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STUDIES OF BISMUTH ALLOYS, II.
DISTRIBUTION OF SMALL ADDITIONS OF Cu, Ag, OR Au
BETWEEN SOLID AND LIQUID PHASES IN Bi-Cu, Bi-Ag, AND Bi-Au

Marcel W. Nathans and Marjorie Leider

May 23, 1961

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ABSTRACT

The distribution of small amounts of radioactive Cu, Ag, and Au between precipitates of these elements and their solutions in bismuth was investigated at different temperatures by sampling the liquid. In all cases the Doerner-Hoskins law was obeyed. Approximate distribution ratios were calculated and plotted against $1/T$. Extrapolation to the melting temperature of the major component X in these Bi-X-Y systems yields values which compare well with the distribution constants obtained either from the binary X-Y phase diagrams or with those calculated from thermodynamic data. The data support solid solution formation as the mechanism of coprecipitation. This investigation also suggests a new method of obtaining significant portions of solidus curves.

* This work was performed under the auspices of the U. S. Atomic Energy Commission.

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Introduction

A few years ago, a program was initiated at the Argonne National Laboratory to study in some detail the coprecipitation of miscellaneous fission products with U_2Zn_{17} from a solution of irradiated uranium in zinc.¹ This followed a few isolated studies by Kaufmann² on the coprecipitation of rare earth tracers with uranium compounds from solutions in bismuth or lead-based alloys; by Teitel³ on similar systems, by Teitel and Brodsky,⁴ and by Teitel⁵ on uranium and protactinium tracers in thorium-bismuth and thorium-bismuth-lead alloys.

¹H. M. Feder and R. J. Teitel, Proc. 2nd U. N. Internat. Conf. on Peaceful Uses of Atomic Energy, Geneva, 1958, Paper No. 540, Vol. 17, p. 383.

²D. F. Kaufmann, Thesis, Mass. Inst. of Technology, June, 1955.

³R. J. Teitel, Chem. Eng. Prog., Symposium Ser. 53, No. 20:25 (1957).

⁴M. Brodsky and R. J. Teitel, quoted in ref. 1.

⁵R. J. Teitel in Progress Rep. Nucl. Eng. Dept., Brookhaven National Laboratory, Rep. No. BNL-418 (5-32), 1955-56, p. 15.

The most extensive investigation at ANL was conducted with small lanthanum additions in solutions of uranium in zinc.⁶ The experiments were done by cooling an initially unsaturated solution and taking samples along the liquidus. It was found that a logarithmic distribution law (Doerner-Hoskins law) was obeyed:

$$\log (La \text{ in solution}) = \lambda \log (U \text{ in solution}).$$

In these experiments, the effects of cooling rate, stirring rate, and concentrations were investigated. The only effect which these variables had was that λ was increased when the cooling rate was rapid (about 15°C per minute) while stirring was omitted. Subsequently, additional experiments were made with other fission products which showed that coprecipitation occurred to a large degree only with lanthanides and actinides as ternary additions.⁷ It was also observed that the addition of aluminum to the solution had very little effect on λ . Any deviations which were observed were attributed to the formation of compounds between the tracer and impurities in the metal which were insoluble in the melt. An important observation was made by Winsch and Paul,⁸ who investigated the coprecipitation of plutonium with UCd_{11} from molten U-Cd and U-Cd-Mg alloys. They found that no coprecipitation occurs

⁶M. W. Nathans, quoted in ref. 1; see also M. W. Nathans and K. E. Anderson, Quarterly Progress Report, Chem. Eng. Div., Argonne National Laboratory, Jan-March 1958, ANL-5858, p. 76.

⁷I. Johnson and K. E. Anderson, in Quarterly Progress Report, Chem. Eng. Div., Argonne National Laboratory, July-Sept. 1958, ANL-5924, p. 135.

⁸I. O. Winsch and R. C. Paul, in Quarterly Progress Report, Chem. Eng. Div., Argonne National Laboratory, Jan-March, 1959, ANL-5996, p. 111.

in the region where uranium crystallizes, but it does occur in the region of primary crystallization of UCd_{11} . This observation is of great interest for the determination of the mechanism of coprecipitation. Apparently plutonium can be substituted for uranium or otherwise incorporated in the lattice in UCd_{11} , but not in uranium itself. This leads us to a further examination of the mechanism.

A discussion of coprecipitation can be found in various places (see ref. 1 and Bonner and Kahn⁹ for example). Three of the mechanisms must be considered here: (a) true solid solution formation, (b) compound formation in the solid, and (c) adsorption on exposed surfaces during or after the crystallization process.

It was our purpose to determine which mechanism would prevail. In order to do so, simpler systems than U-Cd or U-Zn were chosen. Perhaps the simplest of these are melts of pure metals to which small amounts of additions were added. Systems of this type have been investigated extensively with germanium as the principal component.¹⁰ Except for diffusional effects, the coprecipitation of impurities with germanium was considered as a purely solid-solution phenomenon.

⁹N. A. Bonner and M. Kahn, "Radioactivity Applied to Chemistry," ed. by A. C. Wahl and N. A. Bonner, John Wiley & Sons, New York, 1951, ch. VI.

¹⁰J. A. Burton, E. D. Kolb, W. P. Slichter, and J. D. Struthers, J. Chem. Phys., 21, 1991 (1953); C. D. Thurmond and J. D. Struthers, J. Phys. Chem., 57, 831 (1953); C. D. Thurmond, F. A. Trumbore, and M. Kowalchik, J. Chem. Phys., 25, 799 (1956); and others.

Next in simplicity are the simple eutectic systems. We have chosen the Bi-Cu and Bi-Ag systems with small amounts of copper, silver, or gold as ternary additions. In order to complete the cycle, we have also looked at the Bi-Au system, although there is an incongruently melting compound, Au_2Bi , formed below 371°C . In all our experiments, the precipitate was a metal (or solid solution) but not a compound. The solid solubilities in all terminal phases were either zero or small, with the exception of the solid solubility of Ag in Bi.¹¹

Experimental

All data were obtained by sampling a melt at various temperatures. The experimental arrangement and the general procedure have been described in the previous paper.¹² The ternary additions, consisting of about 100 mg of copper, silver, or gold, were activated by irradiation in the Livermore Pool Type Reactor (LPTR), so that we could analyze for them by counting techniques. Convenient irradiation times in the employed flux of 2×10^{12} were about 15 minutes for copper, 1 to 2 hours for silver, and 15 to 30 minutes for gold. The half-lives of the radioactive isotopes used were checked in order to make sure that we were counting the right isotopes. The half-life of Cu^{64} was found to be 12.77 hours, compared to literature values of 12.80, 12.74, 12.88, and 12.87 hours.¹³ The half-life for Au^{198} was found

¹¹M. Hansen and K. Anderko, "Constitution of Binary Alloys," 2nd ed., McGraw Hill, New York, 1958.

¹²M. W. Nathans and M. Leider, University of California Lawrence Radiation Laboratory, Livermore, Calif., UCRL-6452. Part I.

¹³D. Strominger, J. M. Hollander, and G. T. Seaborg, "Table of Isotopes," Rev. Mod. Phys. 30, 585 (1958).

to be 2.75 ± 0.10 days, compared to literature values around 2.70 days.¹³ The half-life of $\text{Ag}^{110\text{m}}$ was found to be 253 days, compared with literature values of 253, 270, and 225 days.¹³ These results show the radiochemical purity of the tracers.

The purity of the metals used for the two major components was as stated in the previous paper¹² in which the analytical methods used were also discussed.

Treatment of the Data

The experimental data were first plotted as

$$\log \left(\frac{\text{tracer in solution}}{\text{total tracer}} \right) \text{ vs } \log \left(\frac{\text{Cu, Ag, or Au in solution}}{\text{total Cu, Ag, or Au}} \right)$$

as suggested by the exact form of the Doerner-Hoskins law. Corrections were made for the amount of material removed by sampling. This can easily be done if the original weight and composition of melt are known as well as the weight and composition of the samples. The sample weights allow the calculation of the total amounts of tracer and macro-components; the sample composition is equal to the composition of the liquid phase. It was assumed that the solid solubility of Bi in Cu, Ag, and Au was negligible,¹¹ so that all the bismuth was in the liquid phase.

The data also allow the calculation of average distribution ratios,

$$K_x = (X)_{\text{solid}} / (X)_{\text{liquid}}$$

where X indicates the tracer. The concentration of X in the solid is the amount of X precipitated between two consecutive samplings per unit weight of the macro-component that has precipitated. The concentration of X in the liquid was taken to be that at the lower sampling temperature. Since the sampling was done at different temperatures, an average temperature had to be chosen. We arbitrarily chose the harmonic mean.

The calculation of K involves the determination of relatively small differences between numbers. Consequently, the errors inherent in K may be rather large. We were not interested so much in the true values of K at different temperatures. If one plots $\log K$ vs $1/T$, the curve should properly extrapolate to the distribution constant of the binary system Y-X as the bismuth content becomes zero, that is, at the melting point of Y. (Small addition of X to the binary system Bi-Y.) The data allowed this procedure with some confidence only for Cu tracer in Bi-Au and Au tracer in Bi-Cu, where it was also possible to determine an experimental value of K at 10 atom % Bi or less.

Results

The data are presented in Fig. 1 as a Doerner-Hoskins plot of the systems investigated. Table I lists the values of λ determined graphically from Fig. 1. Figure 1 shows that the plots are straight lines over a considerable range. The two lines for the Au tracer in Bi-Cu correspond to a slow cooling and a fast cooling (about $20^\circ\text{C}/\text{min}$) run. They do not coincide, but are essentially parallel. The Cu tracer in Bi-Au (above the peritectic was done twice with the same charge. The runs agree very well (points for the second run are not shown).

It is clear that considerable coprecipitation occurs in the Bi-Cu-Au system but not in the Bi-Cu-Ag system. This is in agreement with the relative shapes of the binary phase diagrams of the Cu-Ag and Cu-Au systems.

Figures 2 and 3 show the calculated values of K plotted as $\log K$ vs $1/T$. The intercept with the line $1/T = 7.37$ at the melting point of copper is about 0.35 (Fig. 2); the intercept with the line $1/T = 7.48$ at the melting point of gold is about 0.85 (Fig. 3). These values can be compared with values obtained directly from the phase diagram, and with values calculated from

thermodynamic data (Table II). The phase diagram data were taken from a paper by Broniewski and Wesolowski.¹⁴ These data are very poor for our purpose, but can be smoothed somewhat by the use of a log (atom %) vs 1/T plot. Such a procedure yields a value of about 0.7 for the distribution ratio of Au between solid and liquid Cu, and of about 0.9 for the distribution ratio of Cu between solid and liquid Au. For the thermodynamic calculations, the data in Hultgren's compilation were used.¹⁵ The distribution coefficient is equal to the ratio of the activity coefficients:

$$K = x_s/x_l = \frac{(a_s/\gamma_s)}{(a_l/\gamma_l)} = \gamma_l/\gamma_s$$

when the activities are referred to the same standard states. The tabulation for Au-Cu gives data for disordered solid alloys at 720°K and for liquid alloys at 1300°K. In the following calculations, the pure solids are taken as the standard states. For convenience, the distribution coefficients at 1300°K are calculated:

a) distribution of Cu between solid and liquid Au, $X_{Cu} \rightarrow 0$

$$\frac{d \ln \gamma}{dT} = - \frac{\Delta \bar{H}}{RT^2}, \quad \Delta \bar{H} = \Delta \bar{H}_{720} + \int_{720}^{1300} \Delta \bar{C}_p dT$$

$\Delta \bar{H}_{Cu} = -2840$ at 720°K. The integral will be neglected.

$$\text{Then } \ln \gamma_{1300} = \ln \gamma_{720} - \frac{2840}{1.99} \left(\frac{1}{1300} - \frac{1}{720} \right).$$

¹⁴W. Broniewski and K. Wesolowski, Ann. acad. sci. tech. Varsovie 1, 44 (1935).

¹⁵R. Hultgren, Project Supervisor, "Selected Values, Thermodynamic Properties of Metals," Prepared for the USAEC at the Minerals Res. Lab., University of California, 1950.

With $\gamma_{720} = 0.137$, one finds $\gamma_{1300} = 0.33$ for the solid.

The compilation lists for the liquid: $\gamma = 0.20$,

so $K = 0.20/0.33 = 0.6$.

b) distribution of Au between solid and liquid Cu, $X_{\text{Au}} \rightarrow 0$.

With $\Delta\bar{H} = -4315$, $\gamma = 0.049$

one finds in a similar manner: $\gamma_{1300} = 0.19$ for the solid.

Since $\gamma_{1300} = 0.04$ for the liquid, $K = 0.04/0.19 = 0.2$.

It is clear that the distribution coefficients in the ternary systems tend toward those in the binary systems. This supports the supposition that the "coprecipitation" mechanism is solid solution formation. This is confirmed to some extent for the Ag-Cu system. The coprecipitation of Ag with Cu and of Cu with Ag is slight, as can be seen from Fig. 1. Hence the calculation of K has inherently larger errors than in the previous case, and the values show considerable scatter. This is shown in Table III. Values of K at the melting points of Cu and Ag obtained from the phase diagram¹¹ are also listed.

We believe that the results suggest a new method for the determination of the solidus in certain binary systems over as yet undetermined ranges of composition. The method involves the determination of the distribution ratio at the temperature of the liquidus, in the manner described in this paper. An example is in the composition of the solid solution of Cu in Au at a liquidus composition of 5 atom % Cu. One determines a plot such as Fig. 2 with a ternary alloy with a Cu-Au ratio of about 5:95 and extrapolates to the Cu-Au liquidus temperature, where the ternary component (Bi, for example) has zero concentration. Such a procedure requires, of course, an improvement in the precision obtained in this work.

TABLE I
VALUES OF LAMBDA, THE DOERNER-HOSKINS
DISTRIBUTION CONSTANT

<u>Binary System</u>	<u>Tracer</u>	<u>λ</u>
Cu-Bi	Au	1.1 - 1.2
	Ag	0.1
Ag-Bi	Cu	0.1
Au-Bi	Cu	2.8

TABLE II
THE DISTRIBUTION RATIOS OF COPPER AND GOLD
IN THE COPPER-GOLD SYSTEM AT
THE MELTING POINTS OF THE PURE COMPONENTS

	<u>$K = X_{\text{solid}}/X_{\text{liquid}}$</u>	
	at 1063°C	at 1083°C
from phase diagram	0.9	0.7
from thermodynamic data	0.6	0.2
this work	0.8 ₅	0.3 ₅

TABLE III
DISTRIBUTION COEFFICIENTS IN THE Bi-Cu-Ag SYSTEM

Ag tracer in Bi-Cu		Cu tracer in Bi-Ag	
$(1/T)_{\text{ave}} \times 10^4, ^\circ\text{K}$	K	$(1/T)_{\text{ave}} \times 10^4, ^\circ\text{K}$	K
12.3	0.34	17.5	0.63
11.7	0.26	16.8	0.39
11.3	0.44	16.1	0.70
10.6	0.23	15.4	0.98
9.8	0.18	8.10	0.6 ₅ ^a
7.37	0.4 ^a		

^aFrom phase diagram, at the melting point of the pure component.

Fig. 1. Doerner-Hoskins plot of systems investigated.

Fig. 2. Distribution of Au in Bi-Cu.

Fig. 3. Distribution of Cu in Bi-Au.

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