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CHEMICAL THERMODYNAMICS OF MATERIALS AT HIGH TEMPERATURES

Technical Report No. 16

THE THERMODYNAMICS OF THE LIQUID SOLUTIONS IN THE TRIAD Cu-Ag-Au:
I. THE Cu-Ag SYSTEM

by

Russell K. Edwards and James H. Downing

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Contribution from the Department of Chemistry, Illinois Institute of Technology

THE THERMODYNAMICS OF THE LIQUID SOLUTIONS IN THE TRIAD Cu-Ag-Au:
I. THE Cu-Ag SYSTEM.[1]

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Russell K. Edwards and James H. Downing

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(1) (a) Presented at the 126th Meeting of the American Chemical Society, New York, September, 1954. (b) Based on part of a thesis by J. H. Downing, submitted to the Illinois Institute of Technology in partial fulfillment of the requirements for the Ph.D. degree, May, 1954. (c) This work was supported by the U. S. Office of Naval Research, U. S. Navy, through Contract N7-onr-329, Task Order II, and Contract NONR 1406, Task Order II.

Abstract

The thermodynamics of the liquid Cu-Ag system have been investigated as part of a general study in the Cu-Ag-Au triad to consider the energetic relationships and chemical bonding among these elements. The study was conducted by the method of determination of the partial pressures over the liquid solutions as a function of composition and temperature. Partial pressures were measured by the molecular effusion technique and were related to the vapor pressures of the pure liquids similarly measured, and activities were calculated. The related thermodynamic properties for the mean temperature 1428°K. are reported, based on the temperature and composition dependencies of the activity data. The activities of both components demonstrate marked positive deviation from ideal solution behavior in the system, as might have been expected in view of the fact that a wide miscibility gap exists in the solid state for this system. Large positive values for partial and integral enthalpies of mixing were found. The partial and integral excess entropies of mixing are positive.

Introduction

The investigation in the liquid Cu-Ag system was chosen to institute a general thermodynamic study in the triad, Cu-Ag-Au, to consider the energetic relationships and chemical bonding among these elements. The atomic radius for Cu is about 12 per cent less than that of Ag, and the atomic radius for the latter is practically identical to that of Au. On the other hand, the cohesive energy of Cu is about 17 per cent greater than that of Ag whereas the value for Au is about 27 per cent greater than that of Ag. An investigation of the binary permutations among the three elements offers an opportunity of observing the effects of the major variables--cohesive energy and atomic radius--while other variables, in particular valence, can reasonably be expected to remain relatively constant.

The study was conducted by the method of determination of the partial pressures over the liquid solutions as a function of composition and temperature. Partial pressures were measured by the molecular effusion technique and were related to the vapor pressures of the pure liquids similarly measured, to obtain self-consistent data from which activities were then calculated. It was imperative that activities be determined only from self-consistent data obtained by relative measurements under identical conditions since reported(2) absolute vapor pressure data by various different investigators have varied by as much as 100 per cent.

The thermodynamic properties for the liquid solutions were calculated from the temperature and composition dependencies of the

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(2) Herbert N. Hersh, J. Am. Chem. Soc., 75, 1529 (1953).

activity data. Inasmuch as the vapor pressure of Cu in the temperature range studied (1300 to 1700°K.) is approximately a factor of ten lower than that of Ag, Cu was a minor but not negligible constituent in most of the effusates. Consequently the activities of Ag were subject to more accurate direct determination than were the activities of Cu, and the best values of the activities of Cu were taken from Gibbs-Duhem integration of the Ag activity data. However, in addition directly obtained Cu activity data were evaluated in order to check the validity of the Gibbs-Duhem integration.

Experimental

Apparatus:--The vacuum apparatus used for the effusion measurements is shown in Fig. 1. The essential features of the apparatus are (a) an evacuated porcelain tube section heated by, (b) a furnace, shown schematically, having Glo-bar elements, (c) a graphite crucible with a small effusion orifice, (d) a thermocouple, enclosed in a silica glass protection tube, for measuring the temperature in the region of the crucible, and (e) a water-cooled cold finger which served to collect samples of the Cu-Ag gas mixture which effused from the crucible as a molecular beam. The crucible was detachable through a polished sliding fit from the graphite support rod shown in the figure. The support rod itself was capable of being moved as desired while under vacuum by means of an external electromagnetic coil acting on an iron section affixed to the end of the rod. Vacuum pumping from both ends of the apparatus was used to insure a high speed system. The mercury diffusion pumps used were isolated from the system by liquid nitrogen traps and so operated as to prohibit exposure of the system to any mercury vapor.

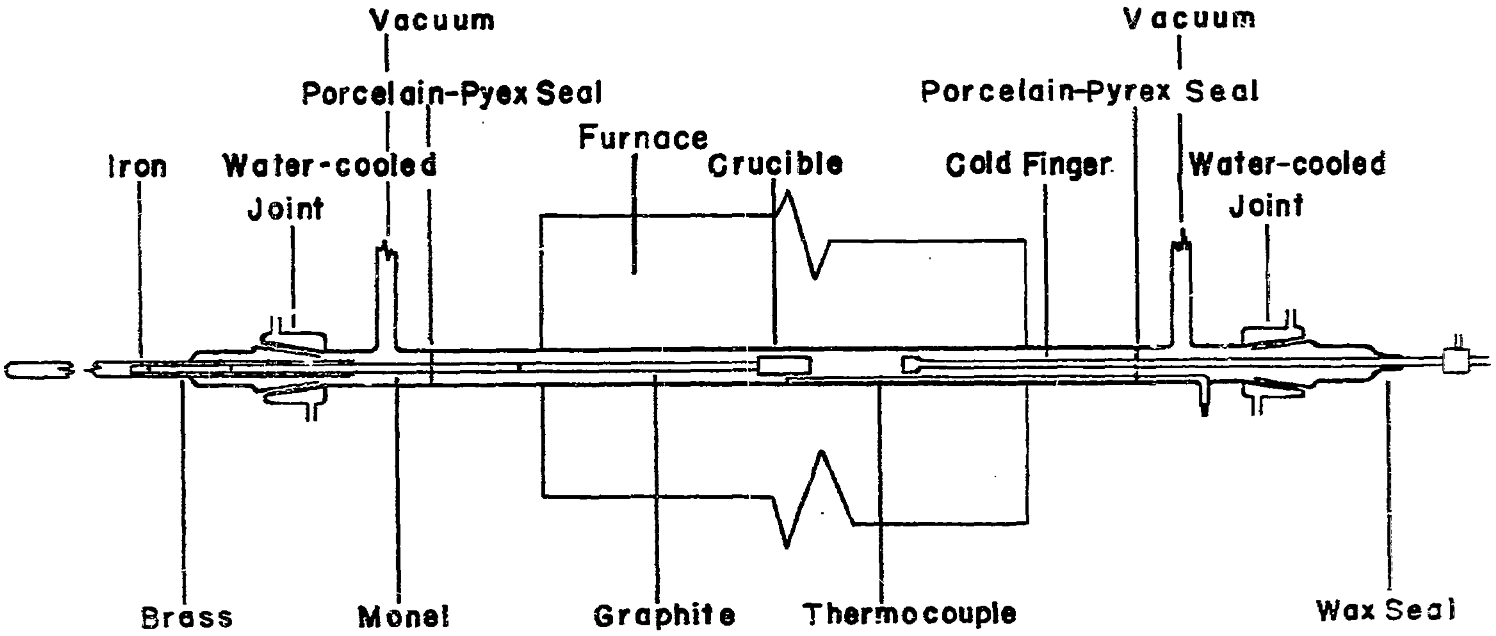

Fig. 1 Effusion Apparatus

Vacuum pressures were measured by means of a Pirani gauge mounted just outside the main vacuum chamber along one of the 20 mm. tubing sections and also by means of an ionization gauge similarly mounted along the other 20 mm. tubing section. Dynamic vacuum pressures of less than 10^{-4}mm. were maintained during the vapor pressure measurements.

Furnace Temperature Control.--The furnace temperature was controlled by means of a Micromax automatic potentiometer with recorder and controller, operating on the signal from a Pt, Pt-Rh(10%) thermocouple located in the vicinity of the furnace heater elements. In general this arrangement could hold the temperature of the heater element environment to a $\pm 5^{\circ}$, and the temperature of the effusion crucible to a much better tolerance. However, to compensate for the tendency of the temperature to drift within the above tolerance due to thermal lags in the system, a manual resetting of the Micromax controller was performed from time to time.

Rate of Effusion.--The rate of effusion was determined from measurement of the time of effusion and weight loss of the crucible plus contents. Weight losses were determined by use of an Ainsworth semi-micro balance. The sensitivity and zero point were determined at the time of each weighing. Careful, systematic procedures were adopted to eliminate errors due to adsorption of gases or moisture by the cell while outside the vacuum line. The cell was never touched except with a rubber test tube holder or a dry cloth. One hour was allowed after removal of the crucible from the vacuum line so that it would attain a steady state relationship with the weighing environment, both with respect to gas adsorption and to temperature. Check measurements showed that the weight uptake during this period was of the order of a few hundredths of a milligram and contributed no significant error to the results since the same systematic procedure was always followed. Errors due to buoyancy factors were less than one per cent. Blank effusion runs with the empty crucibles showed that the crucibles themselves suffered no measurable weight loss under the normal experimental conditions.

Effusion Crucibles.--Three different effusion crucibles, with significantly different effusion orifice sizes, were used; thus crucibles could be used which had orifices appropriate, in terms of true effusion conditions, to the various pressure ranges. Calibration of the effective effusion orifice areas by measurement of the rate of vaporization of mercury from these crucibles has been discussed elsewhere.[3]

As was anticipated at the outset of this study, some diffusion of the metals through the graphite crucible walls was encountered. It had been expected that the diffusion mechanism would be that of capillary flow through the graphite pores. Since such a mechanism is equivalent to effusive flow out of an orifice, it was supposed that the extraneous weight loss contribution would be accountable through the "effective" orifice area obtained by the calibration procedure. In any case, error in the effective orifice area would cancel out in the calculation of activities. Edwards and Downing[3] found that silver does diffuse through graphite by the capillary flow mechanism, but that copper diffuses through by activated diffusion. Even so, activities are relative and therefore still calculable; however, this surprising circumstance complicates the calculation of gas phase compositions as is noted below.

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(3) Russell K. Edwards and James H. Downing, to be published.

Composition of the Gas Phase.--Samples of the effusates were collected on the cold finger, the face of which was located three inches from the crucible effusion orifice. The stainless steel surface was highly polished to facilitate removal of condensate samples. Samples could either be brushed off or scraped off with a steel knife. Care was taken to avoid marring the polished surface. The cold finger was afterward cleaned with fine steel wool and washed with carbon tetrachloride.

Micro-analytical techniques were required for chemical analysis of the effusate materials because of the very small amounts, ranging from two to ten milligrams. In the effusates copper was always the minor constituent; therefore analysis for copper was requisite but silver could be obtained by difference. Spectrographic analyses showed that no other components were present in the effusates to any significant amount. The concentration of the colored cupric ammonia complex can be spectrophotometrically determined in the presence of silver without interference. The wave length of the absorption peak for this complex is 620 millimicrons; however, the height of the peak is a function of the ammonia concentration.[4] In order to avoid difficulties arising from this concentration dependence, a peak of 580 millimicrons[5] was used in the present investigation since at this wave length the absorption is independent of the ammonia concentration. Beer's law has been reported[4] to hold under these conditions, a fact that was amply verified in the present work.

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(4) F. Snell and C. Snell, "Colorimetric Methods of Analysis," Third Edition, D. Van Nostrand, Inc., New York (1949).

(5) C. Milner, Ind. and Eng. Chem., Anal. Ed., 18, 94 (1946).

Had all the weight loss been by the effusive and capillary flow mechanisms, it would have been simple to obtain the weight loss of each species from knowledge of the total weight loss and the composition of the collected effusate sample on the cold finger. Since, however, extraneous loss of copper took place by activated diffusion, it was necessary to apply a correction to the composition nominally obtained from the analysis of the collected material. Therefore we experimentally measured the collection probabilities for both orifice loss and for the extraneous loss by the diffusion processes. The latter measurement was carried out by using one of the crucibles with a cap having no orifice. From this information, and that available from the study of the rates of the diffusion processes,[3] the correction could be made. The correction produced only a small alteration of the calculated partial pressures of silver but considerably altered the calculated partial pressures of copper, as would be expected since the latter was the minor constituent in the effusates. As anticipated, the size of the correction required was significantly larger for the crucible of the smallest orifice.

Agreement of partial pressures obtained using the crucibles of three different orifice sizes, shown in Fig. 2, attests to the validity of the correction treatment. There the data points on the curve representing the partial pressure of silver in equilibrium with a liquid solution of composition 49 atom per cent silver belong about equally to the three different crucibles with different orifice sizes. A similar plot (not shown) for the partial pressure of copper over this solution was equally consistent.

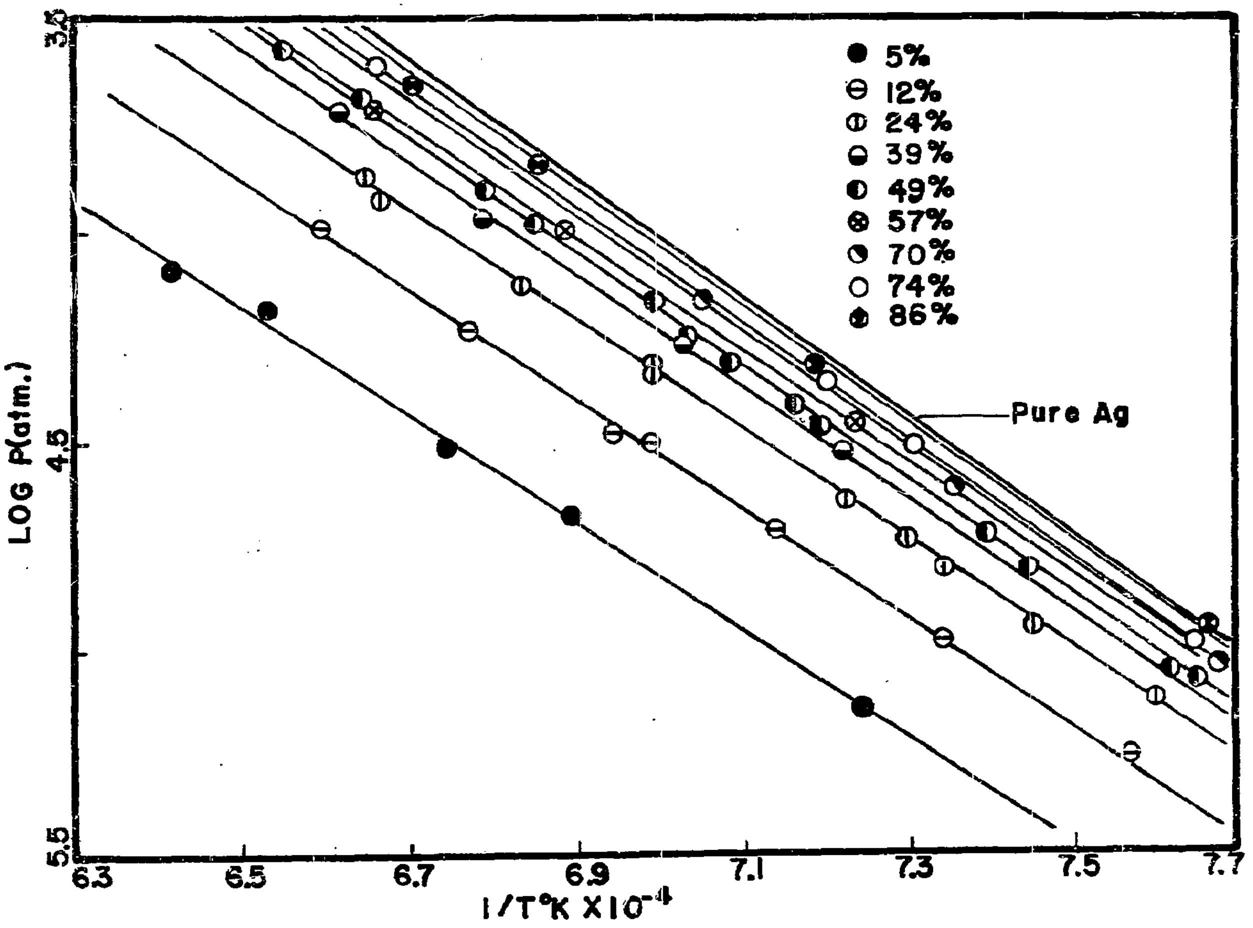

Fig. 2 Silver Partial Pressures over Cu-Ag Liquid Solutions
(Compositions given in atom % Ag)

Composition of the Liquid Phase.--Homogeneous two-phase Cu-Ag alloys were prepared by melting under vacuum the appropriate mixtures in a long graphite tube of about 1/4 inch diameter. The preparations were stirred and then quenched by rapid cooling so that segregation of phases could be avoided. The solid rod obtained was then machined until free from any adhering graphite particles. The reductive action of the graphite was expected to remove any oxide contamination.

Portions of the rods used were analyzed iodimetrically for copper before introduction into the effusion crucibles; residues in the crucibles after a series of runs on a liquid of a given composition were again analyzed for copper to ascertain the change in composition that took place during the effusion runs. The change was always less than one atom per cent, and the mean value was used.

Emptying and Cleaning the Crucibles.--An auxilliary apparatus consisting of a graphite holder with a long graphite handle permitted shaking out the liquid metal solutions from the inverted crucibles (with caps removed) while in an argon atmosphere. Thereafter the crucible was baked out at high temperature under vacuum until it came to constant weight. This procedure was carried out whenever a change in the liquid composition was made.

Freedom from Errors Due to Impurities.--High purity silver and copper of better than 99.98% and 99.99% respectively, were used. However, in such a study as this it is more important to establish that no impurities of high volatility contribute to effusion loss. In the present work effusates from first runs on the pure materials were analyzed by semi-quantitative spectrographic examination. Less than 0.1 per cent impurity was found in the effusates for either of the two materials and thus the maximum error due to impurities was established.

Sequence of Determinations.--Some revaporization of the material which had condensed along the cooler portion of the porcelain tube was inevitable, and the following sequence of operation was adopted in order to minimize error in effusate compositions arising from condensations of some of this revaporized material. Before a series of runs with a new alloy composition was begun, the apparatus was held under vacuum at a temperature appreciably higher than that at which any of the subsequent experimental runs were to be carried out. In this way condensates would be moved down along the porcelain walls to a cooler region. When the series of runs with the new alloy were begun, the highest temperature run was made first and so on toward decreasing temperatures. Thus the condensing zone would gradually advance toward the center of the furnace and revaporization of the condensate would likely be of negligible importance.

Temperature Measurement and Calibration.--Two Pt, Pt-Rh(10%) thermocouples, made from the same original wires, were used in this work. One, which we shall call the "proximate" thermocouple, is shown in Fig. 1. It served as the working thermocouple. The cold junction of this thermocouple was external to the vacuum and was held at the ice point in an ice-water-air mixture, external to the vacuum, under which it was joined to copper lead wires. These were connected to a Brown Electronik recording potentiometer, in series with a Rubicon portable precision potentiometer. The latter was used to buck out excess millivoltage. A continuous temperature record for any run was thus obtained. At periodic intervals the recorded millivoltage on the Brown instrument was checked by a direct reading on the Rubicon potentiometer. The other thermocouple we shall term the laboratory "reference" thermocouple. It was calibrated at the melting points of National Bureau of Standards' tin and zinc and also at the melting point of the high purity silver used here in the vapor pressure work. Its millivoltage-temperature curve was found to be in good accord in this temperature interval with National Bureau of Standards tabulations for high quality thermocouples of this kind.

Calibration of the proximate thermocouple in terms of the actual temperature existing within the graphite effusion crucible was accomplished as follows. A replica was made of the graphite effusion crucibles used, except that the hole normally in the base for the support rod was bored completely through to the interior of the effusion chamber. The reference thermocouple, with its junction in the center of the effusion chamber and its porcelain two-hole protection tube, now served to support the crucible. In this calibration work and in all effusion runs, the crucible position at the center of the uniform temperature zone of the furnace was carefully reproduced by referring to index markers along the apparatus. Comparison under normal vacuum conditions showed the two thermocouples to agree precisely over the complete temperature range when under steady state temperature conditions. This calibration procedure was periodically repeated throughout the entire study in order to apprehend any possible deterioration of the proximate working thermocouple; this could readily have occurred if any cracks developed in the silica glass protection tube, permitting alloying with the effusate material. No deterioration was found; the proximate thermocouple remained completely equivalent to the laboratory reference thermocouple throughout the work.

Since the fundamental temperature scale in the range pertinent to these vapor pressure measurements is based on the radiation laws, an additional calibration of the proximate thermocouple in terms of a Leeds and Northrup optical pyrometer was performed to ascertain whether the thermocouple millivoltage-temperature relationship remained compatible with the National Bureau of Standards' tabulated values at these higher temperatures. A long thin-walled porcelain support tube was fitted into the base of the replica crucible so that it served also as a sighting tube, giving a view of the "black body" interior of the effusion chamber. An optical window was affixed in the appropriate position and the comparison between the optical pyrometer and the proximate thermocouple was made from the silver melting point temperature on up, under normal vacuum conditions. The silver point having been previously established, the optical pyrometer constant, C, containing the window absorption corrections, was obtained for the relationship

$$1/T_t = 1/T_o + C$$

where T_t refers to the true temperature and T_o refers to the observed optical pyrometer temperature, both on the absolute scale. Thereafter the equation was used to obtain the true temperature in the higher temperature range from the observed pyrometer temperature. The correlation between the two scales was good to within the reproducibility of the optical pyrometer readings. These deviations were random, with an average deviation of $\pm 3^{\circ}$.

The optical pyrometer used was itself calibrated against a similar optical pyrometer which had been calibrated by the National Bureau of Standards.

Effective Average Temperature of a Run.--The procedure used in starting a run was to first bring the furnace temperature to a value about 50° higher than desired and to permit time for final degassing. Just before the crucible was rapidly introduced into the hot zone by use of the external electromagnet, the furnace power was reduced to meet the anticipated new lower temperature produced by the heat loss to the crucible. Rapid withdrawal of the crucible at the end of a run was also simply accomplished. The usual method[2] of obtaining the effective average temperature was employed; this corrects for finite heating up and cooling off time as well as for temperature fluctuations during a run. In only a few of the shortest runs was this temperature significantly different from our arithmetically averaged temperature.

Results and Discussion

Silver partial pressure curves for the several liquid solutions investigated are shown in Fig. 2. A similar family of curves was obtained for copper partial pressures. Activities with reference to the pure components were derived from three different temperatures, and the curves for the mean temperature of 1428°K. are shown in Fig. 3. The data for the silver activities are shown, with carefully estimated maximum uncertainties indicated. These data were then treated by the Gibbs-Duhem integration to obtain the curve shown for copper activities. The directly evaluated copper activities, as we have pointed out, are subject to considerably greater uncertainties than are the silver activities, and the best values are without doubt those obtained through the Gibbs-Duhem integration. The agreement of the values directly obtained with the latter is substantial, and the deviations therefrom are random.

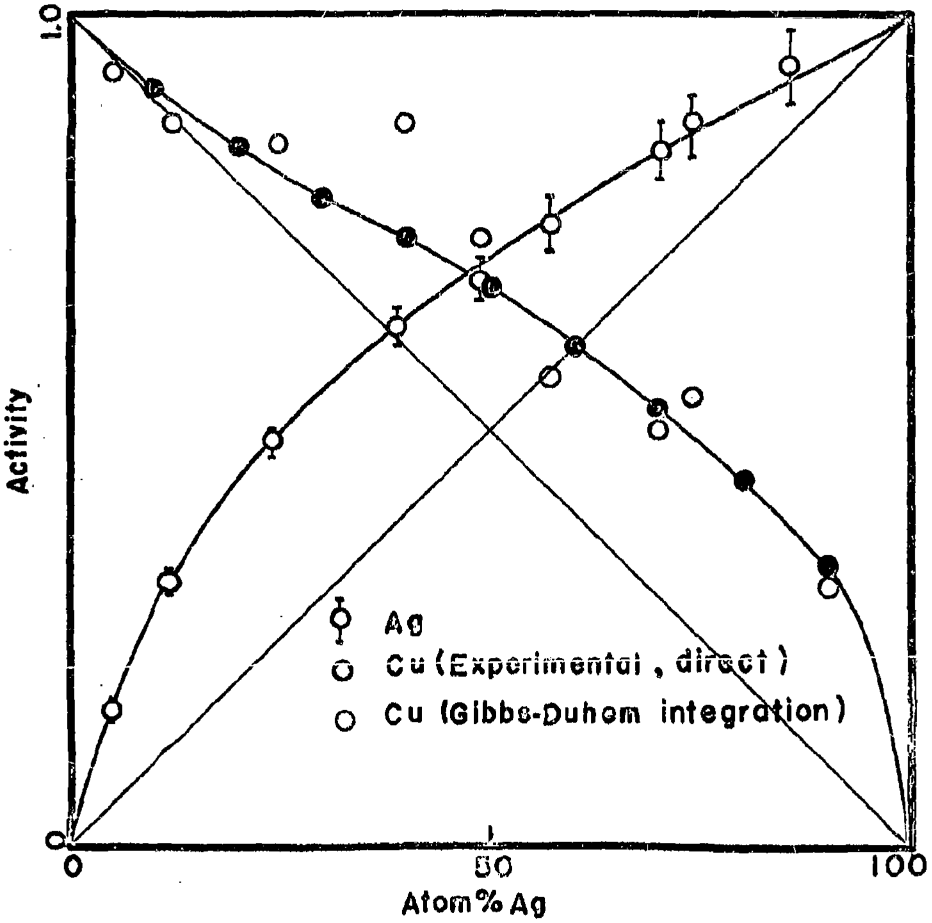

Fig.3 Activities in Cu-Ag Liquid Solutions at 7.0 x 10^{-4} 1/°K. (1428°K)
(Experimental data for Cu are from direct evaluation of data; Gibbs-Duhem data for Cu are from a Gibbs-Duhem treatment of the Ag data).

The thermodynamic quantities listed in Table 1 have been derived through the appropriate temperature dependencies of the smoothed activity curves. The partial molar entropies of mixing for copper-silver liquid solutions are compared with ideal solution values in Fig. 4. The partial molar enthalpies of mixing are displayed in Fig. 5. Shown also in that figure is one point for copper obtained by Edwards, Downing and Cubicciotti[5] in a somewhat limited study by the galvanic cell method. The integral molar thermodynamic quantities for the mixing process are shown in Fig. 6. Shown there also are the enthalpies of mixing obtained calorimetrically by Kawakami,[7] whose results are appreciably lower than ours.

An error analysis of our work leads to probable errors of ± 600 cal. per mole in the enthalpy data, ± 0.45 cal. mol.$^{-1}$ deg.$^{-1}$ in the entropy data, and 40 cal. per mole in the free energy data. With regard to the discrepancy between the enthalpy data and that of Kawakami, it is of note that he obtained[7] essentially zero enthalpy of mixing in the copper-gold liquid system whereas both Edwards and Brodsky,[8] and Oriani,[9] by the vapor pressure method and the galvanic cell method, respectively, have obtained large negative values.

The marked positive deviation from ideality of the liquid Cu-Ag solutions is well in accord with the fact that the Cu-Ag system shows a

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(5) R. K. Edwards, J. H. Downing and D. Cubicciotti, to be published.

(7) M. Kawakami, Sci. Rep., Tohoku Imp. Univ., 19, 521 (1930).

(8) R. K. Edwards and M. B. Brodsky, to be published.
(9) R. A. Oriani, private communication, July 27, 1954.

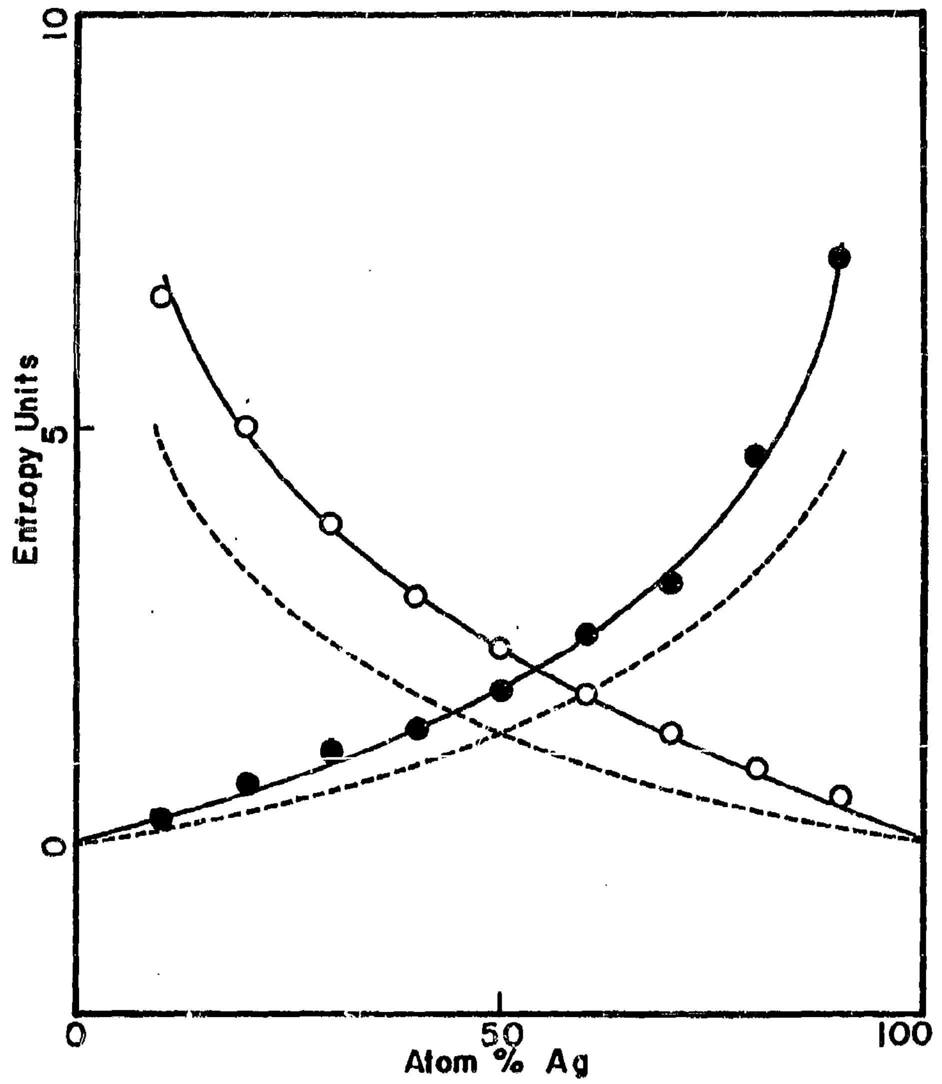

Fig. 4 Partial Molar Entropy of Mixing

○ - Silver
○ - Copper
--- Ideal solution

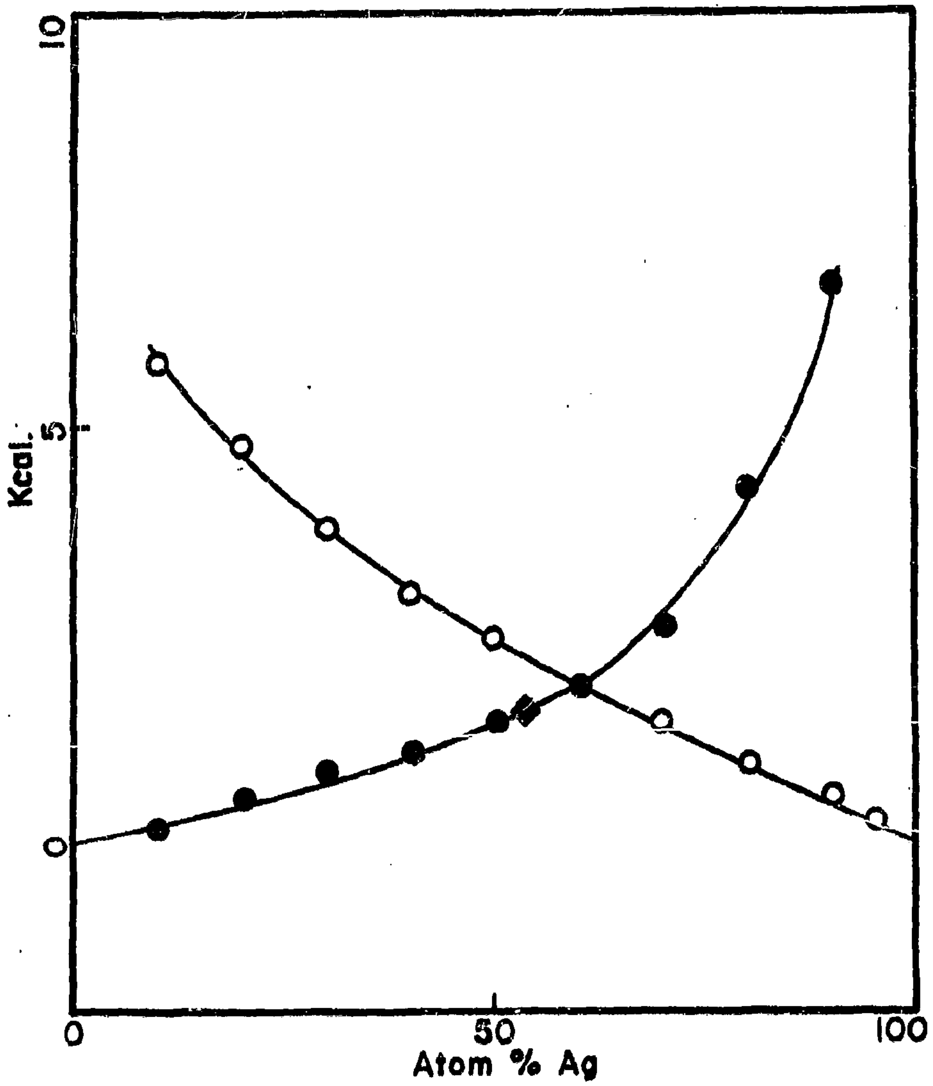

Fig. 5 Partial Molar Enthalpy of Mixing

○ - Silver
● - Copper
◇ - Copper from e.m.f. measurements(6)

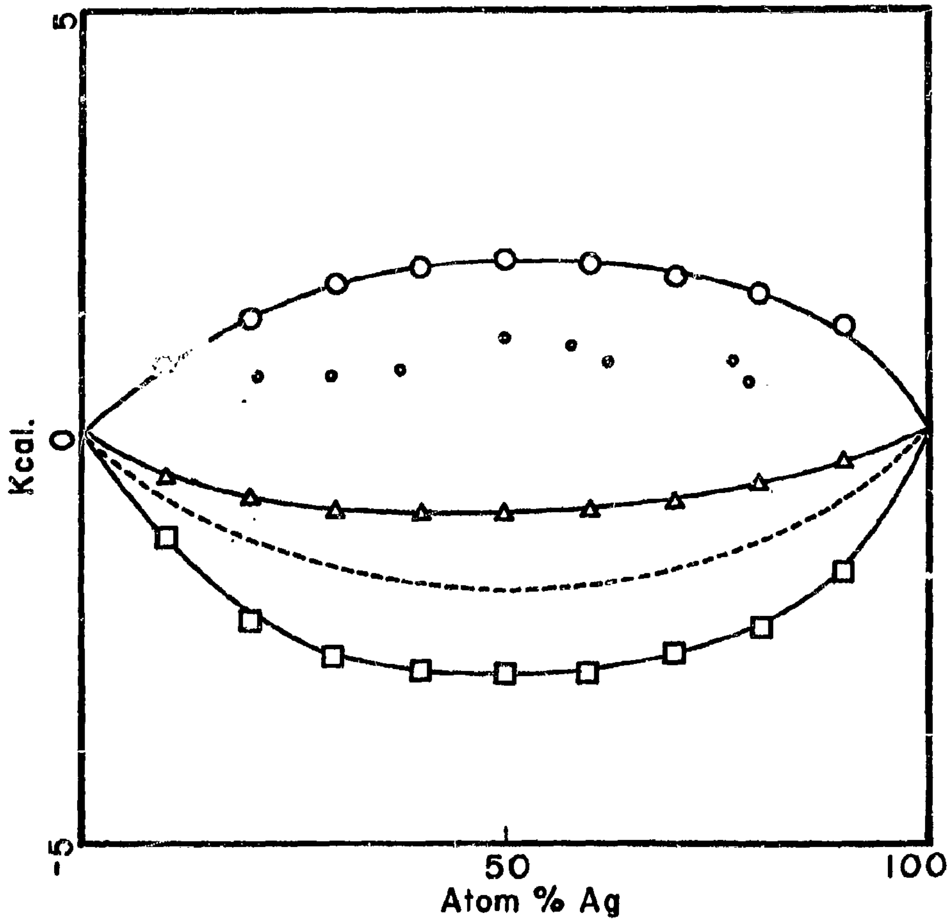

Fig. 6 Integral Molar Thermodynamic Values for Mixing

○ - Enthalpy, this study
● - Enthalpy, calorimetric by Kawakami
△ - Free energy, this study
--- Free energy, ideal solution
□ - Negative value of (temperature times entropy) product

Table 1.

Thermodynamic Functions for Mixing at 1428°K for Cu-Ag Liquid Solutions

Composition (atom % Ag)	Silver, Partial Molar Quantities			Copper, Partial Molar Quantities			Integral Molar Quantities		
	$\overline{\Delta F}^{o}$ cal./mol.	$\overline{\Delta H}^{o}$ cal./mol.	$\overline{\Delta S}^{o}$ cal./mol.-deg.	$\overline{\Delta F}^{o}$ cal./mol.	$\overline{\Delta H}^{o}$ cal./mol.	$\overline{\Delta S}^{o}$ cal./mol.-deg.	ΔF^{o} cal./mol.	ΔH^{o} cal./mol.	ΔS^{o} cal./mol.-deg.
0.10	3,510	5,700	6.6	260	200	0.3	590	800	0.9
0.20	2,330	4,800	5.0	490	600	0.7	860	1,300	1.6
0.30	1,730	3,800	3.9	690	900	1.1	1,000	1,700	1.9
0.40	1,310	3,000	3.0	890	1,100	1.4	1,050	1,900	2.0
0.50	990	2,500	2.3	1,140	1,500	1.9	1,070	2,000	2.1
0.60	740	1,900	1.8	1,440	2,200	2.5	1,020	1,900	2.1
0.70	510	1,500	1.4	1,820	2,600	3.1	910	1,800	1.9
0.80	330	1,000	0.9	2,280	4,300	4.7	720	1,600	1.7
0.90	160	600	0.6	3,060	6,700	7.0	450	1,200	1.2

miscibility gap in the solid state. Moreover, the extent of the positive deviation decreases with temperature, as would also be expected. When the results of the related studies in the Cu-Au and Ag-Au liquid systems are available for comparison, we will discuss the fundamental significance of this study more thoroughly.