-6}, because at the higher scan rate the partial dissolution of the solid intermetallic near the Hg surface is lower.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Cu amalgam was prepared by its dissolution in Hg. Equal portions of Zn were introduced by electrolysis into the hanging mercury drop electrode and the hanging copper amalgam electrode. Potentials of both electrodes vs. SCE were measured in time. Anodic stripping voltammetry curves were recorded after 150 s from the deposition of Zn at -1.2 V from a solution of 10^{-4} mol dm^{-3} $ZnSO_4$, 0.5 mol dm^{-3} KCl, pH = 3. The solubility products were calculated from the potential differences and the oxidation currents from voltammetry.

SOURCE AND PURITY OF MATERIALS:

Spectrally pure Cu, triply distilled H_2O, twicely distilled Hg and analytically pure reagents from POCh were used.

ESTIMATED ERROR:

Solubility product: precision ± 15 % in the potentiometry (private communication).

Temperature: ± 0.2 K.

COMPONENTS:

(1) Copper-zinc 1:1; CuZn; [12019-27-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Rodgers, R.S.; Meites, L.

J. Electroanal. Chem. 1981, *125*, 167-76.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of CuZn in Hg at 298.2 K is (3.8±0.6)x10^{-6} mol^2 dm^{-6}, as overall average.

$10^3 c_{Zn}{}^i$/ mol dm^{-3}	$10^3 c_{Cu}{}^i$/ mol dm^{-3}	$10^3 c_{Zn}{}^f$/ mol dm^{-3}	$10^3 c_{Cu}{}^f$/ mol dm^{-3}	10^6 K_{CuZn}/mol^2 dm^{-6}
12.64	16.28	1.06	4.71	5.0
	10.87	3.31	1.54	5.1
	2.72	10.3	0.37	3.8
6.32	5.43	2.43	1.54	3.7
	2.72	4.53	0.93	4.2
	1.36	5.39	0.43	2.3
3.16	4.07	1.19	2.10	2.5
	2.72	2.26	1.81	4.1
1.57	2.72	1.04	2.19	2.3
	1.34	1.57	1.34	---
				Mean: 3.7±0.9

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The complex Cu-Zn amalgams were obtained by electroreduction of the ions under potentiostatic conditions. Stock solutions of Cu(II) and Zn(II) were standardized by conventional techniques. The amalgams were oxidized with constant current and potentials were recorded. Complementary stripping convective chronoamperometry experiments were also performed.

SOURCE AND PURITY OF MATERIALS:

Reagents grade chemicals were used.

ESTIMATED ERROR:

Solubility product: precision ± 15 %.

Temperature: ± 0.05 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper-zinc 1:1; CuZn; [12019-27-1] (2) Mercury; Hg; [7439-97-6]	Rodgers, R.S.; Meites, L. *J. Electroanal. Chem.* 1981, *125*, 167-76.

EXPERIMENTAL VALUES (continued)

On the same basis, the constant concentration of unbonded Zn (0.58 ± 0.05 mmol dm^{-3}) in amalgams saturated with Cu may be combined with the solubility of Cu in Hg to obtain K_s = $(4.0 \pm 0.3) \times 10^{-6}$ $mol^2\ dm^{-6}$. Some complementary chronoamperometric experiments showed that soluble forms of Cu-Zn compounds, apart from CuZn, are also formed in the amalgam system with excess of Cu or Zn. The solubility value used for Cu in Hg (6.85×10^{-3} mol dm^{-3}) was originally determined at 288 K; however, this value is acceptable at 298 K according to our evaluation; see the Cu-Hg system.

COMPONENTS:

(1) Copper-zinc 1:1; CuZn; [12019-27-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Ma, X.S.; Kao, H.; Chang, C.G.

J. Electroanal. Chem. 1983, *151*, 179-92.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of CuZn in Hg at 25 °C is 2.9×10^{-6} mol^2 dm^{-6}. Concentrations of Cu and Zn were changed in the ranges $(0.22\text{-}3.30)\times10^{-3}$ mol dm^{-3} and $(0.81\text{-}3.83)\times10^{-3}$ mol dm^{-3}, respectively.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Cu amalgam was prepared by electrolysis on an Hg cathode from $(1.0 - 4.5)\times10^{-4}$ mol/dm^3 $CuSO_4$, 0.3 mol/dm^3 triethyloamine (sic) and 0.1 mol/dm^3 NaOH. The Zn amalgam was prepared by electrolysis on an Hg cathode from $(1.0 - 4.0)\times10^{-4}$ mol/dm^3 $ZnCl_2$ and 1 mol/dm^3 NaOH. Both amalgams were mixed, aged 3-5 min, and hanging drop electrodes were prepared. Electrooxidation of Zn from the complex amalgam was carried out under chronoamperometric conditions at -0.8 V. When the product of the concentrations of Cu and Zn was higher than the value of the solubility product reported above, the diffusion coefficient of Zn decreased and the oxidation curves were distorted. This decrease is caused by the precipitation of CuZn in Hg.

SOURCE AND PURITY OF MATERIALS:

Analytical reagents were used without further purification.

ESTIMATED ERROR:

Standard deviation of diffusion coefficient determination 4 %; solubility: precision no better than ± 10 % (by compilers).

Temperature: nothing specified.

COMPONENTS:

(1) Copper-zinc 1:1; CuZn; [12019-27-1]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zhang, Z.X.; Pu, D.B.; Zhu, Q.W.

Acta Chim. Sinica 1986, *44*, 460-5.

VARIABLES:

Room temperature measurement

PREPARED BY:

J. Fu; C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The equilibrium constant of the reaction Cu + Zn $\rightleftharpoons$ CuZn in mercury was found to be $10^{8.27\pm0.03}$ (probably at 293 K). The value recalculated by the compilers is $2.7\text{x}10^6$ mol^{-1} dm^3. This suggests that the solubility of CuZn was not reached under the experimental conditions.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A solution of Cu(II) was prepared by dissolution of $CuSO_4\cdot5H_2O$ in H_2O. The solution of Zn(II) was prepared by dissolution of metallic Zn in HCl. The electrolyte for investigation was composed of $7.78\text{x}10^{-6}$ mol dm^{-3} Cu(II) and $(0.8\text{-}7.2)\text{x}10^{-6}$ mol dm^{-3} Zn(II) in 0.1 mol dm^{-3} NH_3 + NH_4Cl. The hanging mercury electrode was introduced into the solution which was freed from O_2 by passing through N_2. Preconcentration electrolysis was carried out at -1.30 V vs. Ag/AgCl/Cl^- for 2 min in a stirred solution. The anodic stripping of Zn from the mixed Cu-Zn amalgam was performed after 30 s of equilibration. The equilibrium constant was calculated from the stripping current using the proper formula.

SOURCE AND PURITY OF MATERIALS:

H_2O: distilled and redistilled from a quartz still.

$CuSO_4\cdot5H_2O$, Zn, HCl, NH_4Cl, NH_3: all analytically pure reagents.

ESTIMATED ERROR:

Stability constant: ± 7 %.

Temperature: nothing specified.

COMPONENTS:	EVALUATOR:
(1) Copper-zinc 1:2; $CuZn_2$; [12174-82-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland December 1986

CRITICAL EVALUATION:

Formation of $CuZn_2$ in Hg was first reported by Speranskaya (1). On the basis of coulometric stripping voltammetry, Shuman and Woodward (2) also postulated formation in the Cu-Zn amalgam of soluble $CuZn_2$ and other compounds. The instability constant of $CuZn_2$ in Hg, K_d = [CuZn][Zn]/[$CuZn_2$], was evaluated to be 7.6×10^{-3} mol dm^{-3}. However, the compilers have reservations as to the fitting procedure applied by the authors. Since the reaction is not fast, it is not clear whether equilibrium in the system was reached after the deposition of Zn on the Cu amalgam electrode and how far the equilibrium was disturbed during the oxidation step. The temperature of the measurement is not stated, so any quantitative values can not be recommended. The paper (2) is not compiled but all experimental details were the same as in the Data Sheet of this paper given for the $CuZn_3$-Hg system. The compound Cu_5Zn_8 is formed rather than $CuZn_2$ in the corresponding composition range of the Cu-Zn binary system (3-5).

Formation of $CuZn_2$, very soluble in Hg, was reported by Piccardi and Udisti (6). The authors determined the stability constant of this compound as K = [$CuZn_2$]/[Cu][Zn]^2 = 100 mol^{-2} dm^6. Note that the numerical results of (2) and (6) only do not agree, since the definition of the constants is different.

References

1. Speranskaya, E.F. *Zh. Anal. Khim.* 1956, *11*, 323.
2. Shuman, M.S.; Woodward, G.P. *Anal. Chem.* 1976, *48*, 1979.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
4. Simic, V.; Marinkovic, Z. *J. Less-Common Met.* 1986, *116*, L7.
5. Kozin, L.F. *Fiziko-Khimicheskie Osnovy Amalgamnoi Metallurgii*, Nauka, Alma-Ata, 1964, p. 186.

COMPONENTS:

(1) Copper-zinc 1:2; $CuZn_2$; [12174-82-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Piccardi, G.; Udisti, R.

Anal. Chim. Acta 1987, *202*, 151-7.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The stability constant, K = $[CuZn_2]/[Cu][Zn]^2$, of soluble $CuZn_2$ was determined to be 100 mol^{-2} dm^6 at 298 K. Soluble $CuZn_2$ is formed as well as CuZn precipitate in Hg. Considering CuZn soluble and $CuZn_2$ insoluble, or both compounds soluble, provided less satisfactory fits.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A mercury film electrode was prepared on a glassy carbon electrode by plating from Hg(II) acetate at -1.0 V for 20 min and then held at -0.1 V for 5 min. The electrode was kept at -0.1 V for 1 min before each experiment. Volume of Hg was calculated from the oxidation charge in KI solution at -0.1 V. The reference electrode was the SCE (to which all potentials are referred) and the auxiliary electrode was a paraffin-impregnated graphite rod. All solutions were deoxygenated with N_2. Stripping voltammetry was applied for determination of Cu and Zn concentrations. The supporting electrolyte for Cu(II) and Zn(II) contained 3 mass % NaCl and $5x10^{-3}$ mol dm^{-3} EDTA. The total and free Zn concentrations in Hg were estimated from charges of the current peaks at -1.11 V in the absence of Cu and with increasing concentration of Cu. The total and free concentrations of Cu were estimated from charges of current peaks at -0.33 V after deposition at -0.85 V and -1.4 V, respectively. Concentration of $CuZn_2$ was calculated from the charge of the current peak at -1.04 V. In further calculations CuZn precipitation was taken into account.

SOURCE AND PURITY OF MATERIALS:

H_2O: demineralized and twice distilled in all-silica apparatus.

Cu(II) and Zn(II) salts: "reagent grade" purity.

Supporting electrolyte salts: "suprapur" from Merck.

ESTIMATED ERROR:

Stability constant: nothing specified.

Temperature: precision ± 0.2 K.

COMPONENTS: (1) Copper-zinc 1:3; $CuZn_3$; [12194-85-3] (2) Mercury; Hg; [7439-97-6]	EVALUATOR: C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland December 1986

CRITICAL EVALUATION:

Shuman and Woodward (1) suggested the formation of $CuZn_3$ in Hg based on stripping voltammetry experiments with coulometric integration of charge. They reported the instability constant, $K_d = [CuZn_2][Zn]/[CuZn_3]$, and the solubility product, $K_s = [Cu][Zn]^3$, equal to 2.1 mol dm^{-3} and 3.1×10^{-5} mol^4 dm^{-12}, respectively. Existence of $CuZn_2$ molecules in Hg is doubtful. Calculating the solubility of $CuZn_3$ in Hg from K_s gives a value several times higher than the solubility of Cu in Hg; see the Cu-Hg system. Such inconsistency may arise from some unexplained experimental observations by the authors, namely a broadened and decreased Zn(II) reduction peak with increased Cu concentration. The authors also assume incorrectly that the reaction investigated is a higher order electrode process. Moreover, it is not known if a real equilibrium in the complex amalgam is reached before the oxidation of the parent metals. Temperatures of the measurements are not given, so any quantitative values can not be recommended.

The compilers express reservations as to the quantitative aspect of $CuZn_3$ formation in Hg only, because in the calorimetric titrations of the Cu-Zn heterogeneous amalgam with Hg performed by Zebreva and coworkers (2) formation of $CuZn_3$ in Hg was detected. The compound $CuZn_3$ was found also by Kozin (5), who carried out conductometric measurements of the Cu-Zn-Hg alloys. In the binary Cu-Zn alloys the compound $CuZn_3$ is stable between 831 and 973 K. At lower temperature only an intermediate phase with a significantly distinct composition occurs (3); also $CuZn_4$ was recently identified (4).

References

1. Shuman, M.S.; Woodward, G.P. *Anal. Chem.* 1976, *48*, 1979.
2. Filippova, L.M.; Zebreva, A.I.; Omarova, N.D. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1977, *20*, 19.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
4. Simic, V.; Marinkovic, Z. *J. Less-Common Met.* 1986, *116*, L7.
5. Kozin, L.F. *Fiziko-Khimicheskie Osnovy Amalgamnoi Metallurgii*, Nauka, Alma-Ata, 1964, p. 186.

COMPONENTS:

(1) Copper-zinc 1:3; $CuZn_3$; [12194-85-3]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Shuman, M.S.; Woodward, G.P.

Anal. Chem. 1976, *48*, 1979-83.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The authors report the solubility product and instability constant of $CuZn_3$ in Hg equal to 3.1×10^{-5} mol^4 dm^{-12} and 2.1 mol dm^{-3}, respectively, at room temperature.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Anodic stripping voltammetry with a thin mercury film plated on a glassy carbon electrode was used. Preelectrolysis of the metal ions was carried out a -1.25 V vs. SCE for 60 s. Then the electrodes were gradually polarized to +0.15 V. The supporting electrolyte used contained 0.05 mol dm^{-3} acetate buffer of pH = 4.5. The K_s and K_d values were obtained by fitting the oxidation currents observed to a model of the process assumed.

SOURCE AND PURITY OF MATERIALS:

Solutions of Cu(II) and Zn(II) were obtained by dissolution of the metals. Glassy carbon was from Chemitrix Corp. No other details are specified.

ESTIMATED ERROR:

Nothing specified. The reservation of compilers to the values determined is described in the Critical Evaluation.

COMPONENTS:	EVALUATOR:
(1) Gallium-nickel 1:1; GaNi; [12183-34-5] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland November 1984

CRITICAL EVALUATION:

Formation of an intermetallic compound of the formula $Ga_7Ni_{10}Hg_x$ in the Ga-Ni-Hg system was reported by Lysenko (1); no solubility data are reported. Using anodic stripping voltammetry Stepanova (2) found the formation of insoluble GaNi in Hg. She calculated the solubility product, K_s = [Ga][Ni], equal to 3.9×10^{-10} $mol^2\ dm^{-6}$ at room temperature, but probably no true equilibrium was reached. One should remember that the solubility of this compound is higher or comparable to the solubility of Ni in Hg, see the Ni-Hg system, which makes the value determined doubtful. The phase GaNi is stable in the Ga-Ni binary system (3).

Abdullah et al. (4) reported formation of $GaNi_2$ in Hg which is, correctly, more stable than NiZn or CuZn. No numerical value of $GaNi_2$ solubility is given.

Value of the solubility of GaNi in Hg (doubtful)

The solubility product of GaNi in Hg at 293 K is, according to (2):

$$4 \times 10^{-10}\ mol^2\ dm^{-6}$$

and the solubility, as calculated by evaluators from K_s:

$$2 \times 10^{-5}\ mol\ dm^{-3}$$

References

1. Lysenko, V.I. *Sbor. Tr., Metall. Tsvet. Met. ikh Anal.* 1962, *7*, 303.
2. Stepanova, O.S. *Izv. Tomsk. Politekhn. Inst.* 1966, *151*, 14.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
4. Abdullah, M.I.; Reusch Berg, B.; Klimek, R. *Anal. Chim. Acta* 1976, *84*, 307.

COMPONENTS: (1) Gallium-nickel 1:1; GaNi; [12183-34-5] (2) Mercury; Hg; [7439-97-6]	ORIGINAL MEASUREMENTS: Stepanova, O.S. *Izv. Tomsk, Politekh. Inst.* 1966, *151*, 14-20.
VARIABLES: Room temperature measurement	PREPARED BY: C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound GaNi is treated as sparingly soluble in Hg; the equilibrium is described by the solubility product equal to 3.9×10^{-10} mol^{2} dm^{-6} at room temperature. The concentration ratio of Ni to Ga was changed in the range 0.1-1.3. The solubility of GaNi is many times higher than the solubility of Ni in Hg.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Stripping voltammetry experiments with the hanging mercury drop electrode were performed. Electrolytic codeposition of Ga and Ni was carried out for 5 min at -1.4 V vs. SCE. The background electrolyte contained acetate buffer at pH = 4.6 and the concentration of Ga(III) was 1.0×10^{-4} or 1.6×10^{-4} mol dm^{-3}. One minute of waiting time between the concentration and stripping stages was applied. The solubility product was calculated from the oxidation currents of the metals using the equation derived in (1). The experiments were performed in a N_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

The solutions contained ions of other heavy metals at concentrations below 10^{-8} mol dm^{-3}.

ESTIMATED ERROR:

Nothing specified. Error of the solubility product determination is not lower than ± 10 % (compilers).

REFERENCES:

1. Stromberg, A.G.; Gorodovykh, V.E. *Zh. Neorg. Khim.* 1968, *8*, 2355.

COMPONENTS:	EVALUATOR:
(1) Indium-antimony 1:1; InSb; [1312-41-0] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland October 1982

CRITICAL EVALUATION:

The In-Sb-Hg system, in the region of Hg-rich compositions, was studied by Levitskaya and Zebreva (1), who used potentiometry and amalgam polarography. Only one, insoluble compound, InSb, is formed in Hg, and the equilibrium is described by the solubility product, K_s = [In][Sb]. The experiments were performed in the temperature range 293 - 353 K. When the concentrations of parent metals were on the order of 4×10^{-4} mol dm^{-3} no interaction between In and Sb was found at 333 and 353 K, which is additional proof that the solubility product is the correct form characterizing the system.

However, Stromberg and coworkers (2) treated the results of the cited paper (1) with their own mathematical procedure. They came to the unexpected conclusion that $InSb_2$ is formed in Hg with the solubility product, K_s = $[In][Sb]^2$, in the range 1.3×10^{-12} - 8×10^{-12} mol^3 dm^{-9} at 293 K. Unexpectedly, Zakharov and coworkers (4) reported no compound formation in the In-Sb amalgams using stripping voltammetry when total concentrations of In and Sb were 3.2×10^{-3} and 7.0×10^{-4} mol dm^{-3}, respectively. The only compound formed in the binary In-Sb alloys is InSb (3).

Value of the solubility of InSb in Hg (tentative)

The solubility products of InSb in Hg at 293 and 313 K are, according to (1):

$$2 \times 10^{-8}\ mol^2\ dm^{-6} \text{ and } 5 \times 10^{-8}\ mol^2\ dm^{-6}$$

and the solubility, as calculated by evaluators from K_s:

$$1.4 \times 10^{-4}\ mol\ dm^{-3} \text{ and } 2.3 \times 10^{-4}\ mol\ dm^{-3}$$

References

1. Levitskaya, S.A.; Zebreva, A.I. *Elektrokhimia* 1966, *2*, 92.
2. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1974, *7*, 42.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
4. Zokharov, M.S.; Mesyats, N.A.; Zaichko, L.F.; Baletskaya, L.G. *Izv. Vyssh. Uchel. Zaved., Khim. Khim. Tekhnol.* 1966, *9*, 355.

COMPONENTS:

(1) Indium-antimony 1:1; InSb; [1312-41-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Levitskaya, S.A.; Zebreva, A.I.

Elektrokhimia 1966, *2*, 92-5.

VARIABLES:

Temperature: 293-313 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

InSb is found to be an insoluble compound in Hg. The solubility product was determined.

Potentiometric results

t/°C	$10^4c_{In}{}^i$/ mol dm^{-3}	$10^4c_{Sb}{}^i$/ mol dm^{-3}	$10^4c_{In}{}^f$/ mol dm^{-3}	$10^4c_{Sb}{}^f$/ mol dm^{-3}	10 k ′ mol^2 dm^{-6}
20	1.115	2.282	0.874	1.041	1.7
	1.261	2.305	0.796	1.840	1.5
	1.280	2.259	0.960	1.939	1.9
	1.577	2.305	1.100	1.828	2.0
	1.600	3.960	1.030	2.400	2.5
	1.600	6.350	1.130	2.400	2.7
	1.680	4.620	1.052	2.400	2.5
	1.760	2.259	1.210	1.709	2.1
	2.087	3.960	1.240	2.400	3.0
				mean value	2.2±0.4

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgams were prepared electrolytically. Potentials of complex In-Sb amalgams were measured versus an In amalgam electrode in a solution of 4.3×10^{-3} mol dm^{-3} $In_2(SO_4)_3$ in 10 % NaCl, pH = 3.4. Amalgam polarography was used. The complex and simple amalgams were anodically oxidized in a solution of 0.5 mol dm^{-3} HCl. The solubility product was calculated from the potential differences as well as oxidation currents of the metals. All operations were carried out in a mixed atmosphere of H_2 and N_2.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility: precision ± 20 % or worse (potentiometry), ± 30 % (polarography).

Temperature: nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Indium-antimony 1:1; InSb; [1312-41-0] (2) Mercury; Hg; [7439-97-6]	Levitskaya, S.A.; Zebreva, A.I. *Elektrokhimia* 1966, *2*, 92-5.

EXPERIMENTAL VALUES (continued)

t/°C	$10^4 c_{In}{}^{i}$/ mol dm^{-3}	$10^4 c_{Sb}{}^{i}$/ mol dm^{-3}	$10^4 c_{In}{}^{f}$/ mol dm^{-3}	$10^4 c_{Sb}{}^{f}$/ mol dm^{-3}	10 K_s/ mol^2 dm^{-6}
40	0.79	6.00	0.55	5.75	3.2
	1.23	5.00	1.05	4.83	5.1
	1.32	6.00	1.03	5.71	5.9
	1.70	5.00	1.42	4.72	6.7
	1.81	6.00	1.42	5.60	8.0
	2.63	2.30	2.25	1.92	4.3
	3.19	3.04	1.96	1.81	3.5
	4.37	3.98	2.52	2.13	5.4
				mean value	5.2±1.6

Amalgam polarography results at 20 °C

$10^4 c_{In}{}^{i}$/ mol dm^{-3}	$10^4 c_{Sb}{}^{i}$/ mol dm^{-3}	$10^4 c_{In}{}^{f}$/ mol dm^{-3}	$10^4 c_{Sb}{}^{f}$/ mol dm^{-3}	10 K_s/ mol^2 dm^{-6}
1.49	1.53	1.00	1.09	1.1
1.53	2.28	1.20	1.70	2.0
2.28	2.28	1.00	1.09	1.1
2.39	2.44	0.95	1.40	1.3
2.60	2.58	1.65	1.52	2.5
3.05	3.04	1.40	1.70	2.4
3.06	2.73	1.20	1.05	1.3
			mean value	1.7±0.5

Using even maximal concentrations of Sb and In equal to 3.98×10^{-4} and 4.37×10^{-4} mol dm^{-3}, respectively, it was found that no soluble compound of both metals forms at 60 or 80 °C.

COMPONENTS: (1) Potassium-sodium-mercury 1:1:2; $KNaHg_2$; [98246-95-8] Potassium-sodium 1:1; KNa; [12056-29-0] (2) Mercury; Hg; [7439-97-6]	EVALUATOR: C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland February 1981

CRITICAL EVALUATION:

The K-Na-Hg system was investigated by Jänecke (1, 2) with thermal analysis. The author determined the melting point of $KNaHg_2$, which is formed at significant concentrations of K and Na in the complex amalgam. This way one may evaluate the solubility of a hypothetical KNa compound in Hg as being 33.3 mol % at 461 K, since only KNa_2 is formed in the binary K-Na alloys.

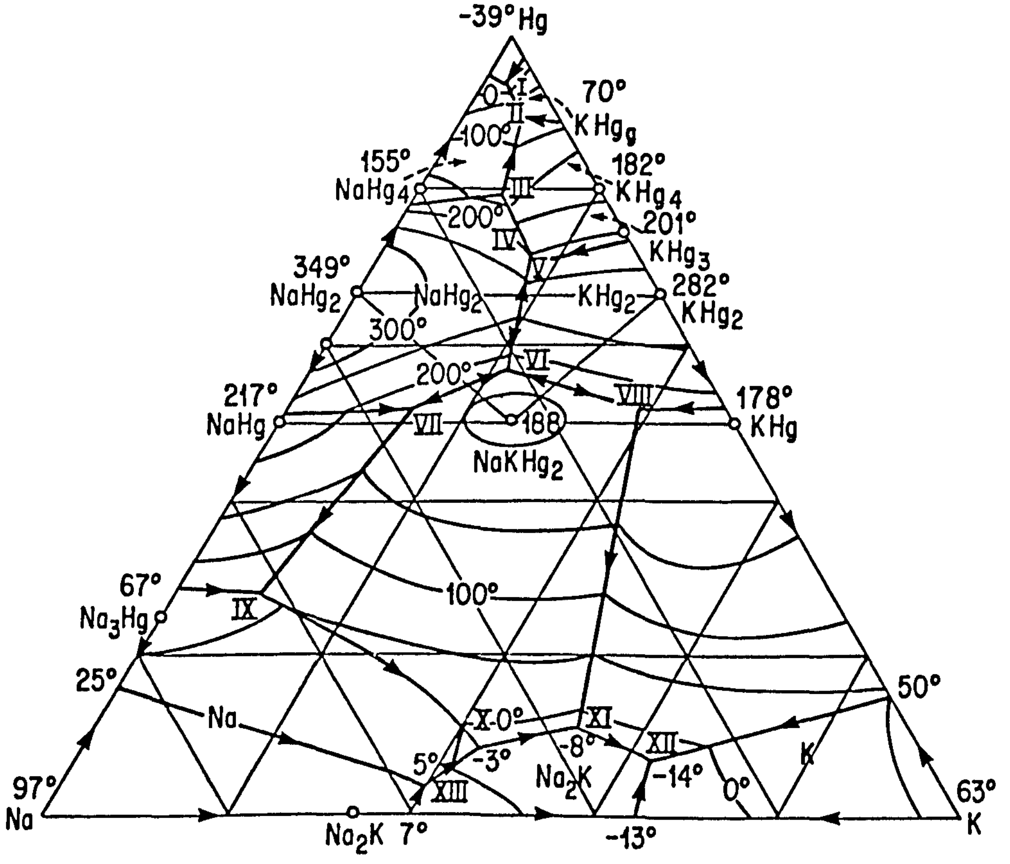
The phase diagram of the K-Na-Hg system taken from (3) is reported below.

Value of the melting point of $KNaHg_2$ (tentative)

The melting point of $KNaHg_2$ is 461 K.

References

1. Jänecke, E. *Z. Phys. Chem.* 1907, *57*, 507.
2. Jänecke, E. *Z. Metallk.* 1928, *20*, 113.
3. Jänecke, E. *Kurzgefasstes Handbuch der Legierungen Universitatsverlag, Heidelberg* 1949.



COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium-sodium-mercury 1:1:2; $KNaHg_2$; [98246-95-8] Potassium-sodium 1:1; KNa; [12056-29-0] (2) Mercury; Hg; [7439-97-6]	Jänecke, E. *Z. Phys. Chem.* 1907, *57*, 507-10. Jänecke, E. *Z. Metallk.* 1928, *20*, 113-7.
VARIABLES:	PREPARED BY:
Composition in the whole range	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The quasibinary system KHg-NaHg was investigated, and the melting point of $KNaHg_2$ was established at 188 °C. Melting points for other compositions of the alloys may be read from the figure given in the Critical Evaluation of the system; no numerical values are reported originally.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Method of preparation of KHg and NaHg amalgams is not known in detail. The amalgams were mixed in various ratios and the cooling curves of the melted samples were recorded in time, in a differential way.	Pure metals were used.
	ESTIMATED ERROR:
	Nothing specified. Temperature: should be no worse than ± 2 K (compilers).

COMPONENTS:	EVALUATOR:
(1) Potassium-lead 1:1; KPb; [12030-93-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland February 1980

CRITICAL EVALUATION:

In the first experiments with the K-Pb-Hg system, Shvedov and Semenyuk (1) did not observe interactions between K and Pb in Hg.

Later, Filippova and coworkers (2) using calorimetric titrations and using higher concentrations of the components found the formation of KPb in crystalline form in Hg. Values of the solubility product, K_s = [K][Pb], of 0.82 and 0.88 mol^2 dm^{-6} at 298 and 313 K, respectively, were reported. They do not agree exactly with those calculated by the compilers and should be corrected for activity coefficients because the amalgams are concentrated. Therefore the values are doubtful. The heats of dissolution of the compound in its saturated amalgam equal to 6.8±1.4 and 8±2 kJ mol^{-1} at 298 and 313 K, respectively, are given.

The most stable solid phase formed in the binary K-Pb system is KPb (3).

Value of the solubility of KPb in Hg (doubtful)

The solubility product of KPb in Hg at 298 and 313 K is, as reported in (2):

0.8 mol^2 dm^{-6} and 0.9 mol^2 dm^{-6}

and the solubility, as calculated by evaluators from K_s:

0.9 mol dm^{-3} and 0.95 mol dm^{-3}, respectively.

References

1. Shvedov, V.N.; Semenyuk, E.Ya. *Zh. Prikl. Khim.* 1971, 44, 80, 282.
2. Filippova, L.M.; Zebreva, A.I.; Korobkina, N.P. *Ukr. Khim. Zh.* 1978, 44, 791.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Potassium-lead 1:1; KPb; [12030-93-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Filippova, L.M.; Zebreva, A.I.;
Korobkina, N.P.

Ukr. Khim. Zh. 1978, 44, 791-3.

VARIABLES:

Temperature: 298 - 313 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of KPb in Hg at 298 and 313 K is 0.82 and 0.88 mol^2 dm^{-6}, respectively.

t/°C	$c_K{}^i$/ mol dm^{-3}	$c_{Pb}{}^i$/ mol dm^{-3}	c_K / mol dm^{-3}	$c_{Pt}{}^f$/ mol dm^{-3}	K_s/ ^{a} mol^2 dm^{-6}
25	1.43	0.95	1.10	0.76	0.84
	1.52	1.00	1.35	0.80	1.08
	1.79	0.69	1.48	0.60	0.89
	1.94	1.00	1.30	0.65	0.85
				mean value	0.91±0.11 ^{a}
40	1.72	1.17	1.08	0.84	0.91
	1.72	1.31	1.10	0.84	0.92
	1.89	0.95	1.45	0.70	1.02

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Homogeneous K and Pb amalgams were mixed in various ratios. Then they were diluted with Hg and heats (Q) were measured. A bend on Q vs. concentrations of K and Pb corresponds to the equilibrium concentrations of the metals. From this the stoichiometry of the intermetallic compound being formed and its solubility product were found. The experiments were carried out in an Ar atmosphere. The Pb amalgam was obtained by dissolution of this metal in Hg and the K amalgam by electrolysis.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

Solubility: precision no better than ± 20 % (by compilers).

COMPONENTS:

(1) Potassium-lead 1:1; KPb; [12030-93-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Filippova, L.M.; Zebreva, A.I.;
Korobkina, N.P.

Ukr. Khim. Zh. 1978, 44, 791-3.

EXPERIMENTAL VALUES (continued)

t/°C	$c_K{}^i$/ mol dm^{-3}	$c_{Pb}{}^i$/ mol dm^{-3}	c_K / mol dm^{-3}	$c_{Pt}{}^f$/ mol dm^{-3}	K_s/ [a] mol^2 dm^{-6}
	2.07	1.33	1.12	0.80	0.90
	2.16	1.21	1.30	0.74	0.96
				mean value	0.94±0.05 [a]

[a] calculated by compilers.

The calculated values of 0.82 and 0.88 mol^2 dm^{-6} do not agree with the original data.

The heat of dissolution of KPb in its saturated amalgam is equal to 6.8±1.4 and 8±2 kJ mol^{-1} at 298 and 313 K, respectively.

COMPONENTS:

(1) Potassium-zinc 2:1; K_2Zn; [98246-96-9]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

February 1980

CRITICAL EVALUATION:

Dzhabarova and coworkers (1) investigated the K-Zn amalgams with stripping voltammetry in DMFA solutions and reported the formation of K_2Zn in Hg in addition to KZn. The solubility product, $K_s = [K]^2[Zn]$, determined was $1x10^{-6}$ mol^3 dm^{-9} at room temperature, but lack of other experimental details obliges one to classify it as a doubtful value. See also the KZn-Hg system. The compound K_2Zn is not known in the binary K-Zn alloys (2).

Value of the solubility of K_2Zn in Hg (doubtful)

The solubility product of K_2Zn in Hg at 293 K is, as given in (1):

$$1x10^{-6} \text{ mol}^3 \text{ dm}^{-9}$$

and the solubility, as calculated from K_s by evaluators:

$$6x10^{-3} \text{ mol dm}^{-3}$$

References

1. Dzhabarova, I.K.; Kaplin, A.A.; Anisimova, L.S. *Usp. Polarogr. s Nakopl., Tomsk*, 1973, p. 39.
2. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Potassium-zinc 1:1; KZn; [98246-97-0]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

February 1980

CRITICAL EVALUATION:

Filippova and coworkers (1) performed calorimetric titrations of the complex K-Zn amalgams. The authors found formation of solid KZn in Hg with the solubility product, K_s = [K][Zn], equal to 1.0 and 3.5 mol^2 dm^{-6} at 298 and 313 K, respectively. The K_s-value should be corrected for activity coefficients of the components, since the amalgam is concentrated. The formation of K-Zn intermetallics in Hg was communicated previously in (2-4). No quantitative data of the solubility are reported in (2, 3). Korshunov and coworkers (2) reported precipitation of $KZn_{10}Hg_{11}$ in the system. Dzhabarova and coworkers (4) investigated the system with stripping voltammetry in DMF solutions. They found two insoluble compounds, KZn and K_2Zn; the determined solubility product of KZn is 2.8x10^{-5} mol^2 dm^{-6} at room temperature, but lack of other experimental details gives no basis for evaluation. There is significant disagreement between the results of (1) and (4), so only doubtful value may be suggested.

KZn is unknown in the K-Zn binary alloys (5).

Value of the solubility of KZn in Hg (doubtful)

The solubility product of KZn in Hg at 298 and 313 K is, as reported in (1):

1 mol^2 dm^{-6} and 3 mol^2 dm^{-6}

and the solubility, as calculated from K_s by evaluators:

1 mol dm^{-3} and 1.8 mol^2 dm^{-6}, respectively

References

1. Filippova, L.M.; Zebreva, A.I.; Omarova, N.D.; Korobkina, N.P. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1978, *21*, 316.
2. Korshunov, V.N.; Selevin, V.V.; Khlystova, K.B. *Elektrokhimia* 1972, *8*, 912.
3. Vorkapic, L.Z.; Drazic, D.M.; Despic, A.R. *J. Electrochem. Soc.* 1974, *121*, 1385.
4. Dzhabarova, I.K.; Kaplin, A.A.; Anisimova, L.S. *Usp. Polarogr. s Nakopl., Tomsk*, 1973, p. 39.
5. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Potassium-zinc 1:1; KZn; [98246-97-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Filippova, L.M.; Zebreva, A.I.; Omarova, N.D.; Korobkina, N.P.

Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 1978, *21*, 316-20.

VARIABLES:

Temperature: 298 - 313 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of KZn in Hg is originally reported as 1.0±0.2 and 3.5±0.5 mol^2 dm^{-6} at 298 and 313 K, respectively. The individual values are as follows:

t/°C	$c_K{}^i$/ mol dm^{-3}	$c_{Pb}{}^i$/ mol dm^{-3}	c_K / mol dm^{-3}	$c_{Pt}{}^f$/ mol dm^{-3}	K_s/ [a] mol^2 dm^{-6}
25	1.43	1.48	0.98	1.02	1.00
	1.46	3.62	0.60	1.48	0.89
	1.49	3.09	0.67	1.39	0.93
	1.50	1.85	0.91	1.12	1.02
	1.52	2.96	0.74	1.24	0.92
	1.52	2.59	0.85	1.45	1.23
	1.52	2.22	0.71	1.33	0.94
				mean value	0.99±0.12 [a]

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Homogeneous K and Zn amalgams were mixed in various proportions. Then they were diluted with Hg and the heats (Q) were measured. A bend on dependence of Q on the concentrations of K and Zn corresponds to the equilibrium concentrations of the metals. From this the stoichiometry of the intermetallic formed and its solubility product as well as the heat of dissolution could be found. The experiments were carried out in an Ar atmosphere. The Zn amalgam was prepared by dissolution of Zn in Hg and the K amalgam by electrolysis.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility: precision ± 20 % (authors) standard deviation between 3 and 8 % (compiler). Temperature: nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium-zinc 1:1; KZn; [98246-97-0] (2) Mercury; Hg; [7439-97-6]	Filippova, L.M.; Zebreva, A.I.; Omarova, N.D.; Korobkina, N.P. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1978, *21*, 316-20.

EXPERIMENTAL VALUES (continued)

t/°C	$c_K{}^i$/ mol dm^{-3}	$c_{Pb}{}^i$/ mol dm^{-3}	c_K / mol dm^{-3}	$c_{Pt}{}^f$/ mol dm^{-3}	K_s/ ^{a} mol^2 dm^{-6}
40	1.88	5.12	1.07	2.88	3.08
	1.93	5.10	1.12	2.98	3.34
	2.49	2.96	1.68	2.00	3.36
	2.89	5.12	1.35	2.38	3.21
	3.44	5.12	1.43	2.19	3.13
				mean value	3.22±0.12 ^{a}

^{a} calculated by compilers.

The heat of dissolution of KZn in the saturated amalgam is 34±4 and 32±2 kJ mol^{-1} at 298 and 313 K, respectively (at confidence level of 0.95).

COMPONENTS:	EVALUATOR:
(1) Lithium-tin 1:1; LiSn; [51404-25-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland April 1983

CRITICAL EVALUATION:

Filippova and coworkers (1, 2) determined the solubility product, $K_s = [Li][Sn]$, of LiSn in Hg as well as the enthalpy of dissolution of this compound in the saturated amalgam. Calorimetric titrations were used.

The compound LiSn is formed in the binary Li-Sn system; however, the phases with higher Li content are more stable (3).

Value of the solubility of LiSn in Hg (tentative)

The solubility product of LiSn in Hg at 298 K is, as calculated by evaluators:

$$8 \times 10^{-2} \text{ mol}^2 \text{ dm}^{-6}$$

and the solubility, as originally given in the paper (1, 2):

$$0.3 \text{ mol dm}^{-3}$$

References

1. Filippova, L.M.; Zebreva, A.I.; Zhumakanov, V.Z. *Ukr. Khim. Zh.* 1981, *47*, 473.
2. Filippova, L.M.; Zebreva, A.I.; Zhumakanov, V.Z. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1982, *25*, 827.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Lithium-tin 1:1; LiSn; [51904-25-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Filippova, L.M.; Zebreva, A.I.;
Zhumakanov, V.Z.

Ukr. Khim. Zh. <u>1981</u>, *47*, 473-6.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of LiSn in Hg at 25 °C is 3×10^{-1} mol dm^{-3} (authors). The detailed results are:

$c_{Li}{}^{i}$/ mol dm^{-3}	$c_{Sn}{}^{i}$/ mol dm^{-3}	$c_{Li}{}^{f}$/ mol dm^{-3}	$c_{Sn}{}^{f}$/ mol dm^{-3}	K_s/ mol^2 dm^{-6}
1.20	0.63	0.42	0.22	0.092
0.85	0.68	0.34	0.27	0.092
0.78	0.65	0.30	0.25	0.075
0.77	0.73	0.29	0.27	0.078
0.68	0.53	0.26	0.33	0.086
0.62	0.73	0.25	0.29	0.073
			mean value	0.083±0.008 [a]

[a] calculated by compilers.

The heat of dissolution of LiSn in its saturated amalgam is 5.2±0.6 kJ mol^{-1} at the 0.95 confidence level. The same results are also reported in (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Li and Sn amalgams were mixed in various proportions. Then they were diluted with Hg and heats (Q) were measured. A bend on dependences Q vs. the concentrations of Li or Sn corresponds to the equilibrium concentrations of the metals. From this titration the stoichiometry, solubility product and heat of dissolution of the compound could be determined. The experiments were carried out in an Ar atmosphere. The Sn amalgam was obtained by dissolution of this metal in Hg and Li amalgam by electrolysis.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified. Solubility: standard deviation ± 10 % (by compilers).

REFERENCES:

1. Filippova, L.M.; Zebreva, A.I.; Zhumakanov, V.Z. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* <u>1982</u>, *25*, 827.

COMPONENTS:

(1) Magnesium-tin 2:1; Mg_2Sn; [1313-08-2]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

September 1982

CRITICAL EVALUATION:

The Mg-Sn-Hg system was investigated by potentiometry. Tammann and Jander (1) reported a value of the stability constant of Mg_2Sn in Hg, $K = [Mg_2Sn]/[Mg]^2[Sn]$, equal to 1.1×10^{10} (mol fraction)$^{-2}$ at 291 K. However, Dergacheva and Kozin (2), after reexamination of the system under similar conditions, observed no interaction between Mg and Sn in Hg up to concentrations of 0.56 and 0.11 mol dm^{-3}, respectively; the corresponding concentrations in (1) were 0.68 and 1.9 mol dm^{-3}, respectively. It seems that the amalgam in work (1) was additionally attacked by corrosion, which simulated formation of a stable intermetallic. No value of the solubility of Mg_2Sn in Hg is suggested because K and $K_s = [Mg]^2[Sn]$ are almost constant in a certain range of concentrations, as was shown by compilers in the data sheet. The stable phase Mg_2Sn is formed in the Mg-Sn binary system (3).

References

1. Tammann, G.; Jander, W. *Z. Anorg. Chem.* 1922, *124*, 105.
2. Dergacheva, M.B.; Kozin, L.F. *Vestn. Akad. Nauk Kaz. SSR* 1974, no. 6, 56.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Magnesium-tin 2:1; Mg_2Sn; [1313-08-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Tammann, G.; Jander, W.

Z. Anorg. Chem. 1922, *124*, 105-122.

VARIABLES:

One temperature: 291 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The authors detected the formation of Mg_2Sn in Hg at 18 °C and, assuming it is soluble, they determined its stability constant as equal to 0.5×10^{10}, 1.1×10^{10} and 1.8×10^{10} (mol fraction)$^{-2}$. The mean value was originally reported as 1.1×10^{10} (mol fraction)$^{-2}$. Compilers, based on primary data from the paper, calculated the following values of the stability constant and solubility product.

w_{Mg}^{i}/ mass %	w_{Sn}^{i}/ mass %	ΔE/ ^{a} mV	c_{Mg}^{f}/ mol dm^{-3}	c_{Sn}^{f}/ ^{a} mol dm^{-3}	K_s/ ^{a} mol^{3} dm^{-9}	K/ ^{a} mol^{-2} dm^{6}
0.124	1.725	140	8.1×10^{-6}	1.59	1.0×10^{-10}	3.3×10^{9}
0.116	0.946	120	8.8×10^{-5}	0.76	5.9×10^{-9}	5.5×10^{7}
0.170	0.734	120	1.3×10^{-4}	0.36	6.1×10^{-9}	8.1×10^{7}
0.191	0.540	110	3.2×10^{-4}	8.7×10^{-2}	8.9×10^{-9}	5.7×10^{7}
0.156	0.408	100	5.9×10^{-4}	3.3×10^{-2}	11×10^{-9}	3.7×10^{7}
0.128	0.252	20	1.4×10^{-1}	2.0×10^{-3}	3.8×10^{-5}	7.0×10^{3}
0.122	0.141	20	1.3×10^{-1}	-	-	-
0.100	0.085	10	-	-	-	-

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Pieces of Mg were dissolved in warm Hg in a glass apparatus filled with dry H_2. Small pieces of Sn were added to the Mg amalgam. The ternary and Mg amalgams were transferred into another cell to form electrodes. The potential of the amalgams in a water-free pyridine solution of Mg(II) were measured vs. the calomel electrode. The equilibrium concentration of Mg in the ternary amalgam was found from the potential differences between Mg binary and ternary amalgams. The Sn concentration was calculated from mass balance.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified. Precision of metal concentrations is no better than ± 20 %, since ΔE is ± 5 mV at minimum (compilers).

COMPONENTS:

(1) Magnesium-tin 2:1; Mg_2Sn; [1313-08-2]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Tammann, G.; Jander, W.

Z. Anorg. Chem. 1922, *124*, 105-122.

EXPERIMENTAL VALUES (continued)

w_{Mg}^{i}/ mass %	w_{Sn}^{i}/ mass %	ΔE/ [a] mV	c_{Mg}^{f}/ mol dm^{-3}	c_{Sn}^{f}/ [a] mol dm^{-3}	K_s/ [a] mol^3 dm^{-9}	K/ [a] mol^{-2} dm^6
0.171	0.078	20	-	-	-	-
0.152	0.056	10	-	-	-	-
0.107	0.019	0	-	-	-	-
0.149	0.017	10	-	-	-	-

[a] calculated by compilers.

It is difficult to decide which value K_s or K better describes the equilibrium of the system, since both are variable in the same degree.

COMPONENTS:

(1) Manganese-lead 1:5; $MnPb_5$; [71512-79-3]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

December 1984

CRITICAL EVALUATION:

Shirinskikh and coworkers (1, 4) did not find any Mn-Pb compound formed in the Mn-Pb-Hg ternary system. On the contrary Kaplin and coworkers (2) determined the solubility product of $MnPb_5$ in Hg, $K_s = [Mn][Pb]^5$, by stripping voltammetry. The reported value is 1×10^{-6} and is expressed in "mol cm^{-3}" which, after recalculations to molar concentration, leads to a paradoxical result of 1×10^{12} mol^6 dm^{-18}. However, if one compares the oxidation currents recorded during the investigation of the Mn-Pb-Hg (2) system with those for the Mn-Zn-Hg or Cu-Mn-Hg (3) systems under similar conditions, one comes to the conclusion that the solubility of $MnPb_5$ is similar to that of $MnZn_4$ or Cu_3Mn; consequently it should be of the order of 10^{-3} mol dm^{-3}. No $MnPb_5$ compound was found in the binary Mn-Pb system (5). Therefore, the equilibrium phase of solid may also contain Hg as a third component. Any value may be suggested in such situation.

References

1. Shirinskikh, A.V.; Lange, A.A. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1976, *42*, 16.
2. Kaplin, A.A.; Mamontova, I.P.; Stromberg, A.G. *Zavod. Lab.* 1979, *45*, 484.
3. Kaplin, A.A.; Mamontova, I.P. *Zh. Anal. Khim.* 1978, *33*, 703.
4. Shirinskikh, A.V.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1983, no. 5, 17.
5. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Manganese-lead 1:5; $MnPb_5$; [71512-79-3]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kaplin, A.A.; Mamontova, I.P.;
Stromberg, A.G.

Zavod. Lab. 1979, *45*, 484-7.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of $MnPb_5$ in Hg at room temperature of 20 °C is:

$$1 \times 10^{-6}\ mol^6\ cm^{-18}$$

The concentration ratio of Mn(II)/Pb(II) in the solution was changed in the range 8.8 - 38.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Thin film mercury electrodes with Ag support were used. The amalgams were prepared by electrolysis at -1.9 V vs. SCE from $MnCl_2$, $PbCl_2$ in 1 mol dm^{-3} NaCl. Then voltammetric oxidations of the mixed amalgams were carried out and the solubility product was calculated with the help of the height of the oxidation current peaks. The experiments were performed in an N_2 atmosphere with maximum 10^{-3} % O_2.

SOURCE AND PURITY OF MATERIALS:

Super pure or chemically pure reagents were used. The solutions contained no more than 10^{-9}-10^{-10} mol dm^{-3} of other heavy metal ions.

ESTIMATED ERROR:

Solubility: determination of oxidation currents ± (5-10) %.

Temperature: nothing specified.

COMPONENTS: (1) Manganese-lead 1:6; $MnPb_6$; [71512-80-6] (2) Mercury; Hg; [7439-97-6]	EVALUATOR: C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland December 1983

CRITICAL EVALUATION:

Shirinskikh and coworkers (1, 4) did not find any evidence of Mn-Pb formation in the Mn-Pb-Hg system; however Kaplin and coworkers (2) determined the solubility product of $MnPb_6$ in Hg, $K_s = [Mn][Pb]^6$, by stripping voltammetry. The result reported, 2.4×10^{-7} mol^7 cm^{-21}, corresponds to a value expressed on the molar scale of 2.4×10^{14} mol^7 dm^{-21} which has no physical sense. However, if one compares oxidation currents observed during the experiments with the Mn-Pb-Hg (2)and with the Mn-Zn-Hg or Cu-Mn-Hg (3) systems investigated under similar conditions, one concludes that the solubility of $MnPb_6$ is of the same order as of $MnZn_4$ or Cu_3Mn (10^{-3} mol dm^{-3}). Similar comments are presented for the solubility equilibrium of $MnPb_5$ in Hg.

The compound $MnPb_6$ was not found in the Mn-Pb binary system (5), so it is possible that the solid equilibrium phase contains Hg as the third component. Any value of the solubility may be suggested in such situation.

References

1. Shirinskikh, A.V.; Lange, A.A. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1976, *42*, 16.
2. Kaplin, A.A.; Mamontova, I.P.; Stromberg, A.G. *Zavod. Lab.* 1979, *45*, 484.
3. Kaplin, A.A.; Mamontova, I.P. *Zh. Anal. Khim.* 1978, *33*, 703.
4. Shirinskikh, A.V.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1983, no. 5, 17.
5. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Manganese-lead 1:6; $MnPb_6$; [71512-80-6] (2) Mercury; Hg; [7439-97-6]	Kaplin, A.A.; Mamontova, I.P.; Stromberg, A.G. *Zavod. Lab.* 1979, *45*, 484-7.
VARIABLES:	PREPARED BY:
Room temperature measurement	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of $MnPb_6$ in Hg at room temperature, probably 293 K, is:

$$2.4x10^{-7}\ mol^7\ cm^{-21}$$

The concentration ratio of Mn(II)/Pb(II) in the solution was changed in the range 1.3 - 2.6.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Thin film mercury electrodes with an Ag base were used. The mixed amalgams were prepared by electrolysis at -1.9 V vs. SCE from a solution of $MnCl_2$ and $PbCl_2$ in 1 mol dm^{-3} NaCl. Then voltammetric oxidation of the amalgam was carried out and the solubility product was calculated with the use of heights of the current peaks. The experiments were performed in an N_2 atmosphere with maximum 10^{-3} % O_2.

SOURCE AND PURITY OF MATERIALS:

Super pure and chemically pure reagents were used. The solutions contained no more than 10^{-9} - 10^{-10} mol dm^{-3} of other heavy metal ions.

ESTIMATED ERROR:

Solubility: determination of the oxidation currents ±(5-10) %.

Temperature: nothing specified.

COMPONENTS:

(1) Manganese-tin 1:2; $MnSn_2$; [12032-87-0]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

September 1986

CRITICAL EVALUATION:

Campbell and Carter (2) investigated Hg-rich compositions of the Mn-Sn amalgams. They identified the composition of the solid phase formed as Mn_2Sn_5 and they determined the concentrations of both metals in the liquid phase at temperatures from 303 to 343 K. However, one should treat these results with skepticism because the solubilities of the parent metals in Hg, also established in this work, are considerably higher than the accepted values of the solubilities (see the Mn-Hg and Sn-Hg systems). Perhaps the filtration applied was not effective. Moreover, an analysis of the data points to the formation of $MnSn_2$ or even MnSn, since the calculated solubility products are more independent of the metals concentrations.

Later Zebreva and Kozlovskii (1) determined the solubility product of $MnSn_2$ in Hg, $K_s = [Mn][Sn]^2$, equal to 7.1×10^{-9} mol^3 dm^{-9} at 293 K. There is significant difference between the solubilities of the compound found in (1) and (2), but we evaluate the results of (1) as more reliable and those of (2) as doubtful.

The phase $MnSn_2$ is stable in the Mn-Sn binary system (3) as well as in the amalgam (4). According to the works of Shirinskikh et al. (4, 5) on Mn-Sn-Hg alloys at room temperature, excesses of Mn or Sn in the amalgams lead to precipitation of Mn_2Hg_5 or Sn_7Hg in addition to $MnSn_2$ (4, 5) or Mn_2Sn (5).

Value of the solubility of $MnSn_2$ in Hg (doubtful)

The solubility product of $MnSn_2$ in Hg at 293 K according to ref. (1) is:

$$7 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$$

and the solubility, as calculated by evaluators from K_s:

$$1 \times 10^{-3} \text{ mol dm}^{-3}$$

References

1. Zebreva, A.I.; Kozlovskii, M.T. *Zavod. Lab.* 1964, *30*, 1193.
2. Campbell, A.N.; Carter, H.D. *Trans. Faraday Soc.* 1933, *29*, 1295.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
4. Shirinskikh, Z.V.; Grigoreva, M.J.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1985, no. 5, 86.
5. Shirinskikh, A.V.; Grigoreva, M.I.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1987, no. 5, 19.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Manganese-tin 1:2; $MnSn_2$; [12032-87-0] (2) Mercury; Hg; [7439-97-6]	Campbell, A.N.; Carter, H.D. *Trans. Faraday Soc.* 1933, *29*, 1295-300.
VARIABLES:	**PREPARED BY:**
Temperature: 303-343 K	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Concentrations of Mn and Sn in equilibrium with solid Mn_2Sn_5 are reported.

t/°C	w_{Mn}/ mass %	$x_{Mn}{}^a$/ at.%	w_{Sn}/ mass %	$x_{Sn}{}^a$/ at.%	$K_s{}^{nSn}$ ^{a}/ (at.%)^2	$K_s{}^{nSn_2}$/ (at.%)^3	$K_s{}^{nSn_{2.5}}$^{a}/ (at.%)$^{3.5}$
30	0.12	0.44	0.08	0.13	5.7×10^{-2}	7.4×10^{-3}	2.7×10^{-3}
	0.14	0.51	0.16	0.27	1.4×10^{-1}	3.7×10^{-2}	1.9×10^{-2}
	0.16	0.58	0.20	0.34	2.0×10^{-1}	6.7×10^{-2}	3.9×10^{-2}
	0.18	0.66	0.28	0.47	3.1×10^{-1}	1.46×10^{-1}	1.0×10^{-1}
	0.20	0.73	0.35	0.59	4.3×10^{-1}	2.5×10^{-1}	1.9×10^{-1}
	0.24	0.88	0.45	0.76	6.7×10^{-1}	5.1×10^{-1}	4.4×10^{-1}
	0.27	0.99	0.50	0.84	8.3×10^{-1}	6.9×10^{-1}	6.3×10^{-1}
	0.03	0.11	0.23	0.38	4.2×10^{-2}	1.6×10^{-2}	9.9×10^{-3}
	0.06	0.22	0.30	0.50	1.1×10^{-1}	5.5×10^{-2}	3.9×10^{-2}
	0.09	0.33	0.41	0.69	2.3×10^{-1}	1.6×10^{-1}	1.3×10^{-1}
	0.11	0.40	0.44	0.74	3.0×10^{-1}	2.2×10^{-1}	1.9×10^{-1}
	0.13	0.47	0.50	0.84	3.9×10^{-1}	3.3×10^{-1}	3.0×10^{-1}
	0.16	0.58	0.59	0.99	5.7×10^{-1}	5.7×10^{-1}	5.7×10^{-1}

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The Mn amalgam was obtained by electroreduction from $MnSO_4$-$(NH)_4)_2SO_4$ electrolyte on an Hg cathode. The Sn amalgam was prepared by pouring molten Sn into Hg under a CO_2 atmosphere. Both amalgams were mixed, kept in a thermostat and filtered through chamois leather. The filtrate was treated with HCl. The Sn was determined by reduction with Al powder in A CO_2 atmosphere, followed by I_2 titration. The Mn was determined by addition of H_2SO_4 and titration with $KMnO_4$.	Hg used was cleaned with diluted HNO_3. Sn was 99.7 % pure. $MnSO_4$ and $(NH_4)_2SO_4$ were chemically pure. **ESTIMATED ERROR:** Nothing specified, but in a few cases the equilibrium concentrations of one metal at fixed concentrations of second metal differ significantly. See also comments in the Critical Evaluation.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Manganese-tin 1:2; $MnSn_2$; [12032-87-0] (2) Mercury; Hg; [7439-97-6]	Campbell, A.N.; Carter, H.D. *Trans. Faraday Soc.* 1933, *29*, 1295-300.

EXPERIMENTAL VALUES (continued)

$t/°C$	w_{Mn}/ mass %	$x_{Mn}{}^a$/ at.%	w_{Sn}/ mass %	$x_{Sn}{}^a$/ at.%	$K_s{}^{nSn}$ ^{a}/ (at.%)^2	$K_s{}^{nSn_2}$/ (at.%)^3	$K_s{}^{nSn_{2.5}}$ ^{a}/ (at.%)$^{3.5}$
55	0.05	0.18	0.06	0.10	$1.8x10^{-2}$	$1.8x10^{-3}$	$5.7x10^{-4}$
	0.07	0.25	1.15	1.94	$4.8x10^{-1}$	$9.4x10^{-1}$	1.3
	0.09	0.33	1.34	2.22	$7.3x10^{-1}$	1.63	2.4
	0.10	0.36	1.50	2.53	$9.1x10^{-1}$	2.30	3.7
	0.16	0.58	0.12	0.20	$1.2x10^{-1}$	$2.3x10^{-2}$	$1.0x10^{-2}$
	0.20	0.73	0.23	0.38	$2.8x10^{-1}$	$1.05x10^{-1}$	$6.5x10^{-2}$
	0.23	0.84	0.35	0.59	$5.0x10^{-1}$	$2.9x10^{-1}$	$2.2x10^{-1}$
	0.30	0.99	0.48	0.81	$8.0x10^{-1}$	$6.5x10^{-1}$	$5.9x10^{-1}$
	0.36	1.32	0.55	0.92	1.21	1.12	1.07
	0.40	1.46	0.62	1.05	1.53	1.61	1.65
	0.30	0.99	0.75	1.27	1.26	1.60	1.80
55	0.25	0.91	0.83	1.39	1.26	1.76	2.08
	0.22	0.80	0.98	1.63	1.30	2.12	2.71
	0.18	0.66	1.10	1.84	1.21	2.23	3.02
	0.16	0.58	1.27	2.11	1.22	2.58	3.75
70	0.10	0.36	2.7	4.48	1.62	7.22	15.3
	0.05	0.18	2.4	4.00	0.72	2.88	5.8
	0.58	2.11	0.67	1.13	2.38	2.69	2.9
	0.15	0.54	2.00	3.32	1.78	5.95	10.8
	0.20	0.73	1.80	3.00	2.19	6.57	11.4
	0.13	0.47	2.50	4.14	1.95	8.05	16.4
	0.25	0.91	1.40	2.33	2.12	4.94	7.5
	0.30	0.99	1.20	2.02	2.00	4.04	5.7
	0.40	1.46	0.85	1.43	2.09	2.99	3.6
	0.14	0.51	2.20	3.66	1.87	6.83	13.1
	0.20	0.73	0.15	0.25	0.18	0.46	0.23
	0.25	0.91	0.27	0.45	0.41	0.18	0.12
	0.31	1.13	0.40	0.67	0.76	0.51	0.42
	0.40	1.46	0.50	0.84	1.46	1.03	0.94
	0.48	1.75	0.70	1.17	2.05	2.40	2.6

[a] calculated by compilers. Analysis of the equilibrium solid phase indicates the formula Mn_2Sn_5 or $MnSn_3$.

COMPONENTS:

(1) Manganese-tin 1:2; $MnSn_2$; [12032-87-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zebreva, A.I.; Kozlovskii, M.T.

Zavod. Lab. 1964, *30*, 1193-5.

VARIABLES:

Temperature: 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of $MnSn_2$ in Hg at 293 K is:

$$(7.1\pm0.6)\times10^{-9}\ \mathrm{mol^3\ dm^{-9}}$$

The concentration of Sn amalgam was fixed at 1.25×10^{-3} mol dm^{-3} and the concentration of Mn was changed in the range 5×10^{-4} - 5×10^{-3} mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgams of Mn and Sn were prepared by an unknown method, probably electrolysis. Oxidation of the complex Mn-Sn amalgam was carried out under polarographic conditions. The solubility product of $MnSn_2$ was calculated from oxidation currents of the elements using dependences of current vs. concentration.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility: precision of ± 8 %.

Temperature: nothing specified.

COMPONENTS:

(1) Manganese-zinc 1:4; $MnZn_4$; [60383-49-5]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

June 1986

CRITICAL EVALUATION:

Kaplin and Mamontova (1) determined the solubility product of $MnZn_4$ in Hg, $K_s = [Mn][Zn]^4$. The corresponding solubility of $MnZn_4$ is only slightly higher than the solubility of Mn in Hg; see the Mn-Hg system. However, Shirinskikh and coworkers, (see references in the $MnZn_5Hg_{3.5}$ - Hg system) identified $MnZn_5Hg_{3.5}$ solid phase in equilibrium with the saturated amalgam. The solubility of this compound is much higher than that of $MnZn_4$ or Mn in Hg.

The compound $MnZn_4$ is formed in the Mn-Zn binary system (2) and probably in the amalgam (3). The matter needs further investigation; the result may be classified in the doubtful category only.

Value of the solubility of $MnZn_4$ in Hg (doubtful)

The solubility product of $MnZn_4$ in Hg at 293 K is, as reported in (1):

$$1 \times 10^{-10} \text{ mol}^5 \text{ dm}^{-15}$$

and the solubility, as calculated from K_s by evaluators:

$$3.3 \times 10^{-3} \text{ mol dm}^{-3}$$

References

1. Kaplin, A.A.; Mamontova, I.P. *Zh. Anal. Khim.* 1978, *33*, 703.
2. Romer, O.; Wachtel, E. *Z. Metallk.* 1971, *62*, 820.
3. Lihl, F.; Kirnbauer, H. *Z. Metallk.* 1957, *48*, 9.

COMPONENTS:

(1) Manganese-zinc 1:4; $MnZn_4$; [60383-49-5]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Kaplin, A.A.; Mamontova, I.P.

Zh. Anal. Khim. 1978, *33*, 703-9.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of $MnZn_4$ in Hg at room temperature is

$$9.6 \times 10^{-11}\ \mathrm{mol^5\ dm^{-15}}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Thin film and hanging drop mercury electrodes were used in stripping voltammetry. The amalgams were prepared by 3 min electrolysis of Zn(II) and Mn(II) in 1 mol dm^{-3} NaCl at -1.9 V vs. SCE. Then voltammetric oxidation of the mixed amalgam was carried out and the solubility product was calculated from the height of the oxidation current peaks. The experiments were performed in an N_2 or Ar atmosphere.

SOURCE AND PURITY OF MATERIALS:

Super pure or chemically pure reagents were used. The solutions contained no more than 10^{-9}-10^{-10} mol dm^{-3} of other heavy metal ions.

ESTIMATED ERROR:

Standard deviation of the oxidation currents is in the range ± (5-10) %.

Temperature: nothing specified.

COMPONENTS:	EVALUATOR:
(1) Manganese-zinc-mercury 1:5:3.5; $MnZn_5Hg_{3.5}$; [55929-83-4] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland August 1986

CRITICAL EVALUATION:

During roentgenographic studies of Mn-Zn amalgams of various composition, Lihl and Kirnbauer (1) observed the formation of a solid phase in the system. This phase contained Mn and Zn in the ratio about 1:4. However, Shirinskikh and coworkers (2) did not find any interactions between 5×10^{-2} mass % Zn amalgam and Mn heterogeneous amalgam based on electroanalytical experiments. The second work of the same group of investigators (3) carried out with higher Zn concentration gave some proof that an insoluble form of Mn-Zn-Hg alloy is formed in Hg. It was rather difficult to give an exact formula of the compound being precipitated, because the composition depended on experimental conditions during the formation: the higher the content of Zn in the liquid phase the higher the content of Zn in the solid Mn-Zn-Hg phase. Solid Mn-Zn-Hg alloys of selected composition were dissolved in Hg, and then equilibrium concentrations of Zn and Mn were determined in the temperature range 293-369 K.

Shirinskikh and coworkers (4) returned to the subject. Keen analysis of their new experimental results led them to the conclusion that an equilibrium in this system may be described with the solubility product, $K_s = [Mn][Zn]^5$, from the fact that the estimated ratio of Mn:Zn was about 1:5. The formula of the solid phase was determined as $MnZn_5Hg_{3.5}$. The solubility products of the compound in Hg at 293, 313 and 333 K are given. After an electrochemical removal of Zn from $MnZn_5Hg_{3.5}$ the well known Mn_2Hg_5 solid remains in the amalgam (5). In the last work of this group (8) the formula of the solid phase is reported as $Mn_2Zn_{10}Hg_5$. As in (1), Kaplin and Mamontova (6) found formation of $MnZn_4$ in Hg by stripping voltammetry. They determined the solubility product, $K_s = [Mn][Zn]^4$ (see the $MnZn_4Hg$ system), which corresponds to the $MnZn_4$ solubility value of 3.3×10^{-3} mol dm^{-3}, very close to the solubility of Mn in Hg. On the other hand, the solubility of $MnZn_5Hg_{3.5}$ determined by (4), equals 6.0×10^{-2} mol dm^{-3}, more than one order of magnitude higher than the solubility of Mn in Hg; see the Mn-Hg system. So the result of (6) seems to be more reliable but the works (2-5) are more exhaustive. Therefore only a doubtful value of the solubility of $MnZn_5Hg_x$ in Hg is suggested. Numerical data of the solubility of $MnZn_5Hg_x$ are reported in (3, 5). The temperature dependence of the $pK_s^{MnZn_5}$ was fitted by the least square method to the linear relation:

$$pK_s = -14.24 + 5300\,T^{-1} \qquad r = 0.9994 \qquad (T/K;\ K_s/\text{mol}^6\ \text{dm}^{-18})$$

The compound $MnZn_4$ was found in the Mn-Zn binary system (7).

Values of the solubility of $MnZn_5Hg_x$ in Hg, according to (5) (doubtful)

T/K	K_s/mol^6 dm^{-18}	soly/mol dm^{-3} [a]
293	1.4×10^{-4}	6×10^{-2}
313	2.4×10^{-3}	9.6×10^{-2}
333	2.1×10^{-2}	1.4×10^{-1}

[a] calculated by evaluators from K_s.

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Manganese-zinc-mercury 1:5:3.5; $MnZn_5Hg_{3.5}$; [55929-83-4] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland August 1986

CRITICAL EVALUATION (continued)

References

1. Lihl, F.; Kirnbauer, H. *Z. Metallk.* 1957, *48*, 9.
2. Shirinskikh, A.V.; Lange, A.A.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1971, no. 4, 37.
3. Shirinskikh, A.V.; Lange, A.A.; Bukhman, S.P. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1973, *35*, 54.
4. Lange, A.A.; Bukhman, S.P.; Shirinskikh, A.V. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1975, no. 4, 30.
5. Shirinskikh, A.V.; Lange, A.A.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1975, no. 2, 62.
6. Kaplin, A.A.; Mamontova, I.P. *Zh. Anal. Khim.* 1978, *33*, 703.
7. Romer, O.; Wachtel, E. *Z. Metallk.* 1971, *62*, 820.
8. Shirinskikh, A.V.; Grigoreva, M.J.; Bukhman, S.P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1985, no. 5, 86.

COMPONENTS:

(1) Manganese-zinc-mercury 1:4.2:2.8;
$MnZn_{4.2}Hg_{2.8}$; [55929-83-4]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Shirinskikh, A.V.; Lange, A.A.;
Bukhman, S.P.
Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR
1973, *35*, 54-9.

VARIABLES:

Temperature: 293-369 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of the solid phase 6.2 mass % Mn, 31.4 mass % Zn and 62.4 mass% Hg in Hg in relation to Mn and Zn at various temperatures was determined in replicate experiments:

t/°C	20	40	60	80	88	96
			$10^2 w_{Mn}^{f}$/mass %			
Trial						
1	0.155	0.38	0.66	1.2	1.47	1.92
2	0.155	0.328	0.71	1.31	1.49	2.36
3	0.15	0.334	0.75	1.36	1.55	2.33
4	0.155	0.341	0.80	1.35	1.58	2.28
5	0.15	0.342	0.77	1.35	1.66	2.32
6	-	0.335	0.792	1.28	1.7	2.3
7	-	-	0.78	1.27	1.73	2.3

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The heterogeneous Mn-Zn amalgam was obtained by electrolysis. The Mn(II) was reduced on Zn amalgam obtained previously. The complex amalgams were conditioned for 6 h. Separation of solid and liquid phases were carried out by filtering under pressure of 7500 kg cm^{-2}. Solubilities of Mn and Zn as well as the constitution of solid phases were determined with the use of complexometric and colorimetric methods after dissolution in 1 mol dm^{-3} H_2SO_4 of the corresponding phases. Analysis of solid samples was performed by X-ray.

SOURCE AND PURITY OF MATERIALS:

Analytically pure reagents were used. $MnSO_4$ was twice recrystallized. Zn was 99.9999 % pure.

ESTIMATED ERROR:

Solubility: precision of ± 5 % (compilers).
Temperature: nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Manganese-zinc-mercury 1:4.2:2.8; $MnZn_{4.2}Hg_{2.8}$; [55929-83-4] (2) Mercury; Hg; [7439-97-6]	Shirinskikh, A.V.; Lange, A.A.; Bukhman, S.P. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1973, *35*, 54-9.

EXPERIMENTAL VALUES (continued)

t/°C	20	40	60	80	88	96
			$10w_{Zn}^f$/mass %			
Trial						
1	2.5	2.72	4.06	4.6	6.2	6.3
2	2.5	2.6	4.0	4.6	6.25	2.36
3	2.46	2.6	3.96	4.5	6.25	2.33
4	2.46	2.6	3.94	4.67	6.26	2.28
5	2.46	2.74	3.94	4.5	6.3	2.32
6	-	-	3.96	4.52	6.4	2.3
7	-	-	4.05	4.56	6.6	2.3

In separate experiments an alloy of composition 4.3 mass % Mn, 28.0 mass % Zn and 67.7 mass % Hg was dissolved in Zn amalgams at 20 °C.

$10w_{Zn}^i$/mass %	1.7	2.5	3.0	6.7
		$10^3w_{Mn}^f$/mass %		
Trial				
1	1.37	0.9	0.204	-
2	1.56	0.9	0.146	-
3	1.58	0.78	0.38	-
4	1.67	0.95	0.41	-
5	1.67	*a*	*a*	-
6	1.65	1.08	*a*	-
7	2.02	1.05	*a*	-
		$10w_{Zn}^f$/mass %		
Trial				
1	2.46	2.6	3.08	6.6
2	2.54	2.7	3.08	6.4
3	2.38	2.76	3.08	6.5
4	2.4	2.6	3.04	6.6
5	2.44	*a*	*a*	6.4
6	2.4	2.68	*a*	6.4
7	2.49	2.64	*a*	6.4

The solubility of solid phase 6.85 mass % Mn, 33.0 mass % Zn and 60.15 mass % Hg in Hg in the temperature range 20-96 °C was presented in a small figure given in the paper. The solubility of solid alloy 15 mass % Mn and 85 mass % Zn in 49 g Hg at 20 °C was investigated as a function of the sample weight of the alloy:

(continued next page)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Manganese-zinc-mercury 1:4.2:2.8; $MnZn_{4.2}Hg_{2.8}$; [55929-83-4] (2) Mercury; Hg; [7439-97-6]	Shirinskikh, A.V.; Lange, A.A.; Bukhman, S.P. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* <u>1973</u>, *35*, 54-9.

EXPERIMENTAL VALUES (continued)

t/°C	20	40	60	80	88	96
			$10w_{Zn}{}^{f}$/mass %			
Trial						
1	2.5	2.72	4.06	4.6	6.2	6.3
2	2.5	2.6	4.0	4.6	6.25	2.36
3	2.46	2.6	3.96	4.5	6.25	2.33
4	2.46	2.6	3.94	4.67	6.26	2.28
5	2.46	2.74	3.94	4.5	6.3	2.32
6	-	-	3.96	4.52	6.4	2.3
7	-	-	4.05	4.56	6.6	2.3

In separate experiments an alloy of composition 4.3 mass % Mn, 28.0 mass % Zn and 67.7 mass % Hg was dissolved in Zn amalgams at 20 °C.

$10w_{Zn}{}^{i}$/mass %	1.7	2.5	3.0	6.7
		$10^3w_{Mn}{}^{f}$/mass %		
Trial				
1	1.37	0.9	0.204	-
2	1.56	0.9	0.146	-
3	1.58	0.78	0.38	-
4	1.67	0.95	0.41	-
5	1.67	*a*	*a*	-
6	1.65	1.08	*a*	-
7	2.02	1.05	*a*	-
		$10w_{Zn}{}^{f}$/mass %		
Trial				
1	2.46	2.6	3.08	6.6
2	2.54	2.7	3.08	6.4
3	2.38	2.76	3.08	6.5
4	2.4	2.6	3.04	6.6
5	2.44	*a*	*a*	6.4
6	2.4	2.68	*a*	6.4
7	2.49	2.64	*a*	6.4

The solubility of solid phase 6.85 mass % Mn, 33.0 mass % Zn and 60.15 mass % Hg in Hg in the temperature range 20-96 °C was presented in a small figure given in the paper. The solubility of solid alloy 15 mass % Mn and 85 mass % Zn in 49 g Hg at 20 °C was investigated as a function of the sample weight of the alloy:

(continued next page)

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Manganese-zinc-mercury 1:4.2:2.8; $MnZn_{4.2}Hg_{2.8}$; [55929-83-4] (2) Mercury; Hg; [7439-97-6]	Shirinskikh, A.V.; Lange, A.A.; Bukhman, S.P. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* <u>1973</u>, *35*, 54-9.

EXPERIMENTAL VALUES (continued)

	$w_M{}^f$/mass %		soly/mass %	
sample/g	Mn	Zn	Mn	Zn
1.013	20.0	80.0	$1.78 \cdot 10^{-3}$	$2.29 \cdot 10^{-1}$
0.428	26.7	73.3	$1.87 \cdot 10^{-3}$	$1.72 \cdot 10^{-1}$
0.348	98.5	1.5	$1.58 \cdot 10^{-3}$	$1.95 \cdot 10^{-1}$

COMPONENTS:

(1) Manganese-zinc-mercury 1:5:3.5; $MnZn_5Hg_{3.5}$; [55929-83-4]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Lange, A.A.; Bukman, S.P.; Shirinskikh, A.V.

Izv. Akad. Nauk Kaz. SSR, Ser. Khim. 1975, no. 4, 30-5.

VARIABLES:

Temperature: 293 - 353 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Equilibrium concentrations of Mn and Zn when alloys of the given composition were dissolved in Zn amalgams of the given composition[a]:

w_{solid}/ mass %	t/°C	$10w_{Zn}{}^{i}$/ mass %	$10^3c_{Mn}{}^{f}$/ mass %	$10w_{Zn}{}^{f}$/ mass %
4.3 Mn	20	1.7	1.6	2.4
28 Zn		2.5	0.9	2.7
67.7 Hg		3.0	0.38	3.1
		6.7	<0.1	6.5
4.7 Mn	40	0.77	3.66	3.38
40 Zn		1.58	3.50	2.37
55.3 Hg		2.8	2.25	3.98
		3.50	1.20	4.60
		4.0	0.71	5.05
		5.7	0.27	6.55

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The heterogeneous Mn-Zn amalgam was obtained by electrolysis. Then the amalgam was placed in a funnel and after 6 hrs the particular fractions of the amalgam were analyzed. The samples were dissolved in H_2SO_4. The Zn(II) and Mn(II) were determined in the solution with the use of complexometric (for sum of Zn and Mn) and colorimetric (for Mn) methods.

SOURCE AND PURITY OF MATERIALS:

99.9999 % pure Zn, $MnSO_4$ twice crystallized and analytically pure H_2SO_4 were used.

ESTIMATED ERROR:

Nothing specified. Solubility: precision no worse than ± 5 % (by compilers).

COMPONENTS:

(1) Manganese-zinc-mercury 1:5:3.5;
$MnZn_5Hg_{3.5}$; [55929-83-4]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Lange, A.A.; Bukman, S.P.;
Shirinskikh, A.V.
Izv. Akad. Nauk Kaz. SSR, Ser. Khim. 1975,
no. 4, 30-5.

EXPERIMENTAL VALUES (continued)

w_{solid}/ mass %	t/°C	$10w_{Zn}{}^{i}$/ mass %	$10^3c_{Mn}{}^{f}$/ mass %	$10w_{Zn}{}^{f}$/ mass %
4.7 Mn	60	3.10	6.70	4.90
40 Zn		4.50	3.60	6.00
55.3 Hg		5.40	1.70	6.85
		7.05	1.07	8.30
		8.50	0.46	.5

[a] All data are mean values of 3 determinations.

The solubility of $MnZn_{-5}$ in Hg at 20 °C as a function of the sample weight:

$w_{MnZn_{-5}}$	w_{Hg}/g	$10^3w_{Mn}{}^{f}$/ mass %	$10w_{Zn}{}^{f}$/ mass %	$x_{Zn}{}^{f}/x_{Mn}{}^{f}$	$x_{Zn}{}^{i}/x_{Mn}{}^{i}$
1.750	48.0	1.60	2.50	3.4	4.5
1.013	49.0	1.78	2.29	2.7	6
0.428	49.0	1.80	1.72	1.1	6
0.522	77.2	1.78	1.43	0.77	6
0.500	113.0	1.42	1.23	0	4.5

The solubility product, $K_s = [Mn][Zn]^5$, of the alloy with average composition $MnZn_5Hg_{3.5}$ in Hg at various temperatures:

t/°C	K_s/mol^6 dm^{-18}
20	1.41×10^{-4}
40	2.40×10^{-3}
60	2.09×10^{-2}

Solubility of 5.2 mass % Mn, 35.7 mass % Zn and 59.1 mass % Hg solid alloy in Hg in relation to Mn and Zn at different temperatures:

t/°C	w_{Mn}/mass %	w_{Zn}/mass %
20	1.60×10^{-3}	2.50×10^{-1}
40	3.55×10^{-3}	3.45×10^{-1}
60	7.70×10^{-3}	4.80×10^{-1}
80	1.50×10^{-2}	6.45×10^{-1}

The concentrations of Mn in equilibrium with the intermetallic solid phase are of the same order as the solubility of Mn in Hg.

COMPONENTS:	EVALUATOR:
(1) Ammonium Radical; $NH_4\cdot$; [26497-91-6] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland July 1985

CRITICAL EVALUATION:

It is now well established that the ammonium radical, as well as its alkyl derivatives, forms homogeneous amalgams (1). However, the reported solubilities of $NH_4{}^{\cdot}$ in mercury vary over a wide range. Le Blanc (2) mentioned that mercury absorbs 0.77 mol % $NH_4{}^{\cdot}$ at room temperature. Rich and Travers (3) observed that the melting point of mercury was decreased to 227.55 K upon addition of up to 5.34 mol % of $NH_4{}^{\cdot}$. Stromberg and Konkova (4) observed that the solubility increased from 7.8×10^{-3} to 2.20×10^{-2} mol % as the temperature increased from 283 to 293 K, whereas Syroeshkina and coworkers (5) noticed a slight decrease from 9.7×10^{-4} to 8.9×10^{-4} mol % in the temperature range of 282 to 290 K. The solubility reported by Stromberg and Karbainov (6), 4.6×10^{4} mol % at 298 K, is of similar magnitude as that of (5), but there is disagreement with the other reported data. Syroeshkina and Raimzhanova (7) estimated that the solubility of $NH_4{}^{\cdot}$ at room temperature is 9×10^{-4} mol %. No experimental details for (2, 7) are given.

It appears that the ammonium amalgams were decomposed to different degrees in each of the reported solubility determinations. It is probable that impurities acted as decomposition catalysts, thus resulting in the varied solubility values. There is no evidence for thermodynamic stability in any of the reports. Because of the uncertainty in the experimental values for this system, no recommendation can be made for the solubility. The equilibria may be presented as:

$$NH_4{}^{\cdot}Hg_x \downarrow \rightleftharpoons NH_4{}^{\cdot}(Hg) \rightleftharpoons NH_3 + H(Hg) \rightleftharpoons NH_3(aq) + 1/2\ H_2 \uparrow$$

(Decomposition of the amalgam results in swelling, so named "ammonium amalgam effect".) An $NH_4{}^{\cdot}$-Hg solid phase was identified at 233 and 203 K (8).

References

1. *Gmelins Handbuch der Anorganische Chemie*, 34, Tl.A, Lfg.2, Verlag Chemie, Weinheim, 1962, p. 1006.
2. Le Blanc, M. *Z. Phys. Chem.* 1890, *5*, 467.
3. Rich, E.M.; Travers, M.W. *J. Chem. Soc.* 1906, *89*, 872.
4. Stromberg, A.G.; Konkova, A.V. *Zh. Fiz. Khim.* 1968, *42*, 2063.
5. Syroeshkina, T.V.; Raimzhanova, M.M.; Gladyshev, V.P. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1978, *21*, 933.
6. Stromberg, A.G.; Karbainov, Ya.A. *Zh. Anal. Khim.* 1965, *20*, 769.
7. Syroeshkina, T.V.; Raimzhanova, M.M. *VII Vsesoyuznoe Soveshchanie po Polarografii, Tbilisi*, 1978, p. 196.
8. Baenziger, N.C.; Nielsen, J.W.; Duwell, E.J. *U. S. At. Ener. Comm. Rep., COO-126*, 1957.

COMPONENTS:

(1) Ammonium radical; NH_4; [26497-91-6]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Rich, E.M.; Travers, M.W.

J. Chem. Soc. 1906, *89*, 872-4.

VARIABLES:

Temperature: 228-234 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubilities of ammonium radical in Hg at low temperatures:

t/°C	Soly/g NH_4 in 100 g of Hg
-45.61	0.507
-44.82	0.415
-41.605	0.084
-40.81	0.079 [a]
-40.01	0.027
-39.67	0.0117
-39.62	0.0094

[a] probably inaccurate, as stated by authors.

The melting point of Hg was found to be -39.40 °C instead of -38.9 °C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A Na amalgam of equivalent concentration was cooled in a flask with a long and narrow neck to a temperature just above its freezing points. Anhydrous NH_3 was then condensed in the flask and excess of NH_4I was dissolved. The mixture was shaken from time to time. After 1 h, the NH_3 was allowed to evaporate and the amalgam was filtered several times through a filter paper with a hole pierced in the bottom of it. Finally the filtrate was transferred to an experimental tube. The temperature was carefully kept constant during all operations. The freezing points of the filtrates were measured by the use of a resistance thermometer. After several hours, the tube was warmed to accelerate the evolution of ammonia and finally Hg was gently warmed with acid solution. The quantity of NH_3 evolved was determined by titration and the solution was always examined for the presence of Na, which was absent in all samples. The Hg was dried and weighed.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified. Solubility: probably ± 1 % (compilers). Temperature: precision ± 0.05 K but accuracy ± 0.5 K (compilers).

COMPONENTS:

(1) Ammonium Radical; NH_4; [26497-91-6]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Karbainov, Yu.A.; Stromberg, A.G.

Zh. Anal. Khim. 1965, *20*, no. 8, 769-772.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of NH_4 in Hg at 25 °C is 3.1×10^{-4} mol dm^{-3} or 4.6×10^{-4} mol % (by compilers). There is no proof given that the amalgam contained crystals of the solute.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgam-containing ammonium radical was prepared by electroreduction of NH_4^+ from methanol solution of 0.1 mol dm^{-3} LiCl, 0.2 mol dm^{-3} NH_4Cl, at -2.8 V for 5 min. The hanging mercury drop was used as a working electrode and the potentials were referred to Hg pool as an anode. Introduction of NH_4 into Hg caused swelling of the electrode due to partial decomposition of the solute. The electrode was linearly polarized to positive potentials and the oxidation peak current was observed at -1.2 V. The concentration of NH_4 was calculated from the oxidation current peak. The amalgam was assumed to be saturated when this current was no longer dependent on the amount of NH_4 introduced inside Hg phase.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility: nothing specified.

Temperature: less than ± 1 K.

COMPONENTS:

(1) Ammonium radical [26497-91-6]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Syroeshkina, T.V.; Raimzhanova, M.M.; Gladyshev, V.P.

Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 1978, *21*, 933-5.

VARIABLES:

Temperature: 282-290 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of the ammonium radical in Hg at various temperatures[a]:

t/°C	10^4soly/mol dm^{-3}	10^6soly/mol fraction	soly/mass %	number of determin.
9	6.6±0.2	9.7±0.3	8.8±0.3	6
11	6.8±0.3	10.0±0.4	9.0±0.4	10
15	6.3±0.3	9.3±0.4	8.4±0.4	10
17	6.0±0.4	8.9±0.6	8.0±0.5	12

[a] Above 20 °C the amalgam is unstable (authors).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgam of ammonium radical was obtained by electroreduction from 5 mol dm^{-3} $(NH_4)_2SO_4$, pH~7, with constant current for 1.5 min. Liquation of the amalgam sample proceeded during and after the electrolysis. The lower fraction of the sample was taken for analysis, assuming that the solid phase of the ammonium radical amalgam is lighter than Hg and rises up to the surface. The content of the ammonium radical in Hg was determined by colorimetry with Nessler's reagent, after the fraction of amalgam was decomposed with 0.01 mol dm^{-3} HCl.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility: precision better than ± 6 %.

Temperature: nothing specified, but should be better than ± 0.5 K.

COMPONENTS:

(1) Ammonium radical; NH_4; [26497-91-6]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Stromberg, A.G.; Konkova, A.V.

Zh. Fiz. Khim. 1968, *42*, 2063-5.

VARIABLES:

Temperature: 283 - 293 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Solubilities (stationary concentrations) of ammonium radical NH_4 in Hg were determined by an indirect method:

t/°C	10^2Soly/mol dm^{-3}	10^3Soly/mass %	10^3Soly/mol %
10	0.53	0.70	7.8
16	0.93	1.23	13.5
20	1.55	2.04	22.0

[a] by compilers.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The amalgam was prepared by electroreduction of NH_4^+ from 2 mol dm^{-3} NH_4Cl (pH=7) on Hg laying (sic) drop electrode at -2.06 V vs. SCE. The time of the electrolysis was changed in the range 15-75 s. Since the drop containing $NH_4^{\cdot}$ gets foamy, its radius was measured before the electrolysis and 1-2 s after it was stopped. Because of the total amount of $NH_4^{\cdot}$ (m_o) some decomposed to NH_3 (m') in the solution and to H_2, whose volume is measured in a gas microburette. One may easily find the amount of $NH_4^{\cdot}$ soluble in Hg (m) from the difference: $m = m_o - m'$.

SOURCE AND PURITY OF MATERIALS:

Hg drop was prepared by electroreduction of $Hg(NO_3)_2$ on a Pt wire.

ESTIMATED ERROR:

Solubility: precision ± (5-10) % (authors) but there is no proof that an equilibrium with a solid was reached in the system (compilers).

Temperature: probably better than ± 1 K (compilers).

COMPONENTS:	EVALUATOR:
(1) Sodium-tin 1:1; NaSn; [12439-10-0] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland April 1983

CRITICAL EVALUATION:

Filippova and coworkers (1) determined the solubility product of NaSn, $K_s = [Na][Sn]$, as well as its enthalpy of dissolution in Hg by the calorimetric titration of the mixed, heterogeneous amalgams. However, there is significant disagreement between the originally reported value, 0.25 mol^2 dm^{-6}, and the mean value calculated by compilers, 0.83 mol^2 dm^{-6}. It is impossible to find the reason for this difference; it may be a misprint or it may be caused by a correction of activity coefficients, since the amalgams were concentrated. Therefore only a doubtful value may be suggested.

Matthes and Schuster (2) found formation of solid Na_2SnHg in the amalgam, but NaSn is formed in the binary Na-Sn system (3).

Value of the solubility of NaSn in Hg (doubtful)

The solubility product of NaSn in Hg at 298 K is, as calculated from the solubility by evaluators:

$$0.25 \text{ mol}^2 \text{ dm}^{-6}$$

and the solubility, as reported in (1):

$$0.5 \text{ mol dm}^{-3}$$

References

1. Filippova, L.M.; Zebreva, A.I.; Zhumakanov, V.Z. *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.* 1982, *25*, 827.
2. Matthes, R.; Schuster, H.-U. *Z. Naturforsch.* 1980, *35 B*, 778.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium-tin 1:1; NaSn; [12439-10-0]	Filippova, L.M.; Zebreva, A.I.; Zhumakanov, V.Z. *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1982, *25*, 827-9.
VARIABLES:	PREPARED BY:
Temperature: 298 K	C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of NaSn in Hg at 25 °C is 0.5 mol dm^{-3}. The detailed results, in disagreement with the original value, are as follows[b]:

c_{Na}^{i}/ mol d $^{-3}$	c_{Sn}^{i}/ mol dm^{-3}	c_{Na}^{f}/ mol dm^{-3}	c_{Sn}^{f}/ mol dm^{-3}	K_s/ [a] mol^2 dm^{-6}
1.33	0.87	1.15	0.60	0.69
2.00	0.84	1.44	0.62	0.89
2.20	0.71	1.70	0.56	0.95
1.52	0.75	1.16	0.59	0.68
2.26	0.69	1.72	0.54	0.93
			mean value	0.83±0.13

[a] by compilers.

[b] solubility 0.9 mol dm^{-3} (compilers).

The heat of dissolution of NaSn in its saturated amalgam is 6.0±0.4 kJ mol^{-1} at the 0.95 confidence level.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The Sn amalgam was obtained by dissolution of this metal in Hg. The Na amalgam was prepared electrolytically. Both amalgams were mixed in various proportions. They were diluted with Hg and heat (Q) was measured. A bend on dependences of Q vs. the concentrations of Na or Sn corresponds to the equilibrium concentrations of the metals. From this, one obtains the stoichiometry and solubility product of the compound formed. The experiments were performed in an Ar atmosphere.	Nothing specified. ESTIMATED ERROR: Nothing specified. Solubilities: standard deviation ± 15 % (by compilers).

COMPONENTS:	EVALUATOR:
(1) Nickel-antimony 1:1; NiSb; [12035-52-8] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland November 1982

CRITICAL EVALUATION:

With the use of anodic stripping voltammetry Zakharov and Zaichko (1) found NiSb insoluble in Hg. The solubility product, $K_s = [Ni][Sb]$, was reported to be 1.7×10^{-8} mol^2 dm^{-6}. So the solubility of this compound is slightly lower than the solubility of Sb in Hg and much higher than the solubility of Ni in Hg; see the Sb-Hg and Ni-Hg systems. Therefore one is not sure whether true equilibrium is reached and only a doubtful value may be suggested. Formation of poorly soluble NiSb in Hg was also reported in (3, 4) but no quantitative results are supported. Times of experiments in (4) were prolonged to 15 min yielding a confirmation of data in (1). The phase NiSb is the most stable in the Ni Sb binary alloys (2).

Value of the solubility of NiSb in Hg (doubtful)

The solubility product of NiSb in Hg at 293 K according to (1) is:

$$1 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$$

and the solubility, as calculated by evaluators from K_s is:

$$1 \times 10^{-4} \text{ mol dm}^{-3}$$

References

1. Zakharov, M.S.; Zaichko, L.F. *Izv. Tomsk. Politekhn. Inst.* 1967, *164*, 183.
2. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
3. Stromberg, A.G.; Zakharov, M.S.; Mesyats, N.A.; Zaichko, L.F.; Stepanova, O.S. *Teoria i Praktika Amalgamny kh Profsesov, Alma-Ata*, 1966, p. 68.
4. Zaichko, L.F.; Zakharov, M.S. *Izv. Tomsk. Politekhn. Inst.* 1971, *174*, 66.

COMPONENTS:

(1) Nickel-antimony 1:1; NiSb; [12035-52-8]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zakharov, M.S.; Zaichko, L.F.

Izv. Tomsk. Politekhn. Inst. 1967, *164*, 183-6.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound NiSb is treated as sparingly soluble in Hg and the solubility product value is (1.7±0.2)x10^{-8} mol^2 dm^{-6} at room temperature. The detailed results are:

$c_{Sb(III)}$/mol dm^{-3}	K_s/mol^2 dm^{-6}
1.2x10^{-5}	1.9x10^{-8}
1.0x10^{-5}	1.5x10^{-8}

The concentration ratio Ni:Sb was changed in the range 0-1.0. Since the solubility of Ni in Hg at room temperature is of the order of 10^{-7} mol dm^{-3} (see the Ni-Hg system) it is doubtful whether the amalgam was in equilibrium before the oxidation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Anodic stripping voltammetry with accumulation (5 min. at -1.65 V) on the hanging mercury drop electrode was applied. The reference electrode was SCE. The Ni(II) and Sb(III) were in a solution of 2 mol dm^{-3} KOH and 0.5 mol dm^{-3} EDTA. The solubility product was calculated from the recorded oxidation currents of both metals. The polarograms were recorded 1 min after the accumulation was completed. The experiments were carried out in an N_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

Sb(III) salt was obtained from dissolution of the metal in an acid. Content of heavy metal ions in the solution was below 5x10^{-8} mol dm^{-3}. Source of Ni(II) was $NiSO_4$.

ESTIMATED ERROR:

Solubility: precision of the determination ± 10 % but an absolute error may be significant. Temperature: nothing specified.

COMPONENTS:	EVALUATOR:
(1) Nickel-tin 1:1; NiSn; [12059-11-9] Nickel-tin 3:4; Ni_3Sn_4; [12202-01-6] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland October 1982

CRITICAL EVALUATION:

The Ni-Sn-Hg system was studied at first by Kemula and Galus (1). They found the formation of a stable intermetallic with the composition NiSn using anodic oxidation of the metals from this complex amalgam, preconcentrated in a hanging mercury drop electrode. However, the solubility of NiSn in Hg was not investigated. This finding was later confirmed by Zebreva and Kovaleva (2) who used anodic stripping voltammetry as well as measurements of potentials of the amalgam electrodes. They detected the compound to be sparingly soluble and reported its solubility products, $K_s = [Ni][Sn]$, at 293 and 323 K. In the calculation of K_s, the concentration of Ni in the homogeneous phase was assumed to be equal to its solubility in Hg, which conforms with the value of the solubility of Ni used (see the Ni-Hg system). This leads to relative and doubtful values of the solubility of NiSn in Hg. The level of Sn concentrations was too low to be determined precisely by potentiometry. More correct values are given in the Data Sheet. Starzewski, in the evaluators' laboratory (3), performed an extensive study of the Ni-Sn-Hg system and found, by voltammetry and coulometry, that, as in the Ni-Sn binary alloys, Ni_3Sn_4 but not NiSn is precipitated in Hg (4). No solubility determinations were carried out in (3). Roentgenographic experiments performed earlier showed that the δ-phase of Ni-Sn (with 52 at % Sn) is formed in the complex amalgam (5).

Value of the solubility of NiSn in Hg (doubtful)

The solubility product of NiSn in Hg at 293 and 323 K is, as reported in (2):

$$1 \times 10^{-12} \text{ and } 3 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}, \text{ respectively}$$

and the solubility, as calculated from K_s by evaluators:

$$1 \times 10^{-6} \text{ and } 2 \times 10^{-6} \text{ mol dm}^{-3}, \text{ respectively}$$

References

1. Kemula, W.; Galus, Z. *Roczniki Chem.* 1960, *34*, 251.
2. Zebreva, A.I.; Kovaleva, L.M. *Zh. Fiz. Khim.* 1965, *39*, 855.
3. Starzewski, P. *M. Sc. Thesis*, University of Warsaw, 1974; as cited in Galus, Z. *Crit. Rev. Anal. Chem.* 1975, *5*, 359.
4. Hansen, M.; Anderko, M. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
5. Lihl, F.; Kirnbauer, H. *Z. Metallk.* 1957, *48*, 9.

COMPONENTS:

(1) Nickel-tin 1:1; NiSn; [12059-11-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zebreva, A.I.; Kovaleva, L.M.

Zh. Fiz. Khim. 1965, *39*, 855-8.

VARIABLES:

Temperature: 293-323 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The compound NiSn is considered sparingly soluble in Hg. Its dissolution equilibrium is described by the solubility product K_s.

$t/°C$	$10^3c_{Sn}{}^i$/ mol dm^{-3}	$10^3c_{Ni}{}^i$/ mol dm^{-3}	$10^7c_{Sn}{}^f$/ mol dm^{-3}	$10^{12}K_s$/ mol^2 dm^{-6}
20	0.05	0.50	0.92	1.07
	0.27	0.50	1.09	1.27
	0.11	5.03	1.36	1.58
	0.11	5.03	1.20	1.39
	0.27	5.03	1.41	1.63
	0.49	5.03	1.16	1.35
	0.49	5.03	1.41	1.63
	0.82	5.03	1.80	2.09
	1.13	5.03	1.62	1.83
	1.27	4.00	1.05	1.22
	1.80	4.00	1.05	1.22
	2.34	4.00	0.98	1.14

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The simple amalgams were prepared by electrolytic reduction of Ni(II) and Sn(II) on a Hg cathode. After mixing of these amalgams in various ratios, potentials of the complex amalgam were measured in a solution of 2 mol dm^{-3} KCl + HCl at pH ~ 1. The solubility product was calculated from the potential difference of Sn in the simple and complex amalgams; the concentration of free Ni was assumed to be equal to its solubility in Hg, so taken as constant. The experiments were carried out in a CO_2 atmosphere. In polarographic experiments oxidation currents of Ni-Sn amalgam were on the border of the detection limit.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility standard deviation ± 25 % but the absolute value is relative.

Temperature: nothing specified.

REFERENCES:

1. Baranski, A.; Galus, Z. *J. Electroanal. Chem.* 1973, *46*, 289.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Nickel-tin 1:1; NiSn; [12059-11-9] (2) Mercury; Hg; [7439-97-6]	Zebreva, A.I.; Kovaleva, L.M. *Zh. Fiz. Khim.* 1965, *39*, 855-8.

EXPERIMENTAL VALUES (continued)

t/°C	$10^3c_{Sn}{}^i$/ mol dm^{-3}	$10^3c_{Ni}{}^i$/ mol dm^{-3}	$10^7c_{Sn}{}^f$/ mol dm^{-3}	$10^{12}K_s$/ mol^2 dm^{-6}
	2.70	4.00	0.94	1.09
	2.87	4.00	1.03	1.19
			mean value	1.4±0.3 [a]
50	0.11	0.50	1.75	2.02
	0.17	0.50	1.56	1.82
	0.23	0.50	1.71	2.01
	1.65	5.03	2.85	3.30
	2.21	5.03	2.85	3.30
	2.76	5.03	2.74	3.16
	3.32	5.03	2.74	3.16
			mean value	2.7±0.7 [a]

[a] mean values and standard deviations calculated by compilers.

In the original calculations of the solubility product the concentration of free Ni (its solubility in Hg) was taken to be 1.16×10^{-5} mol dm^{-3} at 20 and 50 °C. This is orders of magnitude higher than the selected values (see the Ni-Hg system). The solubility of Ni at 20 and 50 °C is 5×10^{-7} and 1.8×10^{-6} mol dm^{-3}, respectively (1). This correction makes the final results equal to 1.8×10^{-14} and 4.2×10^{-13} mol^2 dm^{-6} at 20 and 50 °C, respectively.

COMPONENTS:

(1) Nickel-zinc 1:1; NiZn; [12035-62-0]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

November 1983

CRITICAL EVALUATION:

Performing electrochemical oxidation of the Ni-Zn amalgams Bukhman and Nosek (1) and Donten (4) concluded that the solubility of NiZn in Hg is limited, but no data were reported. An extended study of the system was published by Rodger and Meites (2). Using controlled potential electrolysis, the authors proved that NiZn is only slightly soluble and reported its solubility product, K_s = [Ni][Zn], equal to 1.0×10^{-8} mol^2 dm^{-6}, probably at 298 K. When the concentration ratio of Zn to Ni is higher than 2.5 another compound, $NiZn_3$, is formed, soluble but poorly dissociated in Hg.

The solubility of NiZn determined is significantly higher than the solubility of Ni in Hg (see the Ni-Hg system) so only a doubtful value of the solubility may be suggested. The phase NiZn is stable in the Ni-Zn binary alloys (3).

Value of the solubility of NiZn in Hg (doubtful)

The solubility product of NiZn in Hg at 298 K is, according to paper (2):

$$1\times10^{-8}\ mol^2\ dm^{-6}$$

and the solubility, as calculated by evaluators:

$$1\times10^{-4}\ mol\ dm^{-3}$$

References

1. Bukhman, S.P.; Nosek, M.V. *Tr. Inst. Khim. Nauk Akad. Nauk Kaz. SSR* 1964, *12*, 99.
2. Rodgers, R.S.; Meites, L. *J. Electroanal. Chem.* 1972, *38*, 359.
3. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
4. Donten, M. *Ph.D. Thesis*, University of Warsaw, 1987.

COMPONENTS:

(1) Nickel-zinc 1:1; NiZn; [12035-62-0]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Rodgers, R.S.; Meites, L.

J. Electroanal. Chem. 1972, *38*, 359-65.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Values of K_s (solubility product) and K_{eq} (equilibrium constant) obtained from the oxidation of aged nickel-zinc amalgams containing excess nickel at room temperature:

$n_{e,Zn}^{i}$/ μmol^{b}	$n_{e,Ni}^{i}$/ μmol^{b}	$n_{e,Zn}^{f}$/ μmol^{b}	$n_{e,NiZn}^{f}$/ μmol^{b}	Amalgam age/h	$10^{8}K_s$/ $mol^{2}dm^{-6}$	$10^{5}K_{eq}$/ mol dm^{-3}
93.3	101	4.69	88.6	13.2	1.18	0.94
46.4	50.5	3.05	43.4	23.2	0.44	0.71
19.34	30.3	6.43	12.91	1.3	[a]	[a]
19.72	30.3	4.09	15.63	16.8	1.22	5.49
19.34	30.3	4.12	15.22	41.8	1.26	5.84
14.98	20.2	3.93	11.05	65.2	0.74	4.77
				mean value	1.0±0.3	

[a] Equilibrium constants not calculated because amalgam not yet at equilibrium. Volume of the complex amalgam 35 cm^{3}.

[b] Equivalent charge amount for the indicated species.

The solubility of the compound is three orders of magnitude higher than the solubility of Ni in Hg; see the Ni-Hg system.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Ni-Zn and Zn amalgams were prepared by electroreduction of Ni(II) and Zn(II) at a mercury pool cathode at -1.35 V vs. Ag/AgCl/NaCl (salt) electrode. The supporting electrolyte was usually 0.1 mol dm^{-3} dibasic ammonium citrate, 0.2 mol dm^{-3} NH_3 saturated with NaCl; also 0.15 mol dm^{-3} NH_3 saturated with NaCl was used in some experiments. Stripping of Zn from the Ni-Zn and Zn amalgams was carried out at -0.3 V. The currents were integrated and the solubility product calculated from mass balance of the reagents. The experiments were performed in a N_2 atmosphere.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility: precision ± 30 % (authors) but an absolute error may be significant (compilers).

Temperature: nothing specified.

COMPONENTS:	EVALUATOR:
(1) Nickel-zinc 1:3; $NiZn_3$; [12439-59-7] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland November 1984

CRITICAL EVALUATION:

When the concentration of Zn in the Ni-Zn-Hg system exceeds 2.5 times the concentration of Ni then $NiZn_3$ is formed in Hg phase. This compound is soluble in Hg and its dissociation constant, $K_d = [Ni][Zn]^3/[NiZn_3]$, is $(6.0 \pm 0.7) \times 10^{-10}$ mol^3 dm^{-9} at probably 298 K. However, a limit of the solubility of $NiZn_3$ in Hg is not reported. The equilibrium Ni concentration estimated from K_d is more than a thousand times higher than the selected value of the solubility of Ni in Hg (see the Ni-Hg system) which makes the result very questionable. For lower ratios of Zn to Ni insoluble NiZn is precipitated in the system.

COMPONENTS:

(1) Nickel-zinc 1:3; $NiZn_3$; [12439-59-7]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Rodgers, R.S.; Meites, L.

J. Electroanal. Chem. 1972, *38*, 359-65.

VARIABLES:

Room temperature measurement

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

Calculation of K_x assuming that NiZn is insoluble (a_{NiZn}=1) and that $NiZn_x$ is soluble:

$n_{e,Zn}^{f}/\mu mol^{a}$	$n_{e,Ni}^{i}/\mu mol^{a}$	$n_{e,NiZn}^{f}/\mu mol^{a}$	K_2	$K_3/mol\ dm^{-3}$	$K_4/mol^2\ dm^{-6}$
197.2	30.3	46.7	12.0	$6.78x10^{-2}$	$2.86x10^{-4}$
89.9	5.05	9.1	22.2	$5.70x10^{-2}$	$1.10x10^{-4}$
60.7	30.3	32.2	31.9	$\underline{5.54x10^{-2}}$	$7.21x10^{-5}$
				$(6.0\pm0.5)x10^{-2}$	

[a] Equivalent charge amount for the indicated species.

The value of K_3 combined with K_s $(1.0\pm0.3)x10^{-8}$ $mol^2\ dm^{-6}$ for NiZn in Hg yielded the value of K_d reported above. The compound $NiZn_3$ is formed in the binary Ni-Zn system (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The experiments were performed in a N_2 atmosphere. The Ni-Zn and Zn amalgams were prepared by electroreduction of Ni(II) and Zn(II) at a mercury pool cathode at -1.35 V vs. Ag/AgCl/NaCl (salt) electrode. The supporting electrolyte was usually 0.1 mol dm^{-3} dibasic ammonium citrate and 0.2 mol dm^{-3} NH_3 saturated with NaCl; 0.15 mol dm^{-3} NH_3 saturated with NH_4Cl was also used in some experiments. Stripping of Zn from the Ni-Zn and Zn amalgams was carried out at -0.3 V. The oxidation currents were integrated and the dissociation constant calculated by fitting the experimental results to the model assumed (NiZn insoluble and $NiZn_3$ soluble). The invariancy of K_3 points to formation of soluble but poorly dissociated $NiZn_3$ in Hg. Other models were tested without success.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Dissociation constant: precision ± 10 % (authors) but absolute error may be significant (compilers).

Temperature: nothing specified.

REFERENCES:

1. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Palladium-zinc 1:1; PdZn; [23412-51-3]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Dergacheva, M.B.; Kozin, L.F.; Panova, N.L.

Dep. VINITI, 1978, 3595-78.

VARIABLES:

Temperature: 323-363 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product values of PdZn in Hg at various temperatures are:

t/°C	K_s/mol^2 dm^{-6}	Solubility/mol dm^{-3}
50	2.7×10^{-8}	1.6×10^{-4}
75	1.9×10^{-6}	1.4×10^{-3}
90	1.3×10^{-5}	3.6×10^{-3}

Initial concentrations of Pd and Zn were changed in the ranges 1×10^{-3}-3×10^{-2} mol dm^{-3} and 3×10^{-4}-5×10^{-2} mol dm^{-3}, respectively. The experiments performed at 298 K were strongly affected by corrosion of the amalgam so any solubility product calculated under these conditions is doubtful. At higher temperature corrosion seems to be less and the solubility values acceptably correct.

Solid PdZn precipitated in Hg was identified by chemical analysis and roentgenography and it was found to be the same as formed in the Pd-Zn binary system (1).

The temperature dependence of the solubility product estimated by the least square method may be expressed with the following equation:

$$pK_s = -17.1 + 7.97\times10^{3}\, T^{-1} \qquad r = 0.999 \qquad (K_s/\mathrm{mol}^2\mathrm{dm}^{-6};\ T/\mathrm{K})$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Pd amalgam was obtained by a complete electroreduction of Pd salt dissolved in HCl solution. The amalgam was transferred to a cell where a known amount of Zn(II) was electroreduced on it with 100 % efficiency. Potentials of the cell: Zn(Hg) |0.2 mol dm^{-3} $ZnSO_4$, 0.5 mol dm^{-3} $(NH_4)_2SO_4$, 3 mol dm^{-3} NaOH and 50 g dm^{-3} $N_2H_4\cdot H_2SO_4$| Pd-Zn(Hg) were measured. The electrolyte was purified from traces of O_2 by blowing H_2 through the solution. The solubility products at various temperatures were calculated from the potential differences and mass balance.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility: nothing specified; it should be better than ± 10 % (compilers).

Temperature: ± 0.5 K.

REFERENCES:

1. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Platinum-zinc 1:2; $PtZn_2$; [79471-67-3]

(2) Mercury; Hg; [7439-97-6]

EVALUATOR:

C. Gumiński, Z. Galus
Department of Chemistry
University of Warsaw
Warsaw, Poland

January 1984

CRITICAL EVALUATION:

Gumiński and coworkers (1) established the formation of $PtZn_2$ in Hg using potentiometry and voltammetry. The solubility product of the compound, $K_s = [Pt][Zn]^2$, was determined to be 1×10^{-14} mol^3 dm^{-9} at 298 K. The formation of $PtZn_2$ in the amalgam was found earlier by Rodgers and Meites (2) but no solubility was determined.

The compounds $PtZn_3$ (2) and $PtZn_4$ (Pt_5Zn_{21}) (2, 3) are also formed in the Pt-Zn-Hg system when the excess of Zn over Pt is higher and experiments are performed for longer conditioning times (2) and higher temperatures (3).

All of these compounds are known to be formed in the Pt-Zn binary system (4).

Value of the solubility product of $PtZn_2$ in Hg (doubtful)

The solubility product of $PtZn_2$ in Hg at 298 K is, according to (1):

$$1 \times 10^{-14} \text{ mol}^3 \text{ dm}^{-9}$$

and the solubility, as calculated from K_s by evaluators:

$$1.5 \times 10^{-5} \text{ mol dm}^{-3}$$

References

1. Gumiński, C.; Roslonek, H.; Galus, Z. *J. Electroanal. Chem.* 1983, *158*, 357.
2. Rodgers, R.S.; Meites, L. *J. Electroanal. Chem.* 1981, *125*, 167.
3. Barlow, M.; Planting, P.J. *Z. Metallk.* 1969, *60*, 293.
4. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

COMPONENTS:

(1) Platinum-zinc 1:2; $PtZn_2$; [79471-67-3]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Gumiński, C.; Roslonek, H.; Galus, Z.

J. Electroanal. Chem. 1983, *158*, 357-68.

VARIABLES:

Temperature: 298 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of $PtZn_2$ in Hg at 298.2 K is $1x10^{-14}$ mol^3 dm^{-9}. The concentration ratio of Pt to Zn in the amalgam was changed in the range 0 - 1. The solubility product was only calculated for the Pt to Zn ratio equal to 1/2. For other ratios the initial concentrations of both metals were unknown.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

All experiments were performed in a H_2 atmosphere. The mixed Pt-Zn amalgam was obtained by electroreduction of both metals on the hanging mercury drop electrode at -1.3 V vs. SCE from a solution of $ZnCl_2$ and H_2PtCl_6 in 0.5 mol dm^{-3} NaCl. After the electrolysis, the electrode was carefully rinsed and transferred into a separate, deoxygenated solution of $1.00x10^{-3}$ mol dm^{-3} $ZnCl_2$ in 0.5 mol dm^{-3} NaCl. The potential of this electrode vs. SCE was recorded for 400 s; it was practically constant after 180 s. From the measured equilibrium potentials at the concentration ratio Pt to Zn equal 1/2, where a jump of the potential vs. concentration ratio was observed, the solubility product of the compound was calculated from the active Zn concentration and mass balance. Every experiment was repeated at least three times.

SOURCE AND PURITY OF MATERIALS:

All reagents from POCh were of analytic purity. Triply distilled H_2O and twice distilled Hg after chemical purification with acidified $Hg_2(NO_3)_2$ were used. Solutions of $ZnCl_2$ and NaCl were additionally purified by a cathodic electrolysis at -0.9 V.

ESTIMATED ERROR:

Solubility: precision ± 50 %; reproducibility of potentials ± 2 mV.

Temperature: ± 0.2 K.

COMPONENTS:	EVALUATOR:
(1) Antimony-zinc 1:1; SbZn; [12039-35-9] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland October 1983

CRITICAL EVALUATION:

On the basis of the anodic oxidation of the complex Sb-Zn amalgam and potentiometric experiments performed by Zebreva and Kozlovskii (1, 4) the formation of solid SbZn in Hg was established. The solubility product, K_s = [Sb][Zn], was determined to be 2.6×10^{-9} mol^2 dm^{-6} at 291 K. However, Zakharov and coworkers (6) using anodic stripping voltammetry did not observe precipitation of SbZn in Hg even when Sb and Zn concentrations were as high as 7.0×10^{-4} and 6.4×10^{-3} mol dm^{-3}, respectively. On the other hand, precipitation of a Sb-Zn compound was observed during simultaneous codeposition of Sb and Zn on a Hg electrode. Mathematical analysis of Zebreva's potentiometric results by the method of Stromberg and coworkers (2, 3) leads to the mean result 1.8×10^{-9} mol^2 dm^{-6}.

The phase SbZn is stable in the binary Sb-Zn alloys (5).

Value of the solubility of SbZn in Hg (tentative)

The solubility product of SbZn in Hg at 291 K (mean value of (1, 4) and (2, 3)) is:

$$2 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$$

and the solubility, as calculated from K_s by evaluators:

$$4 \times 10^{-5} \text{ mol dm}^{-3}$$

References

1. Zebreva, A.I. *Zh. Fiz. Khim.* 1962, *36*, 1822.
2. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Zh. Fiz. Khim.* 1974, *48*, 2243.
3. Stromberg, A.G.; Mikheeva, N.P.; Belousov, Yu.P. *Tr. Inst. Org. Katal. Elektrokhim. Akad. Nauk Kaz. SSR* 1974, *7*, 42.
4. Zebreva, A.I.; Kozlovskii, M.T. *Zavod. Lab.* 1964, *30*, 1193.
5. Hansen, M.; Anderko, K. *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
6. Zakharov, M.S.; Mesyats, N.A.; Zaichko, L.F.; Baletskaya, L.G. *Tzv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.* 1966, *9*, 355.
7. Abramova, N.S.; Bukhman, S.P. *Fiz.-Khim. Issled. Neorg. Soedin.*, Cheboksary, 1983, p. 81.

COMPONENTS:

(1) Antimony-zinc 1:1; SbZn; [12039-35-9]

(2) Mercury; Hg; [7439-97-6]

ORIGINAL MEASUREMENTS:

Zebreva, A.I.

Zh. Fiz. Khim. 1962, *36*, 1822-5.

VARIABLES:

Temperature: 291 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility product of SbZn in Hg is 2.7×10^{-9} mol^2 dm^{-6} at 18 °C or $(2.6 \pm 0.6) \times 10^{-9}$ mol^2 dm^{-6} as reported in (1).

Results of the potentiometric determination:

$10^5 c_{Zn}^{i}$/ mol dm^{-3}	$10^5 c_{Sb}^{i}$/ mol dm^{-3}	$10^5 c_{Zn}^{f}$/ mol dm^{-3}	$10^5 c_{Sb}^{f}$/ mol dm^{-3}	$10^9 K_s$/ mol^2 dm^{-6}
4.74	9.2	3.43	7.9	2.71
7.14	9.2	4.14	6.2	2.56
8.74	9.2	5.46	5.9	3.20
1.75	14.2	1.60	14.0	2.25
2.92	14.2	1.84	13.1	2.42
4.07	14.2	1.93	12.1	2.34
5.21	14.2	2.02	11.0	2.22
6.96	14.2	2.16	9.4	2.02

(continued next page)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Differences of the potential of Zn and Sb-Zn amalgams in a solution containing Zn(II) were measured. Also constant current anodic oxidation of Sb-Zn amalgams in 0.5 mol dm^{-3} H_2SO_4 or 1 mol dm^{-3} NaOH + 0.07 mol dm^{-3} $KNaC_4H_4O_6$ solutions were performed as supplementary measurements. The solubility product was calculated from the potential differences of the cell and mass balance. The amalgams were prepared by an electrolysis.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility: precision ± 20 % (authors) standard deviation ± 17 % (compilers).

Temperature: nothing specified.

REFERENCES:

1. Zebreva, A.I.; Kozlovskii, M.T. *Zavod. Lab.* 1964, *30*, 1193.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Antimony-zinc 1:1; SbZn; [12039-35-9] (2) Mercury; Hg; [7439-97-6]	Zebreva, A.I. *Zh. Fiz. Khim.* 1962, *36*, 1822-5.

EXPERIMENTAL VALUES (continued)

$10^5c_{Zn}{}^i$/ mol dm^{-3}	$10^5c_{Sb}{}^i$/ mol dm^{-3}	$10^5c_{Zn}{}^f$/ mol dm^{-3}	$10^5c_{Sb}{}^f$/ mol dm^{-3}	10^9K_s/ mol^2 dm^{-6}
8.70	14.2	2.48	8.0	2.00
11.00	14.2	4.50	7.1	3.20
			mean value	2.5±0.4 [a]

[a] mean value and standard deviation calculated by compilers.

COMPONENTS:	EVALUATOR:
(1) Tellurium-thallium 1:2; $TeTl_2$; [12040-13-0] Tellurium-thallium-mercury 2:1:1; Te_2TlHg [98595-01-8] Tellurium-thallium-mercury 4:2:3; $Te_4Tl_2Hg_3$ [67115-70-2] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland April 1984

CRITICAL EVALUATION:

Babanly and coworkers (1) reported on the Te-Tl-Hg system and constructed the phase diagram in form of liquidus lines reproduced below. One may read solubilities of $TeTl_2$ in Hg from the binary $TeTl_2$-Hg cross section. The equation relating the solubility to temperature is:

$$pS = -1.70 + 1.78\times10^{3}\ T^{-1} \qquad r = 0.995 \qquad (S/\text{mol }\%;\ T/K)$$

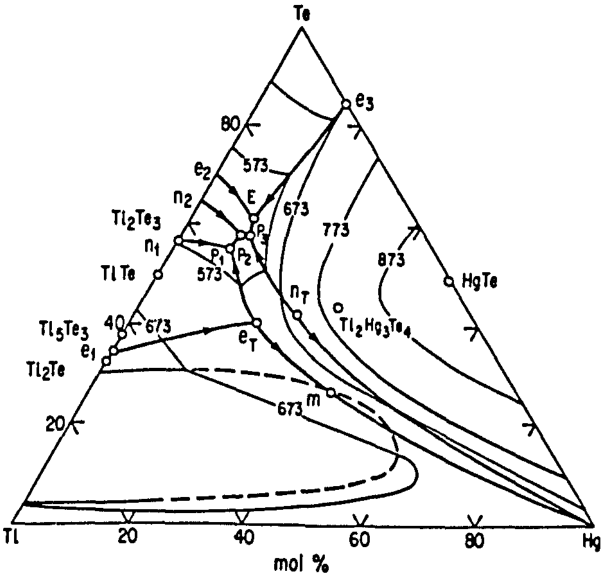
Since the solubility of $TeTl_2$ in the temperature range 518-681 K is higher than the solubility of Te in Hg (see the Te-Hg system) the results obtained are questionable. The only explanation, which may be proposed, is that the equilibrium solid phase is not $TeTl_2$, as found to exist in the binary Te-Tl system (3), but Te_2TlHg (2) or $Te_4Tl_2Hg_3$ (1). The melting point of $Te_4Tl_2Hg_3$ was also established in (1).

Value of the solubility of $TeTl_2$ in Hg (doubtful)

The solubility of $TeTl_2$ in Hg at 568 K is 3 mol % and at 681 K is 13 mol %, according to (1).

References

1. Babanly, M.B.; Asadov, M.M.; Kuliev, A.A. *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1983, *19*, 583.
2. Gyseinov, G.D.; Gyseinov, G.G.; Ismailov, M.Z.; Godzhaev, E.M. *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1960, *5*, 33.
3. Castanet, R.; Bergman, C.; Michel, M.L.; Kehiaian, H.V. *Z. Metallk.* 1977, *68*, 342.



COMPONENTS:

(1) Tellurium-thallium 1:2; $TeTl_2$; [12040-13-0]

(2) Tellurium-thallium 4:2:3; $Te_4Tl_2Hg_3$; [67115-70-2]

ORIGINAL MEASUREMENTS:

Babanly, M.B.; Asadov, M.M.; Kuliev, A.A.
Izv. Akad. Nauk SSSR, Neorg. Mater. 1983, *19*, 583-7.

VARIABLES:

Temperature: 518-681 K

PREPARED BY:

C. Gumiński; Z. Galus

EXPERIMENTAL VALUES:

The solubility of $TeTl_2$ in Hg was determined from the $TeTl_2$-Hg phase diagram by the compilers:

T/K	solubility/mol fraction
518	0.020
568	0.033
630	0.070
658	0.10
681	0.13

The melting point of $Te_4Tl_2Hg_3$ was determined to be 800 K, as read by compilers from the $Te_4Tl_2Hg_3$-Te phase diagram inserted in the original work.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The alloys of Te-Tl were prepared by melting the elements in evacuated quartz ampules. They were homogenized for 400 hours at a temperature 20-30 K lower than the solidus. Differential thermal analysis and measurements of vapor pressure over the amalgams were performed.

SOURCE AND PURITY OF MATERIALS:

High purity elements were used.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:	EVALUATOR:
(1) Tellurium-zinc 1:1; TeZn; [1315-11-3] (2) Mercury; Hg; [7439-97-6]	C. Gumiński, Z. Galus Department of Chemistry University of Warsaw Warsaw, Poland September 1988

CRITICAL EVALUATION:

No experimental values on the solubility of TeZn in Hg are reported. The solubility of TeZn in Hg was predicted by Brebrick (1) to be about one-tenth that of CdTe. Erdenbaeva and Esimbekova (2) did not notice any dissolution of a TeZn suspension in Hg at 298 to 353 K. Some studies of the TeZn-HgTe pseudobinary phase diagrams were reported in (3-6). The compound TeZn is stable in the Te-Zn binary system (7).

References

1. Brebrick, R.F. *J. Cryst. Growth* 1988, *86*, 39.
2. Erdenbaeva, M.I.; Esimbekova, B.B. *Dep. VINITI no. 4582-81*, 1981.
3. Danilyuk, S.A.; Kot, M.V. *Izv. Akad. Nauk SSSR, Ser. Fiz.* 1964, *28*, 1073.
4. Crucheanu, E.; Niculescu, D.; Nictor, N. *Rev. Roum. Phys.* 1964, *9*, 499.
5. Wooley, J.C.; Ray, B. *J. Phys. Chem. Solids* 1960, *13*, 151.
6. Mizetskaya, I.B.; Tomashik, V.N.; Vengel, P.F. *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1983, *19*, 1010.
7. Laugier, A. *Rev. Phys. Appl.* 1973, *8*, 259.

SYSTEM INDEX

Pages preceded by E refer to evaluation texts whereas those not preceded by E refer to compiled tables.

REGISTRY NUMBER INDEX

Pages preceded by E refer to evaluation texts whereas those not preceded by E refer to compiled tables.

AUTHOR INDEX

Pages preceded by E refer to evaluation texts whereas those not preceded by E refer to compiled tables. Page numbers in Roman numerials refer to qualitative data in the Introduction to the volume pp(x-xxiii).

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