one hand, and eq. 12 on the other, it is postulated that

$$fD_a = \lambda_d^2 k_d \qquad (17)$$

and

$$F = -\lambda_d^2 k_d \frac{\partial a}{\partial r_t} \qquad (18)$$

This implies the assumption that the driving force of diffusion is determined by the activity gradient $\partial a/\partial r_t$, rather than by the conventional concentration gradient $\partial C/\partial r_t$.

The activity coefficient of oxygen represents an obvious measure of its relative fugacity in the various media. The fugacities can be visualized as depending on the relative frequency of jumps to the solution surface of oxygen and solvent molecules, *i.e.*

$$f \alpha \frac{k_d}{k_v} = q \frac{k_d}{k_v} \qquad (19)$$

Combining eq. 19, 17, 6 and 9, it is readily seen that

$$D_a\eta = \frac{\lambda_d^2 k_d}{f} \eta = \frac{\kappa T}{q\Lambda} \qquad (20)$$

At a given temperature, eq. 20 indicates that $D_a\eta$ is a constant as long as approximation (9) is valid. Under the experimental conditions this appears to be the case at all viscosities greater than about 2 centipoise. This is accounted for by assuming that with increasing proportions of glycerol or sucrose in the solvent, the over-all packing becomes comparatively closer and the average Λ value remains invariant due to compensatory effects between increased molecular size and decreased intermolecular distances.

The failure of eq. 20 in the low viscosity region ($\eta < 2$ in the presence of glycerol, $\eta < 1.5$ in the presence of sucrose) indicates that approximation (9) does not hold in solutions consisting predominantly of pure water as solvent. This anomaly is attributed to the "ice-like structure" of liquid water at room temperature which implies the availability of appreciable intermolecular space between loosely packed tetrahedral aggregates of water molecules.[24,25] The presence of other molecules, such as sucrose or glycerol, is known to cause the ice-like structure to collapse by a quasi pressure-like strain-action engendering closer packing.[24] The fact that the Stokes–Einstein region extends to lower viscosities in the presence of sucrose than in the presence of glycerol can be ascribed to the reasonably greater efficiency of the larger sucrose molecules in destroying the ice-like structure of water. Qualitatively, increased pressure and/or higher temperatures are expected to have a similar effect. An extensive program of subsequent studies is anticipated in these laboratories with a view to elucidating the relevant quantitative correlations.

Acknowledgments.—This investigation was supported in part by a grant-in-aid from the American Cancer Society upon recommendation of the Committee on Growth of the National Research Council. Thanks are due to Richard A. Javick for carrying out solubility determinations.

(24) J. H. Wang, *J. Phys. Chem.*, **58**, 686 (1954).

(25) R. A. Robinson and R. M. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955, p. 3.

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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. II. The Cu–Au System[1]

BY RUSSELL K. EDWARDS AND MERWYN B. BRODSKY

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The thermodynamics of the liquid solutions in the Cu–Au system have been investigated by effusion vapor pressure measurements carried out over a number of solution compositions in the temperature range 1500–1600°K. The activities of both components demonstrate marked negative deviation from ideal solution behavior over most of the composition range. Corresponding values for the partial and integral enthalpies and the excess partial and integral entropies of mixing are negative. However, for copper the activities, partial molar enthalpies, and excess partial molar entropies of mixing show small positive deviations as the solutions approach pure copper in composition. The work demonstrates the practicability of computing the activities of both components in a series of solutions of a binary mixture from measurements of the total rates of effusion—without experimental measurements of gas phase compositions.

Introduction

Edwards and Downing[2] initiated the titled general study with their investigation of the liquid Cu–Ag system by the effusion vapor pressure method. Concurrent with the present work, Oriani[3-5] carried out experimentally an e.m.f. investigation in the liquid Cu-Au system.

In the present investigation, the thermodynamics of the liquid solutions in the Cu–Au system were obtained from rate of effusion measurements carried out over a number of solutions in the temperature range 1500–1600°K. Partial rates of effusion for both components were related to those of the pure materials, similarly measured in the same apparatus, to obtain self-consistent data from which activities were calculated.

The total rate of effusion from Cu–Au solutions was measured by the weight-loss method. The Cu–Au solutions were contained in porcelain Knudsen crucibles, situated in a heated, evacuated porcelain

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(1) (a) Based on part of a thesis by M. B. Brodsky, submitted by Illinois Institute of Technology in partial fulfillment of the requirements for the Ph.D. degree, May, 1955. (b) This work was supported by the U. S. Office of Naval Research through Contract N7-onr-329, Task Order II, and Contract NONR 1406, Task Order II.

(2) R. K. Edwards and J. H. Downing, *J. Phys. Chem.*, **60**, 108 (1956).

(3) R. A. Oriani, private communication enclosing a manuscript prepared for publication and including large scale plots of his e.m.f. data, June 8, 1955.

(4) R. A. Oriani, private communication, Sept. 13, 1954.

(5) R. A. Oriani, private communication, Oct. 4, 1954.

tube. Inasmuch as the vapor pressure of Au in the temperature range studied is approximately a factor of ten lower than that of Cu, Au was a minor but not a negligible constituent in most of the effusates and of comparable importance in the effusates from solutions of high Au content.

Experimental knowledge of the composition of the gas phase at equilibrium is ordinarily required for a given solution in order to obtain the activities of the individual species under such conditions. However, in principle it is possible to obtain activities at a given temperature and over the complete range of solution compositions from simultaneous treatment of the equations

$$a_1 = Q_1/Q_1^\circ \tag{1}$$

$$a_2 = Q/Q_2^\circ \tag{2}$$

$$Q_1 + Q_2 = Q_{\text{total observed}} \tag{3}$$

$$\text{Gibbs–Duhem Equation} \tag{4}$$

Here, activities are denoted a_1 and a_2 for the components (1) and (2). Rates of effusion from a given orifice are denoted Q_1 and Q_2 for the solutions of measured compositions and Q_1° and Q_2° for the reference states of the pure liquids. The results reported in this paper were obtained by the latter "computational" procedure which was found to be practical and lead to improved accuracy. However, in addition, gas phase compositions were determined experimentally from chemical analyses of samples of the effusates which were collected on a water-cooled cold finger.

Experimental

The general procedures and apparatus used were essentially those which have been described by Edwards and Downing.[2] Certain variations warranting comment are discussed below.

Effusion Crucibles.—The effusion crucibles finally adopted for the present study were of porcelain, fabricated in one piece by the McDanel Refractory Porcelain Co. The design is shown in the paper by Edwards and Brodsky[6] on the vapor pressure of pure liquid Au. Certain other types of crucibles were also tested. Molybdenum crucibles, which were found by Hersh[7] to be satisfactory containers for liquid Cu, permitted considerable extraneous vaporization loss of Au by diffusion through the walls. Tantalum crucibles alloyed with Au and caused very serious extraneous vaporization loss of Au. Fused silica crucibles were found to be wetted by liquid Cu and usually cracked when the metal solidified on cooling.

All of the activity data reported in this study are based on the use of a single crucible; thus equations 1, 2 and 3 hold without introduction of an orifice-area term. The crucible was $^5/_8''$ long, $^3/_4''$ in outside diameter and $^1/_8''$ in wall thickness. Its orifice was a cylindrical tube 0.02293 cm.^{2} in measured area. Its effective area for effusion was 0.00668 cm.^{2} as obtained by calibration based on measured rates of vaporization of mercury by the method described by Edwards and Downing.[8]

Blank determinations at high temperatures and under usual experimental conditions showed that the porcelain crucible, alone, suffered no measurable weight loss. Moreover, comparative runs were carried out for the crucible charged with a Cu–Au solution of 43 weight per cent. copper. When the orifice was plugged with a silica rod, the weight loss was only 4.2% of the normal loss found when the orifice was open. Since the plug was only of casual fit, this amount of loss can be readily attributed to effusion around the plug; therefore, the crucible was considered to be free from any diffusive loss of either Cu or Au through the walls.

An exact replica of the crucible was used as a buoyancy ballast during all weighings.

Materials.—Gold of 99.999% purity was obtained from the Sigmund Cohn Co. in the form of wire 0.5 mm. in diameter. It was washed with benzene before using. Copper of 99.999% purity was obtained from the Central Research Laboratories of the American Smelting and Refining Co., also in the form of wire 0.5 mm. in diameter. The oxidation-resistant coating was removed with steel wool, and the wire was given a final washing with benzene.

Preparation and Composition of the Liquid Solutions.—The solutions were made up by introducing the Cu and Au wire through the effusion orifice. Some of the changes in solution composition were effected by introducing additional portions of the desired component. In this case, computation of the composition was based on a mass balance of the amounts of materials added and the measured amounts which had effused. In other cases, the crucibles were emptied and cleaned before they were recharged.

Before beginning a series of measurements, the following procedure was adopted to obtain mixing of a solution of a given composition. The crucible with its charge (placed in a vertical position within a vertical tube furnace and under high vacuum) was heated to 1100°K. At that temperature the contents of the crucible were molten but their vapor pressures were low enough to prevent appreciable vaporization. Argon was then admitted to slightly over one atmosphere pressure; the cap to the vacuum system was removed, and the crucible was shaken by means of a long-handled silica glass holding device. The tube was re-evacuated and the whole process repeated several times. Finally, the crucible was placed in its horizontal operating position within the effusion apparatus. Some further mixing would be expected to take place on melting in this position.

Emptying and Cleaning the Crucibles.—Early attempts to shake molten solutions out of crucibles through the orifice were unsuccessful. Therefore, when it became necessary to empty the crucibles, the contents were dissolved out with hot aqua regia. A syringe, made of Kel-F, was used to fill the crucible with aqua regia. The crucible was then heated in hot water for 30 minutes and the aqua regia removed with the syringe. It was possible to dissolve all of the contents of a crucible with ten such treatments. Thereafter, the crucible was thoroughly rinsed with distilled water, dried in air and heated under vacuum to constant weight at a temperature higher than those used in normal effusion runs.

Experimental Composition of the Gas Phase.—Effusate samples collected on the cold finger varied in amount from two to ten mg. for the Cu-rich solutions to as little as 0.5–2 mg. for the Au-rich solutions. Micro-analytical techniques were used, and Au was determined as the colored complex with *o*-dianisidine at 445 mμ[9] on a Beckman D. U. spectrophotometer. The calibration curve for this complex followed Beer's law over the desired concentration range and was checked periodically since the strength of the *o*-dianisidine decreased slightly over a period of several months. It was possible to estimate the Au in a 1-ml. aliquot to within 2 μg. Cu was taken by difference between the total effusate weight and the weight of Au. Direct determinations of Cu in the effusates from the Cu-rich solutions by the method used by Edwards and Downing[2] were in good agreement with the values obtained by the difference method. However, appreciable analytical errors were apparent in the experimentally determined gas phase compositions, particularly in the case of the smaller effusates from the Au-rich solutions. Change with temperature in effusate compositions for a series of runs from given solutions was less than the experimental error in the analyses; therefore, the average of all analyses for each of such series was taken as most reliable. This, of course, imputes a greater reliability to activities obtained for the mean temperature of the study when they are based on experimentally determined gas phase compositions. Final evaluations of effusate compositions show that they ranged from about 0.3 to about 95 weight per cent. Au for solutions of compositions 95 to 5 atom per cent. Cu, respectively. The percentage error in the experimentally determined Cu composition of the gas phase is therefore quite small for the Cu-rich solutions but becomes somewhat larger than that for Au in the case of the

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[6] R. K. Edwards and M. B. Brodsky, to be published.

[7] H. Hersh, THIS JOURNAL, **75**, 1529 (1953).

[8] R. K. Edwards and J. H. Downing, *J. Phys. Chem.*, **59**, 1079 (1955).

[9] F. Snell and C. Snell, "Colorimetric Methods of Analysis," 3rd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1949.

Au-rich solutions. Since it is also true that smaller effusate samples were collected for the Au-rich solutions, it is apparent that activities based on experimentally determined gas phase compositions will have an appreciably lower reliability for the Au-rich solutions.

Temperature Measurement and Calibration.—The procedures for the control of the furnace temperature, the measurement of temperature and the temperature calibration have been described elsewhere.[2] The same Pt, Pt–Rh (10%) thermocouples were used in the present work. However, completely new calibrations were carried out periodically throughout the course of this study. The laboratory "reference" thermocouple was calibrated against the additional check point at the melting point of National Bureau of Standards aluminum. The calibration of the "proximate" thermocouple against the National Bureau of Standards calibrated optical pyrometer was performed directly rather than through the use of a secondary optical pyrometer.

Effective Average Temperature of a Run.—Due to the relatively poor thermal shock properties of the porcelain crucibles, it was found impossible to use the technique of rapid introduction and withdrawal of the crucibles to and from the hot zone of the furnace as was used in the previous study.[2] Instead, it was necessary to permit the crucible to heat up and cool off along with the furnace and to apply corrections for the non-isothermal portions of any given effusion run. The method adopted in this work was the common one[7] in which an effective average temperature, T_{av}, was obtained from a continuous record of the observed Kelvin temperature, T, *versus* the time, t, through the relation

$$t_{eff} \times e^{-\Delta H/RT_{av}} = \int_0^{t_{eff}} e^{-\Delta H/RT}\,dt \qquad (5)$$

In the equation, ΔH is the molar heat of vaporization of the substance effusing, and t_{eff} was taken to be the total time the crucible was at a temperature high enough to cause measurable weight loss in 1 hr. In general, it was taken to be the total time the crucible was at a temperature above 1170°K. The molar heat of vaporization in the desired temperature range was taken to be 77 kcal. for Cu and 82 kcal. for Au. For the runs involving effusion of both species, two different values of T_{av} resulted, of course. However, these two values were never more than 2° apart and the average value was used. It is thus clear that only an approximate value for ΔH suffices for the integration.

A Typical Effusion Run.—A crucible with a solution of known composition was weighed, placed on the porcelain support rod and inserted in the vacuum system. A vacuum of 5×10^{-5} mm. was obtained after 0.5 hr. Then, by means of an electromagnetic device, the crucible was pushed into the center of the furnace section to a position directly over the measuring thermocouple. The positioning of the crucible was carefully reproduced each time by matching index markers along the support rod and along the outer Pyrex portion of the vacuum chamber. The furnace was turned on and the controller set for the desired temperature. After 1 hr. of heating, the temperature reached 1170°K. and timing was started. After another 45 to 60 minutes, the temperature reached the desired value. The temperature was continuously recorded on a Brown Electronik potentiometer and was also checked every 15 minutes on a Rubicon portable precision potentiometer. The elapsed time at the desired temperature ranged from 4 to 10 hr. When the furnace power was turned off, the temperature would fall to 1170°K. in a matter of about 15 minutes, and at that point timing was terminated. Cooling to a temperature suitable for removal of the crucible from the hot zone required from 4 to 5 hr. In some cases the crucible was allowed to cool overnight before removal from the operating position. Throughout the work, liquid nitrogen traps were used to exclude from the system any mercury vapors from the diffusion pumps.

The removal of effusate samples from the cold finger has been described previously.[2]

Calculation of the Results

Solution of equations 1, 2, 3 and 4 at three different temperatures was effected by a method of successive approximations. Values of Q_{total} for the selected temperatures were taken from least squares plots of log ($Q_{total} \times T^{1/2}$) *versus* $1/T$, where T is the absolute temperature of a given measurement. Individual plots were made for effusion measurements (on the average, seven measurements) over each individual solution of measured composition. The plots were linear within the random error of the measurements, although in principle they need not necessarily be so. The Gibbs–Duhem equation was used in the form

$$\log \gamma_1 = -X_1X_2 \frac{\log \gamma_2}{(1 - X_2)^2} - \int_{X_1 = 1}^{X_1 = X_1} \frac{\log \gamma_2}{(1 - X_2)^2}\,dX_1 \qquad (6)$$

in which γ_1 and γ_2 are the activity coefficients and X_1 and X_2 are the atom fractions of components (1) and (2) in the liquid solutions. The integration was

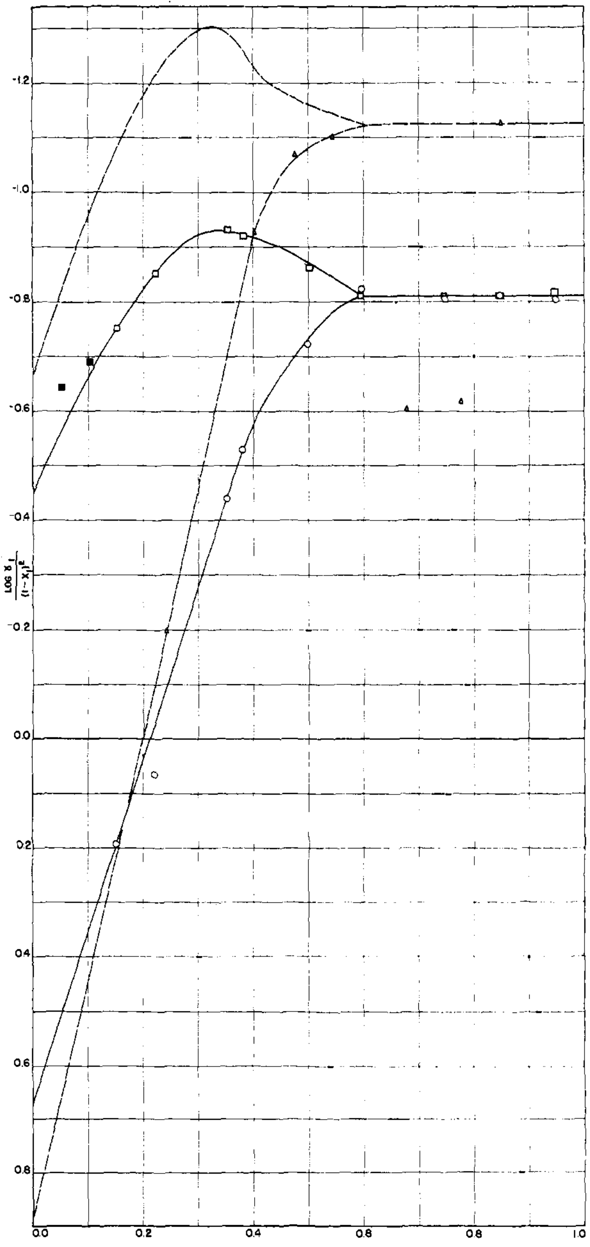

Fig. 1.—Functionality in the Cu–Au liquid solutions: solid lines, this study at 1550°K., ○, Cu; □, Au; dashed lines, Oriani's e.m.f. data, 1283°K., ▲, Cu.

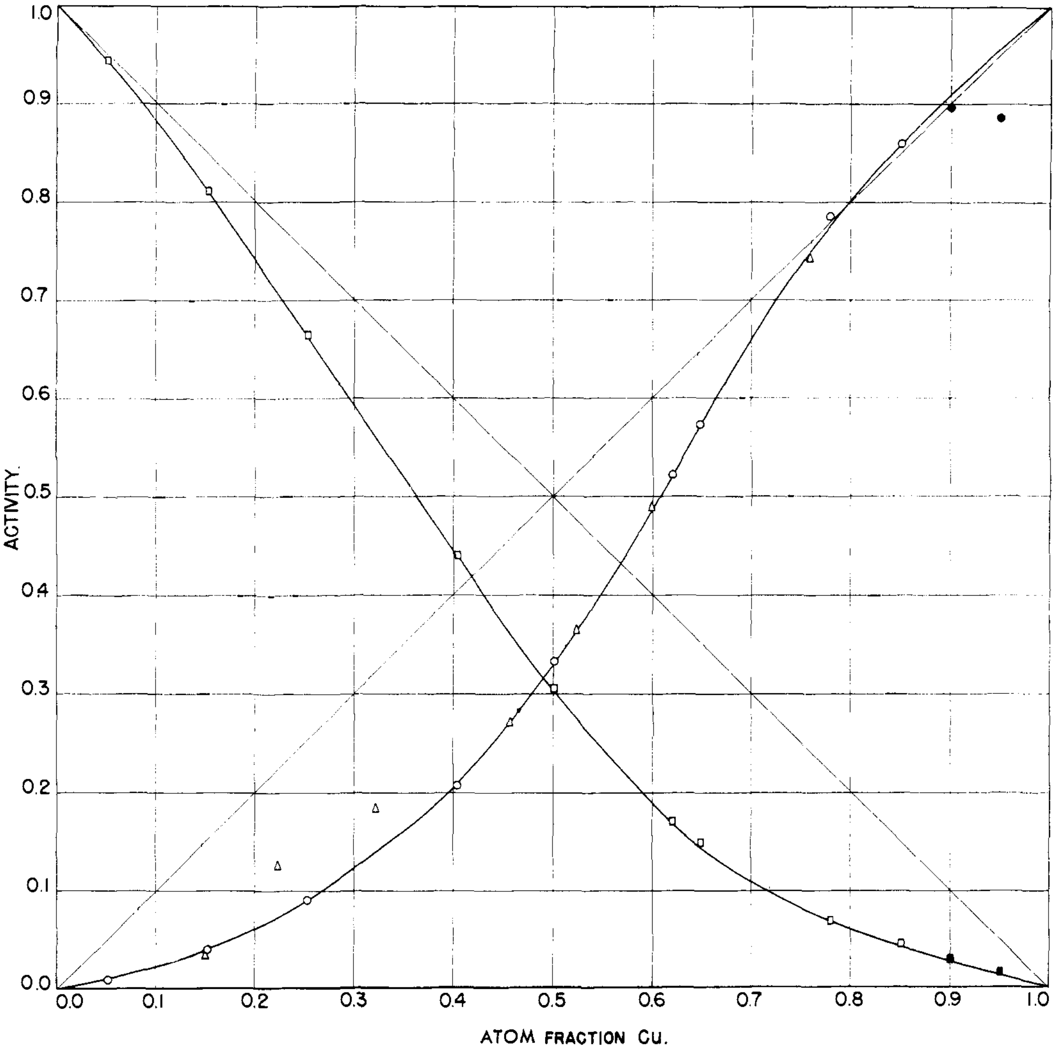

Fig. 2.—Activities in Cu–Au liquid solutions at 1550°K.: □, ○, this study; △, Oriani's data from e.m.f. measurements (extrapolated).

performed from the Au-rich side of the composition range since the functionality proved to be simpler for this case. The solid lines in Fig. 1 show the results of the final calculations plotted in the form log $\gamma_i/(1 - X_i)^2$, which we may call the α-function, *versus* X_i for 1550°K. The areas under the curves lead to the last term in equation 6.

It was found that α_{Cu} was equal to α_{Au} and constant in the region $X_{Au} = 1$ to $X_{Au} = 0.6$. This fact renders values particularly secure for the extrapolation to infinite dilution with respect to Cu. Moreover, when the continuation of the integration is performed on the Cu curve, the contribution of the area under this horizontal portion is of relatively major importance in establishing successive points. Consequently, since we found rather good agreement of the computational values with the directly obtained experimental values for Cu in the region $X_{Au} = 0.15$ to 0.379, we can impute considerable validity to the over-all integration. For example, α_{Cu} obtained directly was identical with the computational value at $X_{Au} = 0.351$, was 0.02 unit low at $X_{Au} = 0.379$, was 0.05 unit high at $X_{Au} = 0.150$ and was 0.08 unit high at $X_{Au} = 0.220$ (as viewed in Fig. 1). In the last case, this would place the directly obtained value almost precisely on the curve drawn in Fig. 1. For the Cu curve we have extrapolated to infinite dilution with respect to Au through the computed point at $X_{Au} = 0.150$, since the data for this point were of highest reliability from the standpoint of temperature. Also to be noted with regard to the neighboring point at $X_{Au} = 0.220$ is the fact that the function α_{Cu} becomes extraordinarily sensitive to small error when it passes through zero, as is approximately the case. Two experimental points at $X_{Au} = 0.100$ and $X_{Au} = 0.050$ were not amenable to computation because of a temperature uncertainty for them of ±3.5°. Neither have the directly obtained values of α_{Cu} for these measurements been shown in Fig. 1, since the temperature uncertainty coupled with the extreme sensitivity of α_{Cu}, as $(1 - X_{Cu})^2$ approaches zero, would permit α_{Cu} to take either large positive or negative values for these measurements. However, the directly obtained values of α_{Au} are shown by the solid points in the figure, and

TABLE I

EXCESS MOLAR QUANTITIES FOR MIXING IN THE Cu–Au LIQUID SYSTEM AT 1550°K.[a]

X_{Cu}	$\overline{\Delta F}^{\circ}_{Cu}$	$\overline{\Delta H}^{\circ}_{Cu}$	$\overline{\Delta S}^{\circ}_{Cu}$	$\overline{\Delta F}^{\circ}_{Au}$	$\overline{\Delta H}^{\circ}_{Au}$	$\overline{\Delta S}^{\circ}_{Au}$	ΔF°	ΔH°	ΔS°
0.000	−5750	−10,800	−3.26	0	0	0	0	0	0
.050	−5190	− 9,740	−2.94	− 14.4	− 27.0	−0.00816	− 273	− 513	−0.155
.100	−4660	− 8,750	−2.64	− 57.5	− 108	−0.0326	− 517	− 972	− .293
.150	−4150	− 7,800	−2.35	− 129	− 243	− .0734	− 732	−1380	− .416
.200	−3680	− 6,910	−2.09	− 230	− 432	− .131	− 919	−1730	− .522
.250	−3230	− 6,070	−1.83	− 359	− 675	− .204	−1080	−2030	− .611
.300	−2820	− 5,290	−1.60	− 517	− 972	− .294	−1210	−2270	− .685
.350	−2430	− 4,560	−1.38	− 704	−1320	− .399	−1310	−2460	− .741
.400	−2070	− 3,890	−1.17	− 919	−1730	− .521	−1380	−2590	− .781
.450	−1680	− 3,320	−1.06	−1210	−2110	− .585	−1420	−2660	− .797
.500	−1300	− 2,920	−1.04	−1550	−2520	− .628	−1430	−2720	− .835
.550	− 956	− 2,520	−1.01	−1930	−2970	− .669	−1400	−2720	− .855
.600	− 652	− 1,880	−0.792	−2340	−3840	− .965	−1330	−2660	− .862
.650	− 380	− 1,070	− .444	−2780	−5240	−1.59	−1220	−2530	− .843
.700	− 178	− 563	− .248	−3210	−6230	−1.95	−1090	−2260	− .757
.750	− 54.0	− 242	− .121	−3530	−7050	−2.27	− 924	−1950	− .659
.800	+ 9.64	− 61.0	− .0456	−3750	−7720	−2.56	− 742	−1590	− .549
.850	+ 31.0	+ 10.7	− .0131	−3840	−8070	−2.73	− 550	−1200	− .419
.900	+ 25.0	+ 31.0	+ .00390	−3790	−8120	−2.79	− 357	− 784	− .275
.950	+ 9.05	+ 23.6	+ .00939	−3590	−7870	−2.76	− 171	− 372	− .130
1.000	0	0	0	−3210	−7290	−2.63	0	0	0

[a] Relative to ideal solution values and in units of calories or calories per °K. The entropy and enthalpy data are derived for the range 1283–1550°K.

they are reasonably close to the computed curve.

Some remarks are in order with respect to the temperature uncertainty noted above. As has been pointed out in the experimental section, the proximate thermocouple was periodically recalibrated. In the case of the series of measurements for solutions of X_{Au} = 0.050, 0.100, 0.220 and 0.351 (carried out in the order given), calibrations before and after were in disagreement by 7°. It was found that the thermocouple position had been altered slightly sometime during the course of these measurements. We presume that the thermocouple may have been bumped by the cold finger on some occasion. Each set of data for runs from a given solution was concordant and thus showed no sudden deviation as would be expected if the thermocouple shift had occurred during the measurements on a given solution. We assumed, therefore, that the shift took place between some two sets of runs. For the results presented, we have used the temperature obtained through the calibration performed after the four sets of runs. The concordance of the points of X_{Au} = 0.351 and 0.220 with the other points on the α_{Cu} curve in Fig. 1 indicates that this procedure was correct for these cases. As will be seen later in the plots of Cu activities, the latter calibration seems to approximately apply also to the case X_{Au} = 0.100. But, had we used the earlier calibration, Cu activities would have been about 8% higher, and this seems to apply approximately to the case X_{Au} = 0.050.

The dashed line was constructed for α_{Cu} at 1283°K. (given in Fig. 1), based on the e.m.f. data of Oriani.[3] Since his measurements were experimentally conducted for the liquid solutions with reference to pure Cu in the solid state, we have recalculated the data to the reference state of pure liquid Cu in order that they may be compared to our data. We have made use of the entropy, heat capacity and heat of fusion data of Kelley[10,11] to this end. The dashed line for α_{Au} is from our Gibbs–Duhem treatment of the smoothed α_{Cu} curve shown. We have ignored the points for X_{Au} = 0.776 and 0.678 in view of the unusual functionality that they would imply and of the smooth functionality which our data at the higher temperature show. We have omitted an additional point at X_{Au} = 0.15 which would have fallen well below the bottom of Fig. 1. Oriani[5] also considered the value obtained in this case to be of low reliability as the temperature coefficient of the e.m.f. was badly out of line with the results of the other measurements.

Results and Discussion

The activity results are shown in Fig. 2. The open circles and squares represent our results based on the computational method discussed above. The solid circles and squares are the results based on experimentally observed gas composition for two cases, for which the temperature error noted previously precluded the possibility of using the computational procedure. Those latter points, whether for Cu or Au, would be subject to nearly the same percentage experimental error; however, because the Au activity is smaller in magnitude, the discrepancy is not as apparent for the Au points. The curves drawn are those obtained from the smoothed curves of Fig. 1.

The triangular points plotted in Fig. 2 for Cu are from Oriani's extrapolation[4] of his e.m.f. data to the temperature of our work. In converting his activities to the reference state of pure liquid Cu, he assumed that the entropy of fusion of Cu could be regarded as constant for the interval of temperature involved.

The mutual support of the two sets of data ob-

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(10) K. K. Kelley, *U. S. Bur. of Mines Bull.*, **476**, 62 (1949).

(11) K. K. Kelley, *ibid.*, **477**, 43 (1948).

tained by the two different experimental techniques leads to the following conclusions: (a) that for the e.m.f. data which agree closely both the values and the temperature coefficients which Oriani obtained must be of high reliability and (b) that we have been correct in assuming the effusion process to involve only a single gas species for each component.

In view of the fact that the relative atomic size factors are essentially identical for the Cu–Ag and the Cu–Ag systems, it is interesting to observe that the extent of the deviations from ideality are nearly the same but of opposite signs for the two systems. That the Cu activity deviation goes from negative to become positive in the range $X_{\mathrm{Cu}} = 0.8$ to 1.0 must be considered quite unusual for a system involving metals of such closely related properties as Cu and Au. The form of the plot in Fig. 1, showing that α_{Bu} passes through zero, leaves little doubt that such is the case.

We calculated activities for the three temperatures, 1500, 1550 and 1600°K., and from the temperature dependencies we were able to obtain enthalpy and entropy data for the mixing process. The results were in rather good agreement, within the experimental error, with those reported by Oriani[4] and with those reported later in this paper. However, in view of the short interval of temperature observed, we would have to allow a fairly large error of about ±50%. On the other hand, as we have pointed out above, although the temperature coefficients for several of Oriani's solutions must be considered excellent, the data for a few of the solutions must be spurious. The consequent difficulty in effecting the Gibbs–Duhem integration of his partial molar enthalpy of mixing data for Cu must reduce the reliability of his reported integral enthalpy and entropy data. In consideration of the excellent complimentarity and large temperature interval between Oriani's work and ours, we believe that the best enthalpy and entropy data would result by obtaining the temperature coefficients through the differences in the α-functions between the two studies (and their involved temperatures) from the smoothed data of Fig. 1. The values that are reported here were calculated in this manner.

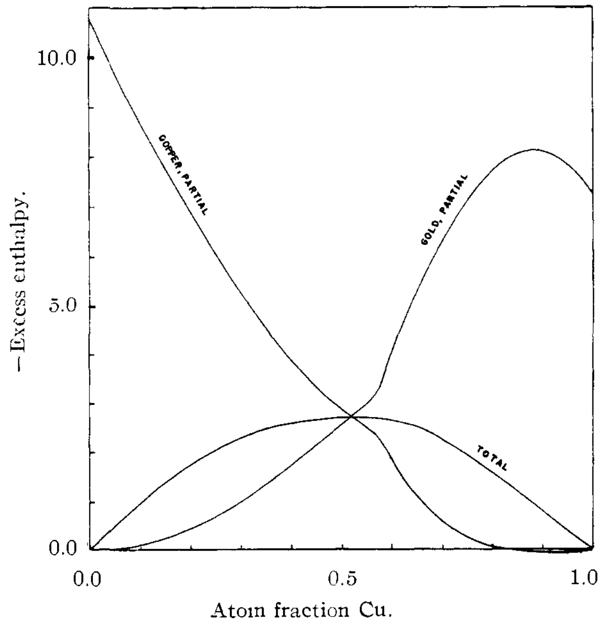

Fig. 3.—Excess enthalpy of mixing in the Cu–Au liquid solutions (kcal. per mole; temperature range 1283–1550°K.).

The excess over ideal solution values of the partial molar enthalpies and total integral molar enthalpies for the mixing process are plotted in Fig. 3, and the corresponding entropy curves are shown in Fig. 4. The irregularities in the curves are of interest. In particular, we notice that the curve of the integral molar excess entropy is asymmetric in such a way as to place the maximum (in $-\Delta S^0$) over the composition region corresponding to the ordered solid phases, AuCu, $\mathrm{Au_2Cu_3}$ and $\mathrm{AuCu_3}$. It appears that some of the factors responsible for the ordering in the solid state are still being reflected for the liquid state. The first inflection in the partial molar excess entropy curves as X_{Cu} increases seems to occur at about the composition corresponding to the minimum in the solidus–liquidus curves.

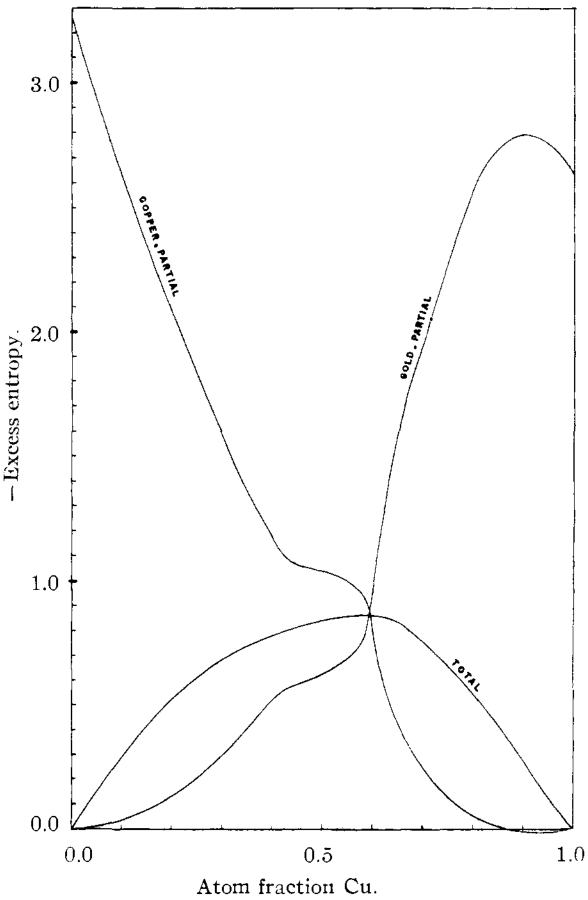

Fig. 4.—Excess entropy of mixing in the Cu–Au liquid solutions (cal./mole/°K); temperature range 1283–1550°K.).

The excess molar thermodynamic properties of the Cu–Au liquid system are shown in Table I. The errors in the several tabulated functions may be derived readily by simultaneous consideration of Fig. 1 and the following estimations of the errors in the α-functions. The error in α_{Au} appears to be about ± 0.01 unit in the region $X_{Cu} = 0$ to $X_{Cu} = 0.4$ and to vary approximately linearly thereafter to ± 0.02 unit at $X_{Cu} = 1$. The error in α_{Cu} appears to be ± 0.01 unit from $X_{Cu} = 0$ to about $X_{Cu} = 0.7$ and to vary approximately linearly thereafter to ± 0.05 unit at $X_{Cu} = 1$, if the nature of the extrapolation has been correctly assumed.

The molar enthalpy of mixing is found to be $-2{,}720 \pm 200$ cal. at $X_{Cu} = 0.5$ which is about 800 cal. more negative than Oriani reported and considerably more negative than the calorimetric value of zero which Kawakami[12] obtained. The general agreement of our work with that of Oriani leads us to discount the calorimetric value. The partial molar enthalpy of mixing of Cu for the solutions infinitely dilute in Cu is found to be $-10{,}800 \pm 700$ cal. The partial molar enthalpy of Au for the solutions infinitely dilute in Au is found to be $-7{,}290 \pm 700$ cal.

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[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Solvent Effects in Gas–Liquid Partition Chromatography

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For the purpose of considering solvent effects in GLPC, the partition coefficient (H^0) is discussed in terms of the vapor pressure of the solute (P^0) and the thermodynamically defined activity coefficient of solute in the solvent (γ^0). This separation of effects leads to a clear understanding of the interrelations of solute and solvent behavior in GLPC operations and provides the basis for exploiting relations which have been found in direct studies of solutions. This in turn leads to a number of observations which are useful in practical GLPC work. The more important of these are: (1) At a given temperature and within an homologous series of solutes the logarithm of the ratio of partition coefficients in solvents may be expected to be a linear function of the solute carbon number. The slopes of such plots for different homologous series may be expected to be the same. (2) Over the restricted ranges in carbon number of interest in a given GLPC separation and except for the first several members of an homologous series, log H^0 for the members of an homologous series may be expected to be linear in carbon number. This observation is closely related to ones already appearing in the literature.

James, Martin and other workers in the field[1-5] have discussed solvent effects in gas–liquid partition chromatographic (GLPC) separations in terms of the fundamental nature of the solute–solvent interactions which occur in the liquid phase and in terms of regularities in GLPC behavior observed among the members of homologous series. A companion paper[6] to the present one has shown that the solvent supports usually used are substantially inert and that GLPC behavior can be largely accounted for in terms of the deviations from ideal behavior in the bulk liquid phase. It is the purpose of the present paper to discuss GLPC solvent effects in more empirical but more quantitative terms than hitherto has been done, exploiting for this purpose observations drawn from direct studies of the non-ideal behavior of solutions.

In the present paper the partition coefficients which characterize GLPC behavior are considered in terms of fundamental solution parameters. Useful and generally applicable relations between solute activity coefficients and structural groupings of solute and solvent are outlined. These are applied in order to illustrate the interplay of solute and solvent properties in setting GLPC behavior in several cases. Useful methods of treating GLPC data are outlined and illustrated.

Experimental

Partition coefficients from GLPC measurements have been determined as described in the previous paper for a number of additional solutes in the two solvents, diisodecyl phthalate and squalane, and in a more polar solvent, Triol. Partition coefficients are shown in Table I; for completeness some of the data presented in the previous paper have been repeated.

Discussion

GLPC Partition Coefficients and Fundamental Solute–Solvent Parameters.—As indicated in the previous paper,[6] the partition coefficient determined from GLPC data is essentially that operative when the solute is at infinite dilution in the solvent phase. In terms of fundamental parameters of the solute and solvent, this may be expressed as

$$H^0 = \frac{M_s RT}{\gamma^0 P^0} \qquad \text{(I)}$$

where M_s is the reciprocal molar volume of the solvent, γ^0 is the activity coefficient of the solute at infinite dilution in the solvent, P^0 is the vapor pressure of the solute and RT has its usual meaning. Equation I leads directly to an expression for the relative partition coefficients of two solute materials, 2 and 1, or to the relative volatility of solute 1 to solute 2, at infinite dilution in the solvent

$$\alpha_{1,2} = \frac{H_2^0}{H_1^0} = \frac{\gamma_1^0 P_1^0}{\gamma_2^0 P_2^0} \qquad \text{(II)}$$

This is identical with the separation coefficient normally used to measure the ease of separation of two components by distillation. Although the number of plates in a column of given geometry varies from solvent to solvent as a result of differ-

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