

Direct Activity Measurements in Liquid Ag-Cu Alloys Using a Valved Knudsen Cell–Mass Spectrometer System

STANLEY M. HOWARD

The primary objective of this investigation was to demonstrate a new method of measuring activities. The mass spectrometric analysis of effusates from a unique valved Knudsen cell was used to determine the activity of Ag in the liquid Ag-Cu system at 1400 K. The alloy compositions were varied from one composition extreme to the other *in situ*. The system exhibits positive deviation from ideal behavior, and the results are in agreement with previous investigations and are summarized by the equation

$$\ln \gamma_{\text{Ag}} = (1.116 \pm 0.034) (1 - X_{\text{Ag}})^2$$

The valved Knudsen cell method is applicable to activity studies of both binary and multi-component systems.

I. INTRODUCTION

MASS spectrometer–Knudsen cell arrangements have been used extensively to determine the thermodynamic properties of liquid metallic alloys. These methods include the double or multiple Knudsen cell method developed by Buchler and Stauffer,^[1] the ion current ratio method proposed by Lyubimov *et al.*^[2] and developed by Belton and Fruehan,^[3] and the polymeric species methods presented by Belton and Fruehan.^[4] A critical review of the various methods employed has been done by Raychaudhuri and Stafford.^[5]

Each experimental method was devised to overcome the same fundamental experimental obstacle, namely, the difficulty of relating the mass spectrometrically measured ion current of an alloy species in the Knudsen cell to the vapor pressure and, ultimately, to the activity of that species. Each of the methods is characterized by the way this experimental obstacle is overcome.

Each method also carries limitations. For example, the polymeric species method is limited to those systems in which there are polymeric or intermolecular species. The ion current ratio method is unlikely to be used for systems containing more than three elements, because it can only be used where the vapor pressures of all the species of interest are within a pressure range of approximately 10^{-2} to 10 Pa over the entire composition range of interest. The double or multiple Knudsen cell method requires precise alignment of each cell orifice and assumes that the effusate beams do not interfere with one another—a condition the current investigator has found difficult to achieve. In addition, considerable quantities of effusate are lost into the furnace region, which in some cases, can cause false contributions to the monitored ion current.

The most stringent limitation shared by all the above methods, except the multiple cell method, is that they require the investigation of many different alloy compositions, each in separate experimental runs, in order

to determine the thermodynamic properties of even a simple binary alloy. This requires considerable experimental effort. This investigation reports the development of a method of determining the thermodynamic properties of liquid metallic alloys which is as direct as the double or multiple Knudsen cell method, yet without the potential beam interaction concerns and the need for laborious, repetitive experiments on a suite of alloy compositions in separate experiments, as required by other methods. The method uses a unique valved Knudsen cell in which the liquid alloy composition is varied during the course of the mass spectrometric analysis of the effusate. This versatile direct method allows *in situ* addition to the sample alloy while mass spectrometrically monitoring the ion current of the element or elements of interest in the Knudsen cell. This not only decreases the time required for activity determination by more than an order of magnitude but also simplifies the mathematical calculations required to obtain activities, compared to most other mass spectrometric–Knudsen cell methods. The purpose of this investigation is to demonstrate the versatility and accuracy of the valved Knudsen cell method through the investigation of an alloy system for which the thermodynamic properties are well established: the Ag-Cu system.

II. LITERATURE SURVEY

Hultgren *et al.*^[6] reviewed the thermodynamic data available for the liquid Ag-Cu system prior to 1968 and concluded that the Ag vapor pressure measurements of Golonka^[7] and those of Edwards and Downing^[8] were in agreement up to $X_{\text{Ag}} = 0.4$, but that Edwards and Downing's results were too endothermic at higher mole fractions of silver. Since that time, seven other investigations have been published on activities in the liquid system.

Golonka *et al.*,^[9] Wagner *et al.*,^[10] and Nakamura *et al.*^[11] have measured the activities using the ion current ratio method. These investigations were conducted over the entire composition range. Golonka *et al.*^[9] studied the liquid Ag-Cu alloy system from 1350 to 1550 K and found midrange activities approximately 10 pct lower

STANLEY M. HOWARD, Professor, is with the Department of Metallurgical Engineering, South Dakota School of Mines and Technology, 501 E. St. Joseph Street, Rapid City, SD 57701.

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than those selected by Hultgren *et al.*^[6] Wagner *et al.*'s^[10] measurements are slightly less endothermic than those selected by Hultgren *et al.*^[6] but are in excellent agreement with Nakamura *et al.*'s.^[11] These three are in good agreement with Nakazawa,^[12] who measured the Ag activity coefficient at infinite dilution using a Knudsen effusion method.

Camersi *et al.*^[11,12,13] measured the activities of Cu in four alloy compositions, using the double Knudsen cell method at temperatures ranging from 1370 to 1398 K. They found approximately 5 to 10 pct more positive deviation from ideal behavior at the midrange compositions than did Edwards and Downing.^[8] Although they performed a Gibbs-Duhem integration, the limited data cast considerable uncertainty on those results.

Choudary and Ghosh^[14] determined the activities of Cu at 1400 K using a solid electrolyte cell from $X_{\text{Cu}} = 0.1$ to 0.8 and are in close agreement with Golonka *et al.*^[9] Taberko and Vaisburd^[15] determined the activity of Ag from vapor pressure measurements for Ag and Cu over the entire composition range and found the system to observe regular behavior described by the equation $RT \ln \gamma_i = (13.8 \text{ kJ/g mole}) (1 - X_i)^2$. Their results are also in close agreement with Golonka *et al.*^[9] at 1400 K. The results of all the investigations were reported for temperatures between 1370 and 1428 K.

III. THEORY

The vapor pressure p_i of the species in the Knudsen cell is given by the relation^[16]

$$p_i = K_g K_m K_s I_i^+ T \quad [1]$$

where K_g is a geometrical constant, K_m is a machine constant, K_s is a species constant, I_i^+ is the measured ion current, and T is the absolute temperature of the cell. It follows from the definition of activity that the activity of a species i in a liquid alloy is given by the following ratio:

$$a_i = \frac{(K_g K_m K_s T I_i^+)}{(K_g K_m K_s T I_i^{+0})} \quad [2]$$

where the superscript 0 denotes the reference state, which throughout this paper is the pure liquid component. As usual, this equation assumes ideal gas behavior and that the two ion currents correspond to the same temperature.

The species constants cancel, because they are independent of experimental conditions. Normally, the remaining constants do not cancel, because changes in the geometry and electronic state of the mass spectrometer occur from one experiment to the next. However, in the valved Knudsen cell method, the geometry remains the same during the course of a run, and the machine constants are also the same, because the experiments take place over a relatively short time period. Therefore, Eq. [2] reduces to

$$a_i = \left(\frac{I_i^+}{I_i^{+0}} \right) \quad [3]$$

for measurements with the valved Knudsen cell-mass spectrometer system.

Equation [3] is the basis of the valved Knudsen cell method. The experimental equipment allows the measurement of I_i^{+0} for pure i , followed immediately by the measurement of I_i^+ for each of many alloys of interest during the course of one experiment. The alloys may be binary or multicomponent.

IV. EXPERIMENTAL

This section includes a description of the valved Knudsen cell-mass spectrometer system and a summary of the procedure followed in this investigation. Words in italics indicate parts of the system which are labeled on the figures.

A. Valved Knudsen Cell-Mass Spectrometer System

The essential feature of the valved Knudsen cell system is shown in Figure 1. The cell is constructed so that small metallic beads, which are directed into the *sample tube*, enter the cell while the sample tube is slid downward, as shown. Once the bead has entered the cell, the sample tube is slid upward to seal the cell.

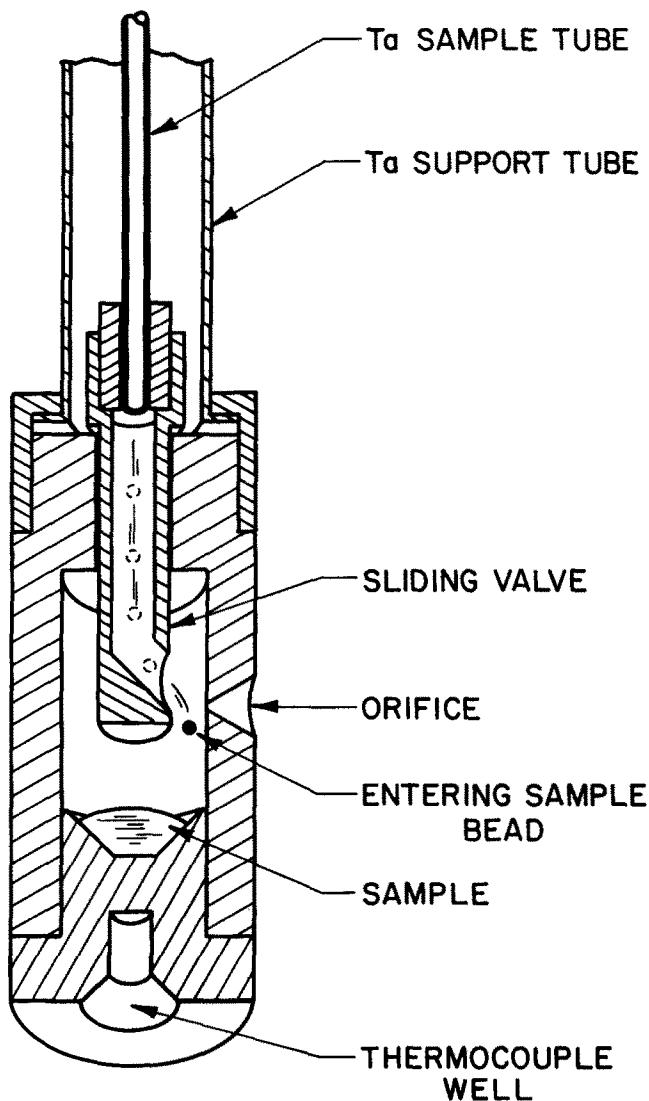


Fig. 1—Valved Knudsen cell assembly.

Figure 2 shows an overall schematic view of the mass spectrometer-valved Knudsen cell inlet system. The valved Knudsen cell hangs by a *support tube* from a *carriage assembly*, which contains the sample beads which are to be dropped into the cell during the course of the experiment. Before an experimental run, the carriage assembly, which is connected to the *thread rod*, is fitted with a *sample wheel*, which holds up to 23 preweighed sample beads. The thread rod with carriage assembly, sample wheel, support tube, and Knudsen cell is placed in the *tower*, and the top tower flange secured. The tower is then evacuated, the *swing valve* opened, and the carriage assembly, including the sample wheel and Knudsen cell, lowered using the *thread rod feedthrough*, which rotates the thread rod. When the Knudsen cell is properly positioned in the furnace, the carriage assembly coincides with the *fork* which, via a system of gear drives and mechanical linkages, simultaneously rotates the sample wheel to drop individual sample beads down the sample tube and opens the Knudsen cell valve to allow

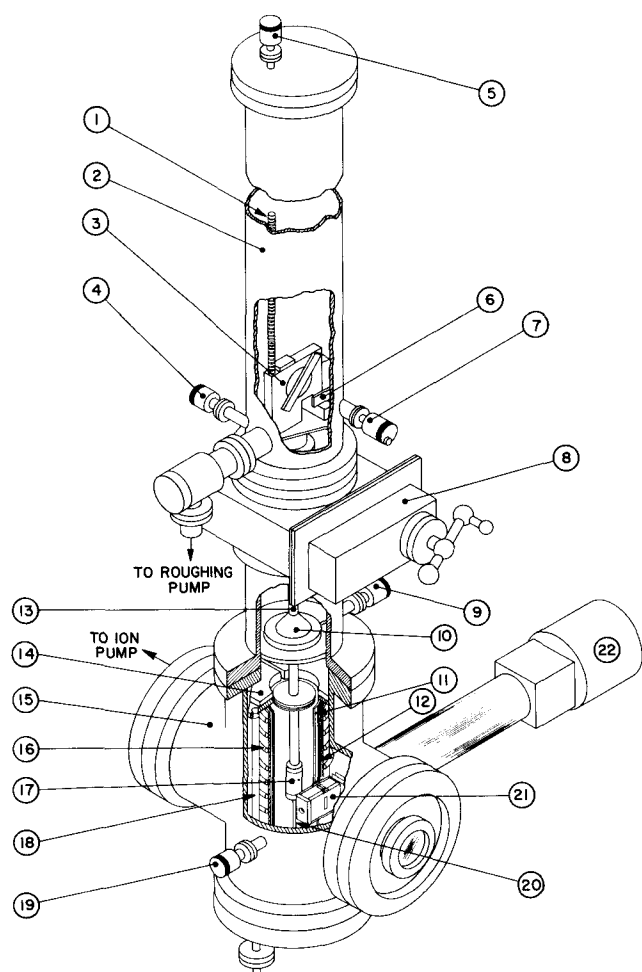


Fig. 2—Overall view of the valved Knudsen cell-mass spectrometer system: (1) thread rod, (2) tower, (3) carriage assembly, (4) radial-alignment feedthrough, (5) thread rod feedthrough, (6) fork, (7) fork feedthrough, (8) swing valve, (9) linear-motion feedthrough, (10) dowel, (11) furnace element, (12) heat shields, (13) support tube, (14) copper clamp, (15) furnace cross, (16) water-cooled jacket, (17) Knudsen cell, (18) power feedthrough, (19) shutter feedthrough, (20) thermocouple, (21) ion source, and (22) detector.

the beads to pass into the cell. The fork is operated by the *fork rotary-motion feedthrough*.

The resistively heated *furnace element* consists of a 30-cm-long by 5-cm-diameter Ta tube. It is split 24 cm along its axis and flanged at the top so that current can pass through a *copper clamp*, down one side of the tube, up the other side of the tube, and out a second copper clamp on the other side. A low-voltage 10 kilowatt power supply is used to feed power to the clamps via two *copper power feedthroughs* mounted on the base of the *furnace cross*. Each power feedthrough is cooled by a fountain-type cooler inserted from the bottom of the feedthrough into an axially bored hole.

The furnace element is surrounded by a series of eight Ta *heat shields* followed by a *water-cooled jacket*. The temperature of the cell is measured by a *thermocouple* located below the cell. The thermocouple extends through the bottom flange of the furnace cross to the bottom of the Knudsen cell.

Effusate from the Knudsen cell passes horizontally 7 cm to the electron beam in the ion source via the slit in the furnace element, slits in the heat shields, and a slit in the water jacket. A rotary-motion *shutter feedthrough* is connected to a shutter, which is used to interrupt the molecular beam as it passes from the cell to the ion source. This allows determination of the background signal, which is subtracted from the ion current measured when the shutter is open. The radial alignment of the orifice is controlled by the *radial-alignment feedthrough*, which is connected to a hook which captures a pin on the support tube clamp. The sideways alignment of the orifice is controlled by the *linear-motion feedthrough*, which moves the collar which has captured the lateral alignment *dowel* laterally. The mass spectrometer is a CVC model MA3A-CB. The entire system is pumped by a 110 L/s triode ion pump.

The Knudsen cell is machined from high-density, high-purity graphite. A 12-mm-diameter tantalum tube serves as a transition material between the graphite cell and the mullite support tube which was fixed to the carriage. The mullite was used to reduce heat conduction along the support tube. Direct connection of the graphite to the mullite was avoided, since intolerable CO gas pressures are generated by such contacts.

B. Procedure

1. Sample preparation

Beads for the sample wheel were preformed into spheres to assure unimpeded fall from the sample wheel through the sample tube and valve into the Knudsen cell. The beads, which have masses of approximately 20 mg, were produced by melting 99.99 pct purity metals in graphite molds under argon or vacuum. This procedure is required, since even minute quantities of oxide form unmanageable quantities of CO in graphite Knudsen cells in high vacuum at high temperatures. The surface tension assures nearly spherical beads at these sizes.

2. Loading the system

With the carriage assembly removed from the tower, the first several holes of the sample wheel were loaded with silver beads. The remaining holes were filled with the preweighed copper or silver beads. Approximately

1 mg of silver was placed in the cell to establish the optimum condition for the silver spectrum before each run.

Once the Knudsen cell was in position, the furnace was brought to temperature, and the instrument tuned to detect the initial silver in the cell. The thermocouple was calibrated using the constant ion current of pure silver at its melting point. The temperature of the cell at this point was determined from a T vs emf plot, where the temperature scale was shifted so that the measured melting point of silver corresponded to the actual melting point of silver (1234 K).

Once the temperature calibration was completed, the cell temperature was raised, and the initial silver completely vaporized. Once the temperature was stabilized at the desired experimental temperature of 1400 K, the first silver beads were dropped into the cell, and the ion current of pure silver measured. The copper beads were then added, and the silver ion current measured for the alloy. The remaining beads were then added one at a time, and the ion current for the new alloy measured after each addition.

V. RESULTS

Figure 3 shows typical results for the Ag-Cu investigation obtained using the valved Knudsen cell. The figure shows 16 measured ion currents of silver for a typical run. The background reading was taken twice during the run, as shown. In actual practice, some of the ion currents are multiplied electronically to permit more precise determination of their values, and the order of the measurements rearranged.

Table I shows the ion currents measured for six different experimental runs. Some of the runs involve considerably fewer beads than the 23 that the sample wheel is capable of holding, but the remaining beads in the wheel were used to enter a ternary field to obtain results which will be presented in a subsequent paper.

Figure 4 shows the activities of silver calculated in accordance with Eq. [3], using the data at 1400 K for the six experimental runs presented in Table I. Also shown in Figure 4 are the results of a Gibbs-Duhem integration for the activity of copper, using the silver activities determined in this investigation. Table II is a summary of the results presented in Figure 4 plus the activity coefficients and estimates of uncertainty.

VI. DISCUSSION

The most likely criticism of the valved Knudsen cell method is that all the activities are based on the measured ion current for the pure alloy. Consequently, an error in that measurement places all the computed activities in error by the same amount. However, this problem is easily overcome. The Darken plot^[17] in Figure 5(a) shows the logarithm of the activity coefficient of silver plotted as a function of $(1 - X_{\text{Ag}})^2$. The primary feature of the results of this study is that the data points fall essentially on a straight line, in accordance with regular solution behavior. The line drawn through the data from this study is the least-squares fit and is the basis of the

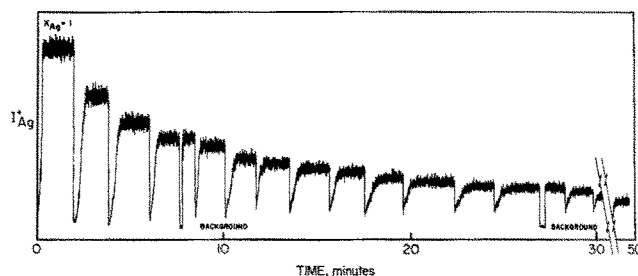


Fig. 3—Measured ion current of silver for a typical run.

activity lines drawn in Figure 4. Now, if the measurement of I_i^{+0} is in error, then the activity coefficients would also be in error. A correction factor c' could correct them according to the equation

$$\gamma_{\text{Ag,true}} = c' \gamma_{\text{Ag,calculated}} \quad [4]$$

which may also be written

$$\ln \gamma_{\text{Ag,true}} = \ln \gamma_{\text{Ag,calculated}} + \ln c' \quad [5]$$

Table I. Measured Ion Currents and Corresponding Activity Data

Run	X_{Ag}	I_{Ag}^+	a_{Ag}	γ_{Ag}
A	1.000	7.10	1.000	1.00
	0.610	5.31	0.748	1.23
	0.395	4.71	0.587	1.48
	0.283	3.55	0.500	1.76
	0.236	3.20	0.451	1.91
	0.188	2.73	0.385	2.05
	0.167	2.53	0.356	2.13
	0.147	2.33	0.328	2.23
	0.133	2.18	0.307	2.31
	0.115	1.94	0.273	2.37
	0.104	1.79	0.252	2.44
	0.093	1.58	0.223	2.37
	0.086	1.52	0.214	2.49
	0.079	1.41	0.199	2.50
	0.068	1.36	0.192	2.84
	0.063	1.28	0.180	2.87
	0.058	1.17	0.165	2.83
B	1.000	28.00	1.000	1.00
	0.103	6.86	0.245	2.37
C	1.000	10.60	1.000	1.00
	0.413	6.40	0.604	1.46
	0.280	5.21	0.492	1.76
	0.195	4.52	0.426	2.18
D	1.000	5.32	1.000	1.00
	0.573	3.77	0.709	1.24
	0.382	3.05	0.573	1.50
	0.271	2.85	0.536	1.98
	0.206	2.22	0.417	2.02
E	1.000	1.90	1.000	1.00
	0.591	1.30	0.684	1.16
	0.389	1.10	0.579	1.49
	0.281	0.94	0.495	1.76
	0.237	0.90	0.474	2.00
F	1.000	8.10	1.000	1.00
	0.713	6.55	0.809	1.14
	0.561	5.75	0.710	1.27

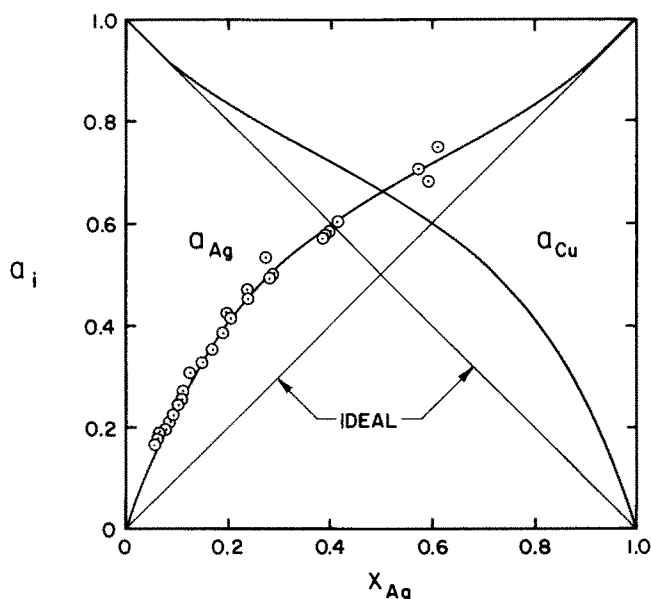


Fig. 4—Activities for the liquid Ag-Cu system at 1400 K.

Then, the least-squares line passing through the calculated data on the Darken plot in Figure 5(a) would not intersect the origin but would have an intercept equal to $-\ln c'$, because $\ln \gamma_{\text{Ag,true}} = 0$ at $(1 - X_{\text{Ag}})^2 = 0$. Therefore, the relationship between $\ln \gamma_{\text{Ag}}$ and $(1 - X_{\text{Ag}})^2$ can be corrected by subtracting an amount equal to the intercept from the $\ln \gamma_{\text{Ag,calculated}}$ values. This is the same as shifting the least-squares line for the computed values upward until it passes through the origin while keeping its slope the same. Therefore, the correct activity coefficient expression is

$$\ln \gamma_{\text{Ag,true}} = b(1 - X_{\text{Ag}})^2 \quad [6]$$

where b is the slope of the least-squares fit.

This result implies that the measured value of the ion current for the pure component is not needed to obtain the activity coefficients. This is true and is proven in the following way. The logarithm of the activity coefficient of component i may be written based on Eq. [3] as

$$\ln \gamma_i = \ln \left(\frac{I_i^+}{X_i I_i^{+0}} \right) \quad [7]$$

The differentiation and integration of this equation from $X_i = 1$ to X_i gives

$$\ln \gamma_i = \int_{X_i=1}^{X_i} d \ln \left(\frac{I_i^+}{X_i} \right) \quad [8]$$

which shows that the error in I_i^{+0} measurement is not only inconsequential but that there is no need to measure it. That is, the value of I_i^+/X_i at $X_i = 1$ can be determined by extrapolation of a line fitted to data at other compositions. Furthermore, Eq. [8] shows that the integration of a plot of $\ln (I_i^+/X_i)$ vs some composition coordinate provides a means of eliminating the computed activity coefficient's dependency on any other one measurement. The composition coordinate $(1 - X_{\text{Ag}})^2$ is recommended, since solutions obeying Darken's quadratic formalism^[17] are described by two straight lines connected by a curved transition region or by one straight line, in the case of a regular solution.

The integration of Eq. [8] is very straightforward in the case of a regular solution, since a least-squares fit of $\ln (I_i^+/X_i)$ vs $(1 - X_{\text{Ag}})^2$ is a straight line. The slope of the fit is the constant of Eq. [6], which, of course, is also known as the alpha function. In the case of non-regular solutions, the curve fitted to the data of such a plot would be shifted in the $\ln (I_i^+/X_i)$ direction until the end at $(1 - X_{\text{Ag}})^2 = 0$ intersected the origin.

Table III shows the results of a least-squares fit of the experimental data in Table I. Run A is the most significant, since it consists of 16 data points. In this run, the intercept was -0.006 . This corresponds to measured γ of 0.994, which, of course, should be 1. Substituting these values into Eq. [5] yields the value of the correction factor $c' = 1.006$, which indicates that the measured I_{Ag}^{+0} was too high by 0.6 pct. The correction factors for the other runs are considerably higher because of the few data included in each run, the distance the data were extrapolated in order to establish an intercept, and the relatively small range in $(1 - X_{\text{Ag}})^2$. Therefore, the intercepts for these runs do not provide an estimate of the precision of any one measurement. However, the intercept from run A does provide a fairly accurate estimate for the precision of I_{Ag}^{+0} for run A. The confidence in the precision so estimated increases with the number of data used to determine the values of the intercept. Since errors in measurement of I_{Ag}^{+0} are random, the intercepts and slopes obtained using all the data yielded

Table II. Results for Ag-Cu System at 1400 K

X_{Ag}	X_{Cu}	a_{Ag}	γ_{Ag}	a_{Cu}	γ_{Cu}
1.0	0.0	1.000 ± 0.000	1.000 ± 0.000	0.000 ± 0.000	3.053 ± 0.106
0.9	0.1	0.910 ± 0.000	1.011 ± 0.000	0.247 ± 0.007	2.469 ± 0.069
0.8	0.2	0.837 ± 0.001	1.046 ± 0.001	0.409 ± 0.009	2.043 ± 0.046
0.7	0.3	0.774 ± 0.002	1.106 ± 0.003	0.518 ± 0.009	1.728 ± 0.039
0.6	0.4	0.717 ± 0.004	1.195 ± 0.007	0.598 ± 0.007	1.494 ± 0.018
0.5	0.5	0.661 ± 0.006	1.322 ± 0.011	0.661 ± 0.006	1.322 ± 0.011
0.4	0.6	0.598 ± 0.007	1.494 ± 0.018	0.717 ± 0.004	1.195 ± 0.007
0.3	0.7	0.518 ± 0.009	1.728 ± 0.039	0.774 ± 0.002	1.106 ± 0.003
0.2	0.8	0.409 ± 0.009	2.043 ± 0.046	0.837 ± 0.001	1.046 ± 0.001
0.1	0.9	0.247 ± 0.007	2.469 ± 0.069	0.910 ± 0.000	1.011 ± 0.000
0.0	1.0	0.000 ± 0.000	3.053 ± 0.106	1.000 ± 0.000	1.000 ± 0.000

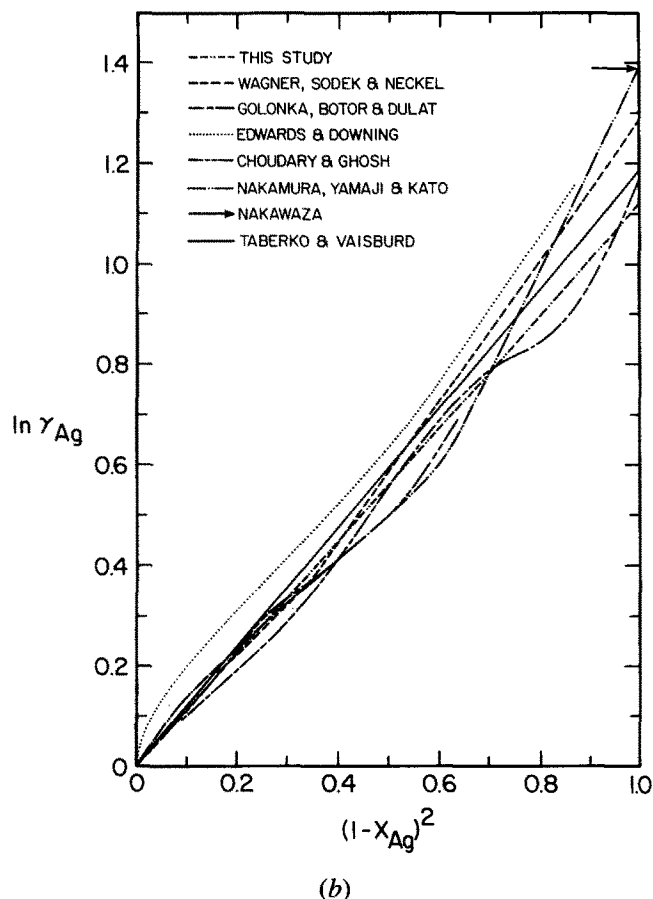
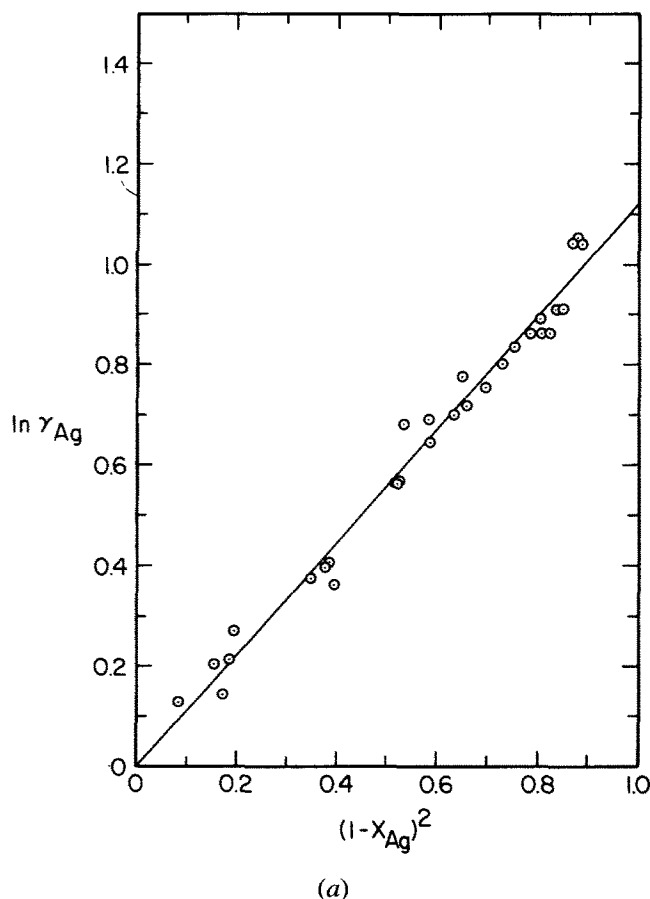


Fig. 5—Darken plot for the liquid Ag-Cu system at 1400 K: (a) this study and (b) other investigations.

the expected result of an intercept closer to zero than did the individual runs.

The least-squares fit for all the data in Table III, in which the intercept was made to pass through the origin, gives

$$\ln \gamma_{Ag} = (1.116 \pm 0.034) (1 - X_{Ag})^2 \quad [9]$$

for the activity coefficients in the liquid Ag-Cu system at 1400 K. The ± 0.034 represents the variation required to include 68 pct of the fitted data, as is the usual meaning of ± 1 standard deviation.

A. Comparison with Other Studies

The comparison of the results of this study with previous investigations is best accomplished by plotting all

the results on the Darken plot^[17] shown in Figure 5(b). The results for the other investigations were brought to 1400 K using the respective heats reported by each investigation. These temperature translations were small, ranging from an increase of 27 K to a decrease of 28 K. Since there is good agreement in the heat data, the differences in results shown are essentially based on the differences in activity measurement. The line for this study is based on Eq. [9]. Each other line is based on the smoothed data reported by the investigators and not this author's interpretation of a smooth curve drawn through the investigators' reported raw data. That is, the substantial undulations in the line representing Golonka *et al.*'s data^[9] are based precisely on their smoothed line through their raw data. The same is true for the minor undulations in the lines representing the results of Edwards and Downing,^[8] Nakamura *et al.*,^[11] and Choudary and Ghosh.^[14] Review of these studies by the current investigator suggests that these undulations are the consequence of undulations drawn through raw data and provide more of an estimate of uncertainty than a definition of actual solution behavior. The smoothing process is determined once the line for the Gibbs-Duhem integration is fixed. Golonka *et al.*'s^[9] integration line is drawn with two inflection points. This results in the undulations shown.

With the exception of the results of Edwards and Downing,^[8] which are more endothermic, and Golonka *et al.*,^[9] which are less endothermic, all the studies are

Table III. Least-Squares Fit for the Results in Table I in the Form $\ln \gamma_{Ag} = a + b(1 - X_{Ag})^2$

Run	N	a	b	r ^{2*}
A	16	-0.006	1.128	0.975
C	3	-0.086	1.310	0.986
D	4	-0.007	1.178	0.959
E	4	-0.071	1.275	0.993
F	2	0.053	0.946	1.000
All	30	0.005	1.116	0.983

*Square of the correlation coefficient.

in very good agreement over the range of $1.0 < X_{\text{Ag}} < 0.35$. Below that range, the activity coefficients at infinite dilution reported by Nakamura *et al.*,^[11] Nakazawa,^[12] and Wagner *et al.*^[10] are 32 to 18 pct higher than the results of this study. The results of Edwards and Downing^[8] do not extend to infinite dilution but fall within this range at low mole fractions of silver. On the other hand, the results of Golonka *et al.*^[9] and those of Taberko and Vaisburd^[15] are in close agreement with this study at infinite dilution.

It is interesting to observe that the results of Nakamura *et al.*,^[11] Golonka *et al.*,^[9] and Choudary and Ghosh^[14] do not conform to Darken's^[17] quadratic formalism. In fact, the results of Golonka *et al.*^[9] and those of Choudary and Ghosh^[14] undulate about this study. The results of Wagner *et al.*,^[10] even though more endothermic than this study, do conform to Darken's^[17] quadratic formalism. The results of Taberko and Vaisburd^[15] and this study both conform to regular solution behavior.

The activity coefficients of Ag obtained by the Gibbs-Duhem integration reported by Camersi *et al.*^[13] are not shown, because they are based on only four compositions. However, there is no doubt that their results are even more endothermic than those of Edwards and Downing.^[8]

B. Errors

The potential problems of surface depletion, hydrodynamic flow, surface effusion, and species diffusion through the graphite cell have been satisfactorily addressed in earlier studies,^[18] and the conditions required to avoid these potential problems were maintained in this study. The only potential problems of special interest, as a consequence of this new experimental method, centered on the size of the initial silver sample used to determine I_{Ag}^{+0} and the uncertainty in sample composition during the course of the investigation, resulting from silver losses.

The first of these concerns was shown to be insignificant by monitoring I_{Ag}^{+0} as a number of very small (~ 2 mg) silver beads were added to the cell. Silver ion current was found to be independent of silver mass above several milligrams of silver.

The potential problem of uncertainties in composition resulting from significant silver losses was dealt with in the following way. The total mass of the alloy bead was determined after each run and subtracted from the total mass of all the beads used to form the alloy. The total mass loss was attributed to silver loss, since the vapor pressure of pure silver (8.09 Pa) is 56 times greater than that of pure copper (0.145 Pa) at 1400 K.^[19] The approximately 1 mg silver losses were then prorated over time, using the area under a curve of silver ion current vs time, since at constant temperature, the rate of silver loss is proportional to its ion current. The values of the mole fractions of silver thus determined were checked by analysis of the final alloy beads and found to be within 0.1 at. pct silver. In systems where losses are likely to be significant, the effect of vaporization may be minimized by initially driving the alloy composition far from the more volatile component, followed by numerous additions of the more volatile component. The advantage

of this procedure is that it (1) increases the amount of the volatile component in the cell, thus minimizing the effect of vaporization losses on composition, and (2) allows the greatest possible traverse of the composition range with one experimental run.

It is important to note that at the very low pressures in the cell, the flow from the cell is molecular rather than hydrodynamic. This means that the tortuous path from the cell's interior to the exterior provides excellent resistance to vapor loss from the cell. Therefore, the loss of vapor along the sliding valve is essentially *nil*.

C. Temperature Gradients

Temperature gradients in the cell were a major concern, since the activity measurements described here require a constant temperature environment. Before the system was built, numerical solutions for the temperature profiles in the Knudsen cell were undertaken. Those studies were used to determine the dimensions and shielding of the furnace and the importance of limiting the length of the Ta support tube. Major factors favoring small gradients were the high conductivity of high-density graphite and the blackbody conditions in the furnace. Numerical solutions showed that the temperature gradients in the cell would be less than 1 K degree. This was confirmed by two experiments. First, a special cell was constructed that held a bead of silver in the upper reaches of the cell's interior and the temperature of the thermocouple noted at the constant ion current of the silver at its melting point. That silver was then vaporized at high temperature, and a second bead was dropped into the cell *via* the valve. This second bead resided at the bottom of the cell. Comparison of the thermocouple temperature at the constant ion current of the second bead with the first showed the temperature differences within the cell to be less than 1 K degree.

A more common, but less precise, method of experimentally confirming the absence of significant temperature gradients was also used. It involved the measurement of the heat of vaporization of silver. The slope of a plot of $\ln(I_{\text{Ag}}^+T)$ vs $1/T$ yielded ΔH_{VAP}^0 values within approximately 4 kJ/g mole of the accepted values.^[19]

D. Limitations

The mass spectrometer-valved Knudsen cell method has some limitations in its applicability. The severest arises from vapor pressure considerations. The vapor pressure of the species monitored should be high enough to be measured by the mass spectrometer over the entire composition range of interest to keep the complexity of the mathematical analysis minimized. However, systems can be investigated by monitoring different species and combining the fragmentary data for two or more components through a Gibbs-Duhem integration. Fortunately, one component usually has a vapor pressure greater than every other species at nearly all compositions.

A second condition that must be met is that the total vapor pressure of the system cannot exceed approximately 10 Pa at any composition of interest, because molecular effusion from the cell is no longer maintained above those pressures, and the cell enters the hydrodynamic flow regime, which would violate Eq. [1].

Another major consideration in using the valved Knudsen cell method is cell materials. The material for the cell should not react with the system under investigation. In the case of Ag-Cu alloys, graphite performs very well, because it machines easily, has a very high thermal conductivity, and does not dissolve or react with copper or silver.

VII. CONCLUSION

The liquid Ag-Cu system at 1400 K was found to exhibit regular behavior. These results are in excellent agreement with Golonka *et al.*,^[9] Choudary and Ghosh,^[14] and Taberko and Vaisburd^[15] but less endothermic than the results of Edwards and Downing,^[8] Nakamura *et al.*,^[11] Nakazawa,^[12] and Wagner *et al.*^[10]

The mass spectrometer-valved Knudsen cell system permits the rapid and accurate measurement of activities in liquid metallic alloys. Although demonstrated for binary alloys in this study, the method is equally well suited for the investigation of multicomponent alloys.

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