

# Effect of Oxygen on the Surface Tension of Liquid Copper

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The influence of oxygen on the surface tension of liquid copper has been determined by the sessile drop technique. The surface tension of pure liquid copper at 1108 °C is found to be equal to  $1.320 \pm 0.015$  N/m. The effect of oxygen is investigated for partial pressures of oxygen ranging from  $10^{-13}$  to  $5 \times 10^{-6}$  atm. The surface activity of oxygen is deduced to equal  $3200 \pm 600$  N/m and the saturation adsorption to equal  $5.72 \times 10^{-6}$  mole/m<sup>2</sup>, which corresponds to a saturation area of  $29 \pm 5 \text{ \AA}^2$  per adsorbed oxygen atom. The adsorption of oxygen on liquid copper is consistent with the formation at the metal surface of a two-dimensional compound of stoichiometry  $\text{Cu}_3\text{O}$ . It is also concluded that equivalent attractive forces operate between neighboring adsorbed atoms.

THE effects of surface-active species on the surface tensions of liquid metals are important in numerous industrial applications. Partially due to the difficulty of their determination, there is a real dearth of reliable experimental data. The sessile drop technique was selected to investigate the effect of oxygen on the surface tension of liquid copper at 1108 °C.

A similar study was conducted by Bernard and Lupis<sup>1</sup> on the Ag-O system at the same temperature (1108 °C). Their theoretical conclusions did not agree with experimental results in the literature on the Cu-O system.<sup>2-4</sup> The present contribution resolves this discrepancy.

## APPARATUS

A sketch of the apparatus is shown in Fig. 1. The equipment was a modified version of that previously used by Bernard.<sup>5</sup>

The furnace was of the global type with a reaction chamber constituted by a McDanel tube of 99.8 pct  $\text{Al}_2\text{O}_3$ . Inside the chamber, a half-cylindrical tray of 99.8 pct  $\text{Al}_2\text{O}_3$ , cut from a tube of 3.5 cm diam, supported the Lucalox substrates used in this investigation.

The temperature of the drop was measured by a Pt/Pt-10 pct Rh thermocouple located under the drop's substrate. It was repeatedly calibrated against the melting points of copper, gold and silver and exhibited an accuracy of 0.5 °C.

Commercial purity gases were used and purified by standard techniques<sup>6</sup> to eliminate reported contaminants (essentially  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{O}_2$ ). Oxygen potentials ranging from  $5 \times 10^{-5}$  atm to  $10^{-16}$  atm, at 1108 °C, were obtained by means of CO-CO<sub>2</sub> mixtures. All gases were metered through capillary flowmeters before entering the reaction chamber. The precision was of the order of 1 pct, even for flowrates as small as 10 cm<sup>3</sup>/min.

Two oxygen probes of calcia-stabilized zirconia were

used. The first probe was placed immediately after the reaction chamber to continuously monitor the oxygen potential during an experiment. The second was mounted directly at the outlet of the gas trains. Its purpose was to verify the composition of the gas flow prior to its introduction in the reaction chamber. Both probes were calibrated against argon-oxygen mixtures of 0.01 pct and 1 pct  $\text{O}_2$ . In this composition range, the agreement between measured and calculated oxygen potentials was within 1 pct.

The oxygen potential corresponding to a CO-CO<sub>2</sub> mixture could also be measured through knowledge of the flowrates and of the concentrations of CO and CO<sub>2</sub>. Agreement between the oxygen potentials resulting from the two methods could only be obtained at very low flowrates. This is probably due to the fact that thermal and thermodynamic equilibria could not be achieved within the small internal volumes of the probes. As a consequence, the following procedure was adopted. The gas mixture was allowed to flow in the probe for a few minutes, the flow was then interrupted and the oxygen potential measured. The uncertainty on  $\log p_{\text{O}_2}$  was estimated at 5 pct.

The sessile drop was viewed through two optically flat windows of fused quartz (surfaces parallel to 30 s of arc). They were mounted on the female joints of the reaction tube by O-ring seals. High resolution photographs of the drop were obtained by a back illumi-

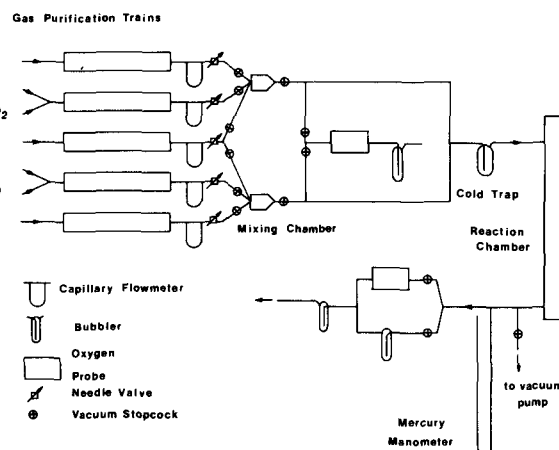


Fig. 1—Schematic of the sessile drop apparatus.

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nation system. The light source was a 500 W tungsten bulb. A lens of long focal length projected an image of the filament immediately behind the drop's meridional section, perpendicular to the optical axis. Several other systems were evaluated but in view of the large filament-to-object and object-to-camera distances, optical alignment was found to be critical. The system adopted provided the sharpest images.

A Gaertner M101 AT telemicroscope was operated at a distance of 65 cm from the drop. Mounted on a micrometric travelling stage, its position was known within  $1 \mu$ .

A Calumet camera, mounted immediately behind the telemicroscope, consisted of an f:5.6 apochromatic lens of 205 mm focal length, bellows and a  $4 \times 5$  sheet-film holder. The drops were photographed at a magnification of 4 to 5 and their images carefully focused on a clear glass plate.  $4 \times 5$  Kodak orthocontrast sheet films were used with an exposure of  $1/60$  s at f16.

Geometric characteristics of the profile of a drop were obtained directly from the negatives with a microcomparator, *i.e.*, a toolmaker's microscope manufactured by Zeiss. Digital micrometers allowed the measurement of horizontal and vertical distances with a resolution of  $1 \mu$ .

## EXPERIMENTAL PROCEDURES

Copper specimens were cut from a rod with a diameter of 1 cm and a purity of 99.999+. They were cleaned in a solution of 1:1 HNO<sub>3</sub> and 1:1 HCl and then rinsed ultrasonically in distilled water. The Lucalox substrates were immersed in boiling aqua regia for 15 min, baked at 1300 °C for several hours, rapidly cooled and introduced in the reaction chamber.

Leveling of a substrate along the longitudinal axis was accomplished at room temperature by inserting a small level mounted on a substrate in the middle of the reaction chamber. A small mirror was positioned at a 45 deg angle to the substrate and the indications of the level could be observed with the telemicroscope. Horizontality of the plaque to within 15 min was achieved by slightly tilting the whole furnace assembly and rotating the working tube about its axis until tests of the image in the telemicroscope indicated the surface of the substrate to be parallel to the horizontal cross hair.

The magnification of the optical system was determined at the beginning and at the end of the experimental run. Both values, usually, differed by less than 0.1 pct.

The metal specimen was heated to about 50 °C below its melting point in an oxidizing atmosphere in order to eliminate any contamination of the copper by adsorbed sulfur. After evacuating the system for 15 min, a reducing mixture of argon and hydrogen was flowed through for several hours. The specimen was then melted, held under this atmosphere for 30 min, and photographed twice. The drop was then solidified, the reaction chamber evacuated and held under static vacuum for 1 h. The solid drop was also measured with the telemicroscope and photographed in order to determine the magnification of the optical train.

After this preparation, the drop was remelted and a flow of pure carbon monoxide in argon was passed in the working tube. A small controlled amount of carbon dioxide was immediately added. After about 10 min, the oxygen probe indicated that equilibrium in the gas phase had been reached. 10 min later, the drop was photographed. A second photograph was usually taken 15 min later. The relative amount of CO<sub>2</sub> in the mixture was increased (effectively raising the oxygen potential) and the photographic procedure was repeated. For each value of the oxygen potential, the gas composition was carefully measured by means of the flowmeters and through readings of the zirconia probe.

## ANALYSIS OF THE PROFILE OF A DROP AND EXPERIMENTAL ERRORS

To deduce the value of the surface tension from the geometric profile of a drop, we adopted the method of Bernard and Lupis<sup>7</sup> which is a modified version of the original method of Bashforth and Adams.<sup>8</sup> It involves the measurement of the maximum diameter,  $X$ , of the drop, and of sets of coordinates  $x$  and  $z$  (see Fig. 2). The parameter  $\beta$ :

$$\beta = \rho g b^2 / \sigma \quad [1]$$

where  $\rho$  is the density of the alloy,  $g$  the acceleration of gravity,  $b$  the radius of curvature at the apex of the drop and  $\sigma$  the surface tension, can be determined by interpolation of the Bashforth and Adams' tables, as expanded by Bernard.<sup>5</sup>

Bernard and Lupis<sup>7</sup> have shown that coordinates of the drop's profile should preferably be measured on two distinct regions of the profile defined by:

$$0.8 < \frac{x}{X} < 0.9 \text{ and } z < Z; \quad \frac{x}{X} < 0.9 \text{ and } z > Z$$

where  $Z$  is the height of the maximum diameter measured from the apex of the drop (see Fig. 2). The relative error on  $\beta$  in the first region is then estimated at 0.3 pct, and in the second region at 0.2 pct. In the calculation of these estimates, we used data representative of a typical drop 1 cm in diam, with a contact angle of 160 deg. The relative uncertainties on  $x$ ,  $z$  and  $X$  were taken to be equal to  $2 \cdot 10^{-4}$ . The equation governing the drop shape, however, was derived under the assumption that it was perfectly axisymmetric. In practice, dissymmetries are often encountered so that  $\beta$

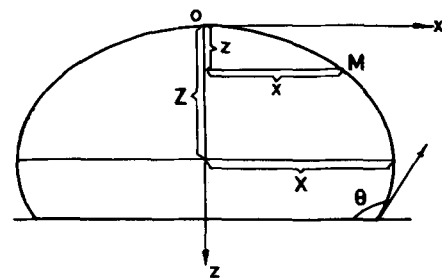


Fig. 2—Illustration of the geometrical parameters measured on a sessile drop profile to calculate the ratio of surface tension to density and the volume of the drop.

values measured in different portions of the drop profile may differ appreciably. Consequently, the adopted procedure consisted in measuring three sets of coordinates in the region  $z < Z$  and two sets in the region  $z > Z$ . The final value of  $\beta$  was taken as the average of these five values.

The fact that high-contact angles are desirable in surface tension measurements has not always been recognized. Some of the most precise determinations<sup>5,9</sup> have been conducted on fine-grained substrates leading to contact angles of 160 deg. When highly polished substrates are used, yielding unfavorable contact angles of 120 deg or lower, erratic values of surface tension have been obtained.

The accuracy of the optical train was verified at room temperature by photographing a calibrated ball with a radius of 1.270 cm. Distortions from a perfectly spherical shape were found to be smaller than  $2 \cdot 10^{-4}$ ; this yielded a relative uncertainty of 0.2 pct on the capillary constant  $\beta$ .

The object-image magnification was determined under vacuum conditions by dividing the maximum diameter measured on the photograph by the value obtained directly with the telemicroscope. The main source of error is due to the difficulty of positioning the telemicroscope cross hair on the drop's profile. The accuracy was improved by repeating this measurement five times to yield a relative uncertainty of 0.1 pct on the magnification.

From Eq. [1], we deduce that:

$$\frac{\Delta\sigma}{\sigma} = 2 \frac{\Delta b}{b} + \frac{\Delta\beta}{\beta} + \frac{\Delta\rho}{\rho} \quad [2]$$

The uncertainty on  $b$  is mainly due to the uncertainty on the magnification; consequently:

$$\begin{aligned} \frac{\Delta\sigma}{\sigma} &= 2 \times 0.1 \text{ pct} + 0.2 \text{ pct} + \frac{\Delta\rho}{\rho} \\ &= 0.4 \text{ pct} + \frac{\Delta\rho}{\rho} \end{aligned} \quad [3]$$

In the absence of any other effects, and ignoring the uncertainty in the density value, the surface tension may thus be determined with a precision better than 0.5 pct.

The absolute value of the temperature coefficient of surface tension is usually smaller than  $0.5 \times 10^{-3}$  N/m $\cdot$  °C for most metals and alloys. An error of 1 °C introduces an error on  $\sigma$  of less than  $0.5 \times 10^{-3}$  N/m, which is negligible in comparison to the errors discussed in the preceding paragraph.

A source of error which has often been mentioned but rarely evaluated is due to heat-induced refraction effects in the gas phase. If the radial temperature gradients are not uniform along the furnace tube, a bending of the light rays will result. Such an effect was observed and, to ascertain its magnitude, the dimensions of a gold drop were carefully measured from 600 to 1050 °C under an argon atmosphere and in vacuum. We note that, in vacuum, such a bending of the light rays will not occur. Our experimental results appear in

Fig. 3. In the presence of argon, the drop appeared smaller than it did in vacuum by about 0.15 pct over the temperature range studied. No shape distortion could be detected. Its image was translated upward by about  $40 \mu$ . This effect may be attributed to the presence of the drop's tray which destroyed the local axial symmetry. Adequate corrections were applied to the data. The calculated volume of a drop under an argon atmosphere, for example, had to be increased by 0.45 pct.

The main source of geometric errors in the sessile drop technique is due to dissymmetries in the drop profile. They usually develop upon melting because the motion of the liquid drop over the asperities of the substrate is not uniform in all directions. Dissymmetries may subsequently appear when the drop spreads on the substrate under the influence of oxygen, or because of a change in temperature. They could be readily detected by determining the tilt in the axis of symmetry from the measurements of the coordinates. Angular dissymmetries as small as 0.2 deg were detected by this method. Large angular dissymmetries led to contact angles which were different on the two sides of the drop's profile.

In the presence of dissymmetries, a definite correlation became evident between the extent of the dissymmetry and the spread in the calculated values of  $\beta$ . In the procedure finally adopted, the values of  $\beta$  were determined in two well-separated regions of the drop's outline. If their difference was larger than 1 pct, the experiment was rejected.

Chemical contamination of the drop is often the most important source of errors and the most difficult to control. The gas purification train and the experimental procedures described above appear to have eliminated any serious contamination. We note that if an accumulation of an impurity (such as sulfur) had occurred in the drop during a run, it would have resulted in a lower value of the surface tension of pure copper at the end of that run. Such a check was sought and satisfactory results obtained in each run.

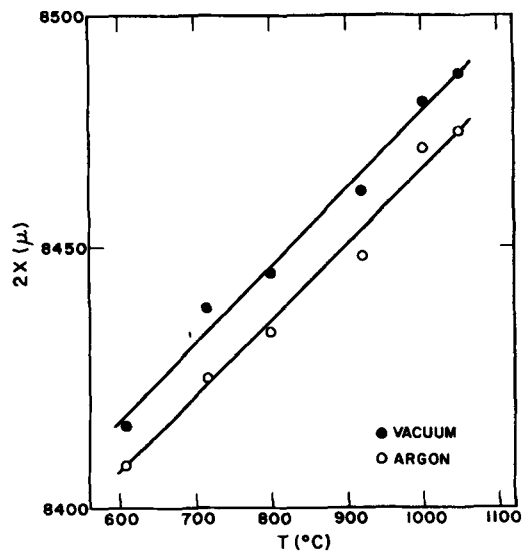


Fig. 3—Influence of heat-induced refraction effects on the apparent size of a gold drop measured in vacuum and under argon between 600 and 1108 °C.

## EXPERIMENTAL RESULTS

### Pure Copper

The sessile drop technique yields the ratio,  $\sigma/\rho$ , of the surface tension to the density. A critical evaluation of the values of the density of liquid copper published in the literature shows a scatter of about 1.3 pct. In spite of the fact that a value of 8.03 g/cm<sup>3</sup> at the melting point of copper (1083.4 °C) is often used, especially in surface tension measurements, we prefer to adopt the data determined by Lucas<sup>10</sup> which appear to be of excellent reliability, and yield a somewhat lower value of 7.94 at 1083.4 °C and 7.92 g/cm<sup>3</sup> at 1108 °C.

Values of the density can also be deduced from the sessile drop technique but with a poor precision. Our measurements gave us an average of 7.92 g/cm<sup>3</sup> with a scatter of about 0.05 g/cm<sup>3</sup> at 1108 °C.

Table I lists our results for the surface tension of the liquid copper at 1108 °C in five independent runs. From these, we deduce the value:

$$\sigma = 1.320 \pm 0.015 \text{ N/m}$$

The highest, and presumably the most reliable, values of the surface tension were obtained after deoxidation treatments of several hours under partial pressures of hydrogen as high as 0.5 atm. The extent of alumina reduction and aluminum dissolution in copper which may occur under such reducing atmospheres is likely to remain negligible. We note that for  $p_{O_2} = 10^{-20}$  atm, the activity of Al in liquid copper in equilibrium with Al<sub>2</sub>O<sub>3</sub> equals  $5 \times 10^{-9}$ . Chemical analyses of the copper specimens could not detect any aluminum.

Over forty separate determinations of the surface tension of liquid copper, by six different methods,<sup>11-13</sup> may be found in the literature. The results which Lang<sup>13</sup> has selected as the most reliable vary from 1.253 N/m to 1.322 N/m at the melting point. (All quoted values have been recalculated on the basis of a density value of 7.92 g/cm<sup>3</sup> at the melting point.) More recent work by Kawai *et al*<sup>14</sup> yielded a value of 1.360 N/m. We note that the authors used a single silica tube in their maximum bubble pressure measurements whereas two tubes may have been preferable for precision work.

The results of the levitation technique used by Soda *et al*<sup>15</sup> should also be cited. From the measurements of the oscillation frequency of a levitated metal droplet about its equilibrium shape, the surface tension is deduced by application of the Rayleigh equation. The calculated value of the surface tension is a sensitive function of the oscillation amplitude, and semi-empirical corrections must be applied to the data. The corrected value for liquid copper was found to be equal to 1.360 N/m. The value of the surface tension of liquid iron measured by this technique<sup>16</sup> was also found to lie above the upper limit of the surface tension data reported by reliable investigators.<sup>11,13</sup> This may imply that either a small additional correction is warranted or that the technique produces very clean surfaces. While the method avoids possible contamination by a crucible, it has not yet been applied to metals such as silver or gold for which more reliable values of the surface tension exist.

Table I. Surface Tension of Liquid Copper at 1108 °C

$\sigma$ (N/m)	Atmosphere	Run Number
1.342	Ar	C11
1.322	Ar-5 pct H <sub>2</sub>	C11
1.310	Vacuum	C11
1.299	Ar	C10
1.305	Ar-5 pct H <sub>2</sub>	C10
1.320	Ar	C8
1.331	Ar-10 pct H <sub>2</sub>	C8
1.305	Vacuum	C8
1.317	Ar	C7
1.308	Ar-8 pct H <sub>2</sub>	C7
1.326	Ar-15 pct H <sub>2</sub>	C7
1.311	Vacuum	C7
1.323	Ar	C3
1.320	Ar-1 pct H <sub>2</sub>	C3

Also recently, Morita and Kasama<sup>3</sup> proposed a value of 1.280 N/m, and Harrison *et al*<sup>17</sup> a value of 1.300 N/m. It is thus difficult to decide unequivocally upon a best value for the surface tension of liquid copper at its melting point (1083.4 °C). Our own value of 1.320 N/m at the slightly higher temperature of 1108 °C\* indicates

\* Correcting for the temperature difference of 25 °C would raise our value of  $\sigma$  by only 0.005 N/m.

that contamination effects were probably negligible.

### Copper-Oxygen Alloys

The fugacity of oxygen was fixed by the ratio of carbon monoxide to carbon dioxide, according to the reaction:



The influence of oxygen on the surface tension of liquid copper was determined at 1108 °C for partial pressures of oxygen extending from  $5 \times 10^{-13}$  to  $5 \times 10^{-6}$  atm. The experimental results appear in Table II. The surface tension isotherm has been plotted in Fig. 4 as a function of  $\log p_{O_2}$ . The isotherm exhibits the characteristic behavior of a surface-active species in a liquid metal: past a certain critical value of its concentration, the slope of the isotherm reaches a practically constant value, *i.e.*, the surface becomes saturated with oxygen.

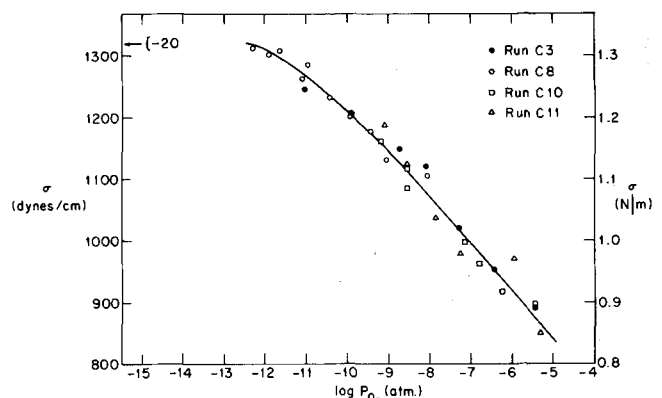


Fig. 4—The surface tension-oxygen chemical potential isotherm of the copper-oxygen system.

**Table II. Effect of Oxygen on the Surface Tension of Liquid Copper at 1108 °C**

Run C3		Run C8		Run C10		Run C11	
log $p_{O_2}$ (atm)	$\sigma$ (N/m)	log $p_{O_2}$ (atm)	$\sigma$ (N/m)	log $p_{O_2}$ (atm)	$\sigma$ (N/m)	log $p_{O_2}$ (atm)	$\sigma$ (N/m)
-11.05	1.243	-12.3	1.311	-9.2	1.161	-9.1	1.189
- 9.9	1.206	-11.9	1.301	-8.55	1.084	-8.55	1.125
- 8.75	1.148	-11.65	1.307	-7.15	0.997	-7.85	1.038
- 8.1	1.120	-11.1	1.262	-6.80	0.962	-7.25	0.978
- 7.2	1.020	-10.95	1.284	-6.20	0.917	-5.9	0.971
- 6.45	0.951	-10.45	1.231	-5.4	0.897	-5.3	0.850
- 5.45	0.892	- 9.95	1.200				
		- 9.45	1.177				
		- 9.05	1.130				
		- 8.55	1.116				
		- 8.05	1.105				

Note: 1 atm = 1.01325 × 10<sup>5</sup> Pa.

Monma and Suto<sup>2</sup> also used CO-CO<sub>2</sub> mixtures corresponding to a  $p_{O_2}$  range of 10<sup>-10</sup> to 10<sup>-4</sup> atm. Despite the inadequate graphical representation of their published data and the absence of tabulated values, a number of serious discrepancies with our results are apparent (see Fig. 5). Their reported value of 1.23 N/m for the surface tension of pure liquid copper is low and suggests possible contamination. The onset of oxygen adsorption differs considerably from our value, as does the limiting slope of the adsorption isotherm. Moreover, as shown by Bernard and Lupis,<sup>1</sup> their results on the copper-sulfur system differ notably from the more reliable data of Baes and Kellogg.<sup>9</sup>

O'Brien and Chaklader<sup>4</sup> obtained values of  $\sigma$  which are nearly constant at 1.23 N/m in the  $p_{O_2}$  range of 4 × 10<sup>-16</sup> to 2 × 10<sup>-10</sup> atm, and have only two data points in the region of saturation (Fig. 5). Their use of highly polished substrates may have introduced dissymmetries in the profile of the drop. Their drops were also too small to yield a good precision on the values of  $\beta$  and  $\sigma$ .<sup>5</sup>

Morita and Kasama<sup>3</sup> investigated the influence of oxygen by means of CO<sub>2</sub>/H<sub>2</sub> mixtures. Starting from very low oxygen partial pressures (10<sup>-20</sup> atm), the surface tension decreases steadily with increasing oxygen potential in a manner quite uncharacteristic of surface-active species in liquid metals. As shown by the investigation of Sasaki and Belton,<sup>18</sup> it is most likely that their gas mixture never reached equilibrium.

### Observations

The control of the oxygen partial pressure by a mixture of CO-CO<sub>2</sub> is no longer possible if carbon deposition occurs, according to the reaction:



For example, it may be calculated that carbon deposition becomes thermodynamically possible at temperatures of 975, 725, and 500 °C when the partial pressures of oxygen at 1108 °C are respectively equal to 10<sup>-16</sup>, 10<sup>-13</sup> and 10<sup>-10</sup> atm.

Several of our runs were conducted with a  $p_{O_2}$  ranging from 10<sup>-16</sup> to 10<sup>-13</sup> atm. Values of  $\sigma$  were observed to be of the order of 1.28 N/m and to slightly increase with increasing oxygen potentials, *i.e.*, with decreasing par-

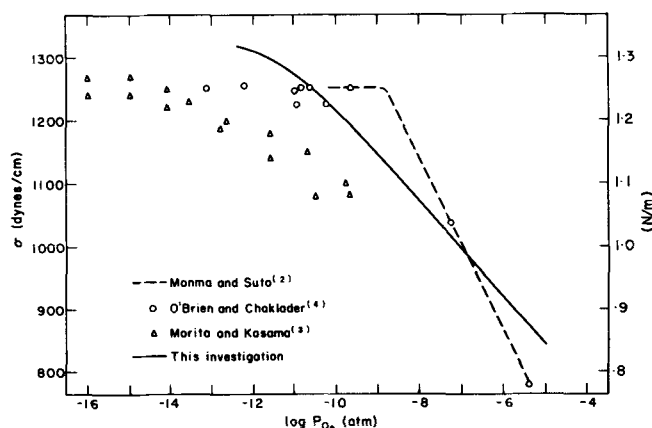


Fig. 5—Comparison of our experimental results on the copper-oxygen system to previous data.

tial pressure of CO. A sudden increase in  $\sigma$  was also registered when, at constant  $p_{O_2}$ , a mixture of Ar-1pctCO was substituted for pure CO. This effect was also systematically observed in a separate investigation of the surface tensions of liquid Ag-Cu alloys. It suggests that CO was adsorbed by liquid Cu and Ag-Cu alloys. Further investigation of this possible adsorption would be worthwhile.

We note that the values of  $p_{O_2}$  calculated from the gas composition were in good agreement with the values measured by the oxygen probes. Consequently, if carbon deposition had indeed occurred, its effect on  $p_{O_2}$  must have been minimal. A number of precautions were also taken to avoid its nucleation or further reduce its impact. A mixture of Ar-1pctCO was used instead of pure CO (since nucleation of graphite from a dilute gas phase would be more difficult), and the oxygen probes as well as the alumina reaction tube were periodically changed to ensure minimum contamination by graphite.

### THERMODYNAMIC ANALYSIS OF THE DATA

The surface activity of oxygen is defined as:

$$J_O = -\left(\frac{\partial \sigma}{\partial X_O}\right)_{X_O \rightarrow 0} \quad [6]$$

It may be rewritten:

$$J_o = \left( \frac{\partial \sigma}{\partial \sqrt{p_{O_2}}} \right)_{X_o \rightarrow 0} \cdot \left( \frac{\sqrt{p_{O_2}}}{X_o} \right)_{X_o \rightarrow 0} \quad [7]$$

The solubility of oxygen in liquid copper follows Sievert's law. From the data of Wilder,<sup>19</sup> we obtain:

$$X_o = 4.85 \sqrt{p_{O_2}} \quad [8]$$

where  $X_o$  is the mole fraction of oxygen in the melt and  $p_{O_2}$  is measured in atmospheres. Rather than calculating the coefficient

$$\left( \frac{\partial \sigma}{\partial \sqrt{p_{O_2}}} \right)_{p_{O_2} \rightarrow 0}$$

from a plot of surface tension vs  $\sqrt{p_{O_2}}$ , it is more advantageous to measure it by plotting  $\sqrt{p_{O_2}}/(\sigma_{Cu}^o - \sigma)$  vs  $\sqrt{p_{O_2}}$ , the ordinate at the origin being equal to the inverse of this coefficient.<sup>20</sup> The curvature at the origin is then well reduced, as shown in Fig. 6, and a simple graphical extrapolation seems adequate in view of the inherent imprecision of this type of determination. The result is:

$$-\left( \frac{\partial \sigma}{\partial \sqrt{p_{O_2}}} \right)_{p_{O_2} \rightarrow 0} = 15,600 \pm 3000 \text{ (N/m)} \times \text{atm}^{-1/2} \quad [9]$$

The surface activity of oxygen in liquid copper can now be deduced from Eq. [7], [8] and [9]:

$$J_o = 3200 \pm 600 \text{ N/m} \quad [10]$$

This value differs substantially from the approximate value calculated from the data of Monma and Suto<sup>2</sup> (1200 N/m), and from the value of Morita and Kasama<sup>3</sup> (>38,000 N/m).

Gibbs' adsorption equation yields the relative adsorption of oxygen with respect to copper:

$$\Gamma_o^{(Cu)} = -\frac{1}{RT} \left( \frac{\partial \sigma}{\partial \ln a_o} \right) \quad [11]$$

where by definition:

$$\Gamma_o^{(Cu)} = \Gamma_o - \Gamma_{Cu} \frac{X_o}{X_{Cu}} \quad [12]$$

Since:

$$d\mu_o = \frac{1}{2} d\mu_{O_2} = \frac{RT}{2} d \ln p_{O_2} \quad [13]$$

consequently:

$$\Gamma_o^{(Cu)} = -\frac{2}{RT} \left( \frac{\partial \sigma}{\partial \ln p_{O_2}} \right) \quad [14]$$

In the range of concentration investigated, the ratio  $X_o/X_{Cu}$  is smaller than  $5 \times 10^{-3}$  and consequently  $\Gamma_o \gg \Gamma_{Cu}(X_o/X_{Cu})$  since  $\Gamma_o$  and  $\Gamma_{Cu}$  have the same order of magnitude. Thus,  $\Gamma_o^{(Cu)} \approx \Gamma_o$ . Within the framework of the monolayer model,  $\Gamma_o$  represents the number of adsorbed oxygen atoms per unit area. Figure 4 shows that the slope of the surface tension-chemical potential of oxygen isotherm is practically constant past a critical

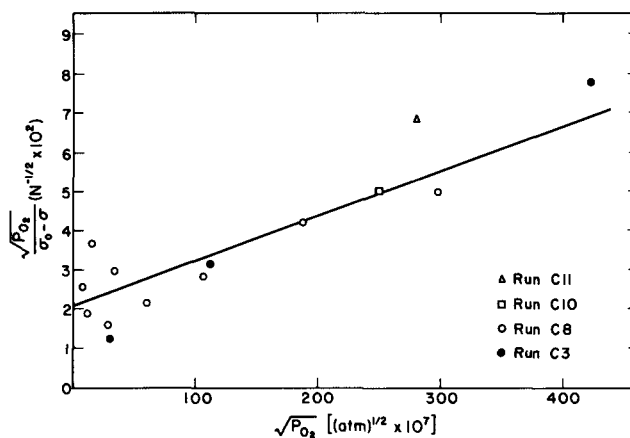


Fig. 6—Determination of the parameter  $(\partial \sigma / \partial \sqrt{p_{O_2}})_{p_{O_2} \rightarrow 0}$

value. In this region, the surface is saturated in oxygen. The limiting adsorption is found to be:

$$\Gamma_{O(sat)} = 5.72 \times 10^{-6} \text{ mole/m}^2 \quad [15]$$

corresponding to an area per adsorbed oxygen atom:

$$\alpha_{O(sat)} = 29 \pm 5 \text{ \AA}^2 \quad [16]$$

Again, this value is in strong disagreement with the data of Monma and Suto,<sup>2</sup> which yield a value of  $14.5 \text{ \AA}^2$ , and the results of Morita and Kasama<sup>3</sup> which suggest that the adsorption of oxygen increases continuously with increasing oxygen potentials.

## INTERPRETATION

### Structure of the Surface Phase

The adsorption of surface active species of the group VI-B on solid metals has been the subject of numerous structural investigations. In many of these systems, very stable three-dimensional compounds such as the metallic sulfides and oxides are known to occur. As a consequence of the strong affinity between the adsorbed metalloid atom and the metal substrate, reconstruction occurs, leading to the formation of a surface layer of definite stoichiometry and structure. Of particular interest to this investigation is the adsorption behavior of oxygen and sulfur on metals of the group IB (copper, silver and gold) which has been extensively studied by one group of investigators.<sup>21-23</sup> The adsorption isotherms of sulfur on these metals have been determined as a function of temperature by sensitive radiotracer techniques and Auger spectroscopy, and the resulting structures have been characterized by low-energy electron diffraction. The absolute adsorption of sulfur at saturation on (111), (110), and (100) planes are virtually identical for the three metals, whereas the stoichiometry of the surface compounds (*i.e.* the ratio of the number of metalloid to metal atoms) varies from 1/2 to 4/5 on the various planes. The three-dimensional sulfides are of the  $M_2S$  type. They have identical crystallographic structures and the bonding is essentially of ionic character. Less detailed information has been obtained in the case of oxygen. However, surface tension measurements have been conducted by the

zero-creep technique on solid copper.<sup>24</sup> The experimental surface tension-oxygen chemical potential isotherm is very similar to that obtained for the liquid metal. It was concluded that the surface stoichiometry was of the type  $M_3O$ .

The large values of the areas occupied at saturation by oxygen and sulfur on many liquid metals suggest similar phenomena. Kozakevitch and Urbain<sup>25</sup> have shown that the saturation coverages determined from the adsorption isotherms are reasonably consistent with the area occupied by the electronegative element in a near close-packed plane of an appropriate solid compound. This idea was further amplified by Bernard and Lupis<sup>1</sup> who showed that this simple geometric model provided an adequate description of their experimental results on the silver-oxygen system as well as of other systems. Table III lists the values of the area occupied by an oxygen atom in a (100) and a (111) plane of the three-dimensional oxides  $Ag_2O$  and  $Cu_2O$ . In both cases, the saturation area is very near to the area occupied in a (111) plane. In this plane, there are three metal atoms per oxygen atom which suggests that the stoichiometry of the surface phase is  $M_3O$ . The oxygen atoms occupy position of hexagonal symmetry in contrast to the square symmetry of the (100) plane. The agreement is also satisfactory for iron.<sup>25</sup>

#### Quantitative Description of the Adsorption Isotherm

In the modelling of the behavior of surface active species in metallic solutions, the dependence of the adsorption  $\Gamma_2$  on the mole fraction  $X_2$  is often described in terms of the Langmuir isotherm. It may be derived by consideration of the reaction:



for which the dissolved element 2 reacts with an empty site at the surface to form a filled site. Applying the law of mass action, we obtain:

$$K = \frac{\Gamma_2}{a_2(\Gamma_2^{(sat)} - \Gamma_2)} \quad [18]$$

where  $a_2$  is the activity of 2 in the solution (with a Henrian reference state),  $\Gamma_2$  is the concentration of 2 at the surface and  $(\Gamma_2^{(sat)} - \Gamma_2)$  is the concentration of vacant sites.

Equation [8] may be combined to the Gibbs adsorp-

tion equation and by integration, we obtain:

$$\sigma = \sigma_1^o - RT \Gamma_2^{(sat)} \ln(1 + Ka_2) \quad [19]$$

The form of this equation was derived empirically by Szyskowsky in 1908. It was shown by Belton<sup>26</sup> to yield adequate representation of the surface tension data for the Fe-O, Fe-S, Fe-Se, Cu-S, and Ag-O systems. More recently, Sasaki and Belton<sup>18</sup> have shown that the Langmuir isotherm (Eq. [19]) cannot represent our experimental values. Strong lateral bonds exist at the surface between adsorbed atoms and the adsorption vs concentration curve exhibits a much steeper rise than predicted by Langmuir's isotherm.

Guttman<sup>27</sup> has discussed a number of interaction models developed essentially for free surfaces but in relation to phenomena of grain boundary embrittlement. In this context, the lattice-gas model developed by Bernard and Lupis<sup>20</sup> presents a number of realistic approximations in dealing with both configurational and energetic contributions to the surface free energy. The model was shown to successfully describe the adsorption behavior of oxygen and sulfur in several systems, and in particular in the silver-oxygen system. In view of the strong similarities already mentioned between this system and the copper-oxygen system, it seems appropriate to review some of the basic assumptions of this model and to test its applicability to our experimental data.

All the sites at the surface are assumed to have a similar area  $\alpha$ . They are all occupied either by an adsorbed atom B or by a solvent atom A. Whenever a B atom is adsorbed, other B atoms are precluded from occupying certain sites in its immediate vicinity. Once the basic lattice and the exclusion pattern have been selected, the stoichiometric ratio  $A_{n-1}B$  is fixed. For example, a lattice with hexagonal symmetry in which first and second neighbors constitute forbidden sites for the adsorbed atom leads to the stoichiometry  $A_3B$ . Even with this simple assumption, the model is a considerable improvement over the Langmuir model since different stoichiometries may be generated for the surface phase. Interactions between adsorbed atoms are introduced as a further refinement. The isotherm corresponding to the stoichiometry  $A_3B$  may be represented with good accuracy by the equation of state:

$$\left(\sigma_o - \sigma - \frac{g\alpha}{A^2}\right)(A - A_{(sat)}) = RT \quad [20]$$

Table III. Area Requirements at Saturation for the Systems Fe-O, Ag-O and Cu-O<sup>5</sup>

System	T (K)	$A_{\frac{1}{2}} (\text{\AA}^2/\text{atom})$			Ionic Radii		Ionic Charge	
		Exp.	Calc.*	Calc.†	$r^-$	$r^+$	$z^-$	$z^+$
1-2								
Fe-O	1823	10.3	6.0	8(111)	1.32	0.83	2	2
Cu-O	1381	29	6.0	18(100) 30(111)	1.32	0.96	2	1
Ag-O	1253	34	6.0	23(100) 38(111)	1.32	1.13	2	1

\* On the basis of a close-packed layer of anions

† On the basis of the solid compound.

where  $A = 1/\Gamma_2 = \alpha/\theta$ , and  $g$  is proportional to a net bonding energy between neighboring impurity atoms.

In our experimental range of  $\theta$  values the isotherm predicted by the model may be represented in parametric form by the equations:<sup>20</sup>

$$\ln \sqrt{p_{O_2}} = \ln \frac{\theta}{1 - 4\theta} + \frac{4\theta}{1 - 4\theta} + \frac{2g\theta}{kT} - \ln c \quad [21]$$

$$\frac{(\sigma_o - \sigma)\alpha}{kT} = \frac{\theta}{1 - 4\theta} + \frac{g\theta^2}{kT} \quad [22]$$

where

$$c = - \frac{\alpha}{kT} \left( \frac{\partial \sigma}{\partial \sqrt{p_{O_2}}} \right)_{p_{O_2} \rightarrow 0} \quad [23]$$

The area per site  $\alpha$  is calculated by assuming that the solvent atoms form a close packed layer. The radius of the solvent atom is calculated from the lattice parameter. For copper:

$$\alpha = 5.78A \quad [24]$$

and using the measured value of

$$\left( \frac{\partial \sigma}{\partial \sqrt{p_{O_2}}} \right)_{p_{O_2} \rightarrow 0}, \text{ we obtain:} \\ c = - (46,000 \pm 9000) (\text{atm})^{-1/2} \quad [25]$$

To test this model it is convenient to plot  $(\sigma_o - \sigma)\alpha/kT$ , the reduced surface pressure, as a function of  $\ln \sqrt{p_{O_2}}$ . We note from Eqs. [21] and [22] that changing the value of  $c$  will shift the theoretical isotherm to the left or to the right, whereas changing the value of  $g$  will quantitatively affect the shape of the curve as well as the limiting adsorption.

Three theoretical isotherms have been plotted in Fig. 7 for values of  $g/kT$  equal to 0, -6 and -12. The theoretical isotherm corresponding to  $g/kT = -6$  provides the most accurate fit to the experimental data. By adjusting the value of  $c$ , the isotherms corresponding to  $g/kT = 0$  and  $g/kT = -12$  could be shifted to follow the experimental data. The resulting values of  $c$  would then be respectively equal to  $1.2 \times 10^5 (\text{atm})^{-1/2}$  and  $1.3 \times 10^4 (\text{atm})^{-1/2}$ . However, these values differ considerably from the experimental value. Furthermore, the limiting slope of the isotherm as well as the transition region are not correctly reproduced. The preceding discussion shows that the theoretical saturation area corresponding to the  $\text{Cu}_3\text{O}$  stoichiometry should be equal to  $4\alpha_{\text{Cu}}$  or  $23.1\text{\AA}^2$  whereas the experimental value is equal to  $29 \pm 5\text{\AA}^2$ . The reason for that apparent discrepancy is that the true saturation area of  $23.1\text{\AA}^2$  is only attained at oxygen potentials which are above the oxidation potential of copper and thus are experimentally inaccessible. It may be seen from Fig. 7 that indeed the slope of the theoretical isotherm increases (and thus the saturation area decreases) with increasing oxygen potentials. The presence of vacancies at the surface may also explain part of the disagreement between theoretical and experimental values.

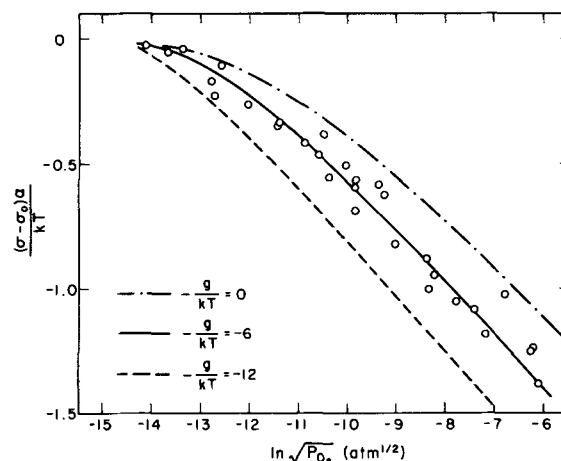


Fig. 7—Experimental test of Eq. [20]. See text for details.

We thus conclude that the experimental isotherm may be satisfactorily described by Eq. [20] with:

$$\frac{g}{kT} = -6 \quad [26]$$

$$c = - (46,000 \pm 9000) (\text{atm})^{-1/2} \quad [27]$$

The negative value of  $g$  indicates that attractive interactions exist between adsorbed oxygen atoms at the surface. Similar conclusions were drawn by Bernard and Lupis for the Ag-O system<sup>20</sup> and by Bénard *et al.*<sup>23</sup> for the adsorption of sulfur on solid gold, copper and silver. The interaction term  $g$  was actually found in the case of the liquid Ag-O system to be in the range of -6 to -8. Although our determination of this parameter is quite imprecise, it is clear that the interaction energies of oxygen atoms adsorbed on liquid silver and liquid copper have similar magnitudes.

## SUMMARY

The surface tensions of Cu-O alloys have been determined by the sessile drop technique. The surface tension of pure liquid copper at 1108 °C is found to be equal to  $1.320 \pm 0.015$  N/m. The surface activity of oxygen,  $-(d\sigma/dX_{O_2})_{X_{O_2} \rightarrow 0}$  equals 3200 N/m and the saturation adsorption,  $5.72 \times 10^{-6}$  mole/m<sup>2</sup>, which corresponds to a saturation area of  $29 \pm 5\text{\AA}^2$  per adsorbed oxygen atom. The saturation stage of oxygen in liquid copper is interpreted through the formation of a two-dimensional compound, corresponding to the stoichiometry  $\text{Cu}_3\text{O}$ . The interaction energies of oxygen atoms adsorbed on liquid silver and liquid copper are shown to have similar magnitudes.

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