values which agree very well with the observed densities over this range. Use was made of this equation to calculate densities down to —52.2°.

2. Surface-tension measurements of liquid carbon dioxide have been made from 25 to —52.2°.

3. The equation of de Block when put into the form $\gamma = .0653(31.35 - t)^{1.24}$ was found to fit the experimental results for the surface tension of carbon dioxide very well except at lower temperatures.

4. From its total energy of surface formation it was found that carbon dioxide had an internal pressure about the same as carbon tetrachloride, toluene and chloroform.

SALT LAKE CITY, UTAH

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

THE EFFECT OF IRON AND OXYGEN ON THE ELECTRICAL CONDUCTIVITY OF COPPER[1]

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RECEIVED JUNE 16, 1927 PUBLISHED NOVEMBER 5, 1927

The electrical conductivity of dilute solid solutions of metallic elements in copper has been the subject of many investigations. The data presented treat the binary systems of copper and practically every metal which may occur as an impurity in commercial copper, namely, silver, gold, zinc, cadmium, aluminum, tin, phosphorus, arsenic, antimony, iron, cobalt and nickel.[2] Unfortunately much discordance is evident in the published results.

In illustration, the solute element iron may be considered. Addicks[3] in his pioneer work upon the impurities of copper attempted to evaluate the effect of the 0.002 to 0.005% of iron present in electrolytic copper. From measurements upon alloys of 0.042, 0.046 and 0.068% of iron and upon pure copper, he interpolated for intermediate iron concentrations and concluded that the conductivity was lowered at the rate of 140% of the International Standard value for each 1% of iron present.

Hanson and Ford[4] at the National Physical Laboratory in England, under Rosenhain's direction, have recently repeated Addicks' work, extending the data to higher iron concentrations. Using the observed conductivity of an alloy of 0.2% of iron, they project a curve to pure copper and suggest a lowering in conductivity at the rate of 235% for 1% of iron.

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[1] A thesis for the degree of Doctor of Philosophy, presented to the Graduate Faculty of the University of Pennsylvania.

[2] Guertler, "Handbuch der Metallographie," Berlin, 1925; *Circular No. 73, Copper*, U. S. Bureau of Standards, 1922.

[3] Addicks, *Trans. Am. Inst. Min. Eng.*, **36**, 18 (1906).

[4] Hanson and Ford, *J. Inst. Metals*, **32**, 335 (1924).

They measured one alloy in this interpolated range. It contained 0.06% of iron. Curiously its conductivity was only about 1% lower than their value for pure copper. Such high conductivity is a considerable deviation from the established behavior of solid solutions. It indicates that the iron in the 0.06% alloy was not present in solid solution.

In an effort, perhaps, to simulate commercial copper, Addicks' and Hanson's alloys all contained cuprous oxide as a soluble component of the liquid phase. The assumption is made in their work that the effect of this oxide is negligible or at least is constant while they perform the interpolation between iron of zero concentration and iron at the measured concentration.

Thermodynamic consideration of the ternary system copper-iron-oxygen shows such assumption to be incorrect. Cuprous oxide is thermally dissociated. Roberts and Smyth[5] measured the equilibrium pressure of liquid copper saturated with cuprous oxide. For the reaction

$$Cu_2O(s) \longrightarrow 2Cu(c_l) + {}^1/_2\,O_2 \qquad (1)$$

they record the data: 1392.3°K. = 0.028 mm. of Hg, 1423.5°K. = 0.035 mm. of Hg; 1457.1°K. = 0.041 mm. of Hg. Selecting solid cuprous oxide and pure liquid copper as the states of unit activity and assuming the activity of copper to equal its mole fraction, the above reaction can be evaluated for ΔF° at 1398°K. and 1336°K. These temperatures are chosen to be, respectively, the temperature of formation of the liquid alloy and the eutectic temperature of the copper-cuprous oxide system. $\Delta F^\circ_{1398} = +17{,}490$ cal.; $\Delta F^\circ_{1336} = +17{,}430$ cal.

Eastman[6] has examined critically the recorded data for equilibrium in the reaction

$$FeO(s) + \xrightarrow{CO} Fe(s) + CO_2$$

Using Lewis and Randall's[7] value of ΔF° for the reaction

$$CO + {}^1/_2\,O_2 \longrightarrow CO_2$$

he evaluates ΔF° for the reaction

$$FeO(s) \longrightarrow Fe(s) + {}^1/_2\,O_2 \qquad (2)$$

for temperatures of 100° intervals from 873 to 1273°K. Extrapolating slightly, $\Delta F^\circ_{1398} = +41{,}295$ cal.; $\Delta F^\circ_{1336} = +42{,}260$ cal.

Combining Equations (1) and (2) to obtain the reaction

$$Fe(s) + Cu_2O(s) \longrightarrow FeO(s) + 2Cu(c_l)$$

$\Delta F^\circ_{1398} = -23{,}805$ cal.; $\Delta F^\circ_{1336} = -24{,}830$ cal.

Assuming the insolubility of ferrous oxide in molten copper and utilizing

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[5] Roberts and Smyth, THIS JOURNAL, **43,** 1061 (1921).

[6] Eastman, *ibid.*, **44,** 875 (1922).

[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

the fact that at the eutectic temperature the activity of cuprous oxide becomes unity, the equilibria are expressed

$$\text{at } 1336^\circ\text{K. } a_{\text{Fe}} = 8 \times 10^{-5} \tag{3}$$

$$\text{at } 1398^\circ\text{K. } a_{\text{Fe}} \times a_{\text{Cu}_2\text{O}} = 19 \times 10^{-5} \tag{4}$$

Equation (4) defines a curve, abc, in Fig. 1 which limits the composition of the ternary alloys which can exist at 1125°. Alloys of composition *M* react to eliminate FeO and arrive at the composition *R*, with very small oxygen content. Alloys of composition *N* react similarly to reach *S*, the equilibrium composition containing little residual iron.

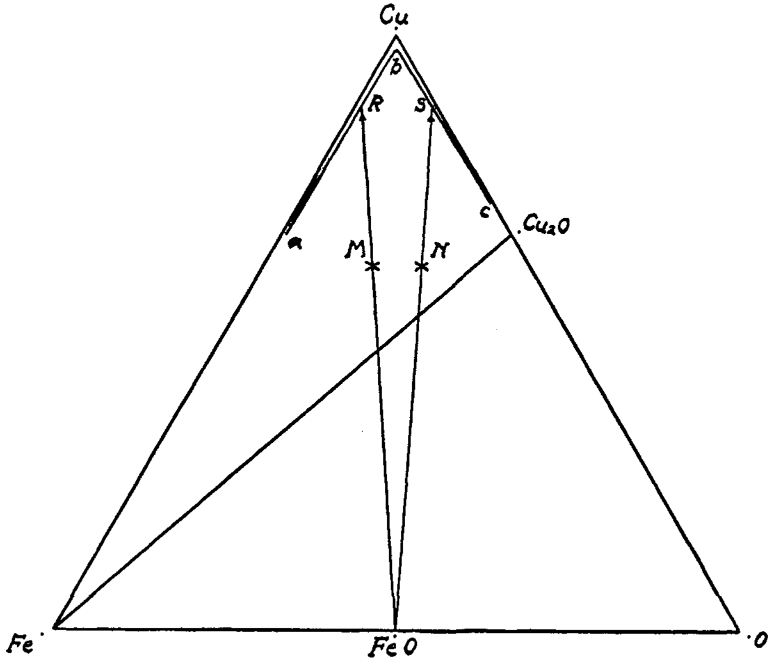

Fig. 1.

Equation (3) defines a line of constant activity, such as TU in Fig. 2, which at 1063° divides the ternary diagram into two areas. Within TUV, iron and eutectic cuprous oxide react, forming ferrous oxide until the iron is reduced to the equilibrium activity 8×10^{-5} or the cuprous oxide phase is consumed. Only within the small area TUWZ can iron and cuprous oxide pass through the eutectic temperature without reacting.

In the absence of data relating the activity of iron and cuprous oxide in copper solutions to the mole fractions, these equilibrium concentrations cannot be calculated. We know, however, that these solutes exhibit quite low solubility in copper. The iron activity in such case doubtless exceeds its mole fraction. The line TU lies, therefore, at or less than 0.008% of iron.

This indicates the presence of indefinite amounts of ferrous oxide in Addicks' and Hanson's alloys. The application of their data to the conductivity of the system copper-iron is thus open to objection.

The present work is planned to take the effect of oxygen into consideration. The alloys are based upon the ternary system copper-iron-oxygen. The copper-rich alloys of the binary systems copper-iron and copper-oxygen are measured. The ternary alloys are then investigated and the lines abc and TU located.

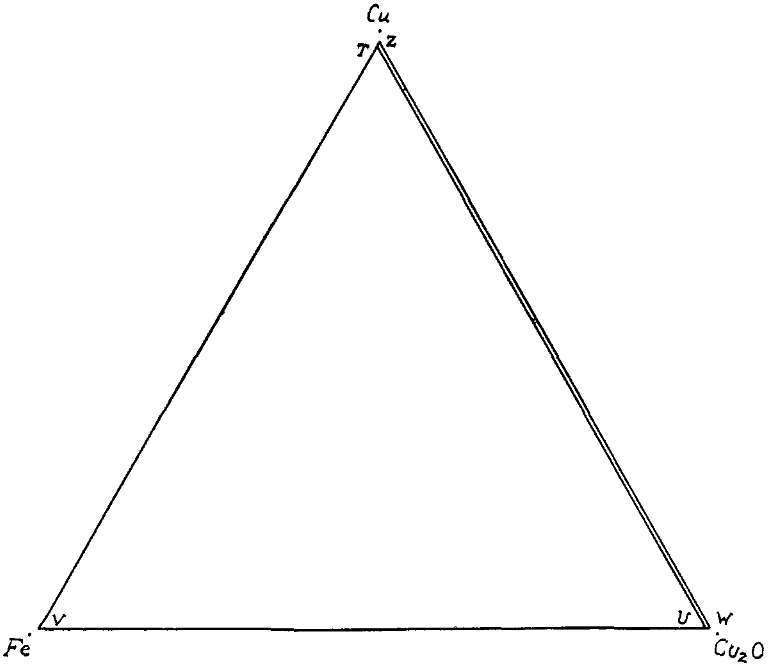

Fig. 2.

Experimental

Pure copper for the alloys was prepared by two successive electrolytic depositions of the metal. Pure electrolyte free of metallic impurities was used in the final deposition. The cathodes analyzed: Ag, 0.0003%; As, 0.0000%; Sb, 0.0001%; Bi, 0.0000%; Fe, 0.0001%; Co, 0.0000%; Ni, 0.0001%; Zn, 0.0000%; Pb, 0.0000%; S, 0.0004%; Se + Te, 0.0000%.

The melts were prepared in a platinum resistance furnace having a vertical heating chamber 12 inches high and 3 inches in diameter. The furnace was evacuated and filled with dry, oxygen-free nitrogen. The system of crucibles and feeders used is shown in Fig. 3. For the binary series copper-iron, electrolytic iron chips to form the desired alloy were placed in the thimble (b). The feeder (a) contained 375 g. of copper and 300 g. of anhydrous barium chloride. Seven hours were required for making each melt, three and one-fourth hours for heating to 1125°, three-fourths of an hour at that temperature and four hours for slow cooling. Practically all the cuprous oxide was removed from the liquid metal by the solvent action of the molten barium chloride.

The solidified melts were sampled for metallographic specimens and forged hot to a $^5/_8$-inch octagon section. Scale and surface defects were removed by machining to $^9/_{16}$-inch diameter, whereupon the samples were annealed to 950° for fifty hours in carbon dioxide and cooled slowly to equalize any cored structure present in the original dendrites. The forgings were then drawn cold to 12 gage (0.080 inch diameter) wire and annealed at 500° by passing an electric current through the wire. The conductivity was measured at 20° with an accuracy of 0.1%, using the standard bridge; 0.15328 ohms per meter gram was considered 100% conductivity.

Chemical analyses for copper, oxygen, sulfur and iron were made on each melt. Copper was determined on turnings removed from the cast piece. Two 10g. electrolytic assays were made, checking within 0.003%. Oxygen and sulfur were determined by ignition in hydrogen at 900° to convert these elements to water and hydrogen sulfide.[8] The sulfide evolved was absorbed in ammoniacal cadmium chloride solution and evaluated by iodine titration. The loss in weight of the sample upon this ignition was attributed to oxygen and sulfur. Knowing the sulfur value, oxygen was determined by difference.

Sixty g. of wire samples from the conductivity measurements were used in this analysis. After cleaning the metal surface, as recommended, with abrasive, dilute alcoholic potassium hydrate, dilute potassium cyanide, distilled water, alcohol and ether, there was no assurance that upon drying at 80° the surface would be free of oxide or adsorbed substances. That adsorbed substances were present seemed proved when metal so prepared was ignited in carbon dioxide and lost 0.0008% in weight. Since all material volatile in carbon dioxide from within the copper had been removed by previous annealing at 950° for fifty hours, this loss must have been a surface effect. Upon further ignition in hydrogen at 900° for five hours, this piece lost 0.0006% as oxygen. Some of this might have been surface oxygen. To overcome these surface effects, a similar sample was given a rapid preliminary heating in hydrogen to 550°, held for three minutes and cooled rapidly. This freed the adsorbed material and removed surface oxygen. Upon further treatment at 900° for five hours, 0.0004% of oxygen was lost. From this the preliminary hydrogen heating was considered more satisfactory than ether drying and carbon dioxide ignition, where such small amounts of oxygen were involved. Iron was determined on the conductivity samples, after electrolytically removing the copper, by double precipitation with gaseous ammonia and weighing as ferric oxide.

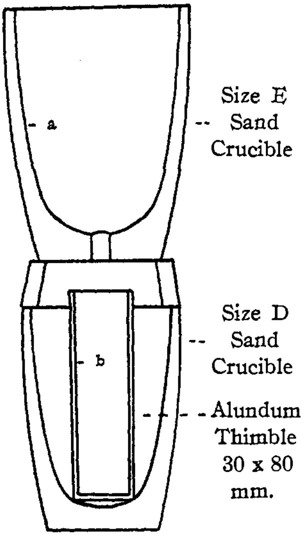

Fig. 3.—Crucible assembly.

It was found impossible to use the crucible assembly shown in Fig. 3 for making copper free of iron, due to a considerable "pick-up" of iron from the crucible. To overcome this, a silica tube ten inches long and seven-eighths of an inch inside diameter, sealed at one end, was substituted for the crucibles. Two hundred g. of copper and 75 g. of barium chloride were charged. The copper used was specially freed from sulfur

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[8] Bassett and Bedworth, *Trans. Am. Inst. Mining. Met. Eng.*, **73**, 784 (1926).

by ignition in hydrogen. The melt piped badly but sufficient metal for one conductivity measurement was obtained.

For the binary series copper-cuprous oxide, methods similar to those employed for the copper-iron series were used. The charge, of course, contained no iron addition and no barium chloride. The oxygen addition was made by allowing the desired amount of oxygen gas to be present in the nitrogen atmosphere of the furnace. No annealing of the forged pieces for fifty hours at 950° was required. In the oxygen determination, ether drying at 80° was used for the preparation of the sample.

For the ternary alloys, the methods of the copper-cuprous oxide series were adopted. A copper-iron alloy containing 2.2% of iron was used for the iron addition. The amount desired was charged in the feeder crucible.

Results

The data for the binary system copper-iron are assembled in Table I. Fig. 4 expresses the relation of conductivity to atomic per cent. of iron. The form of the curve is in accord with the general behavior of solid solutions as expressed by Guertler.[2] For comparison the data of

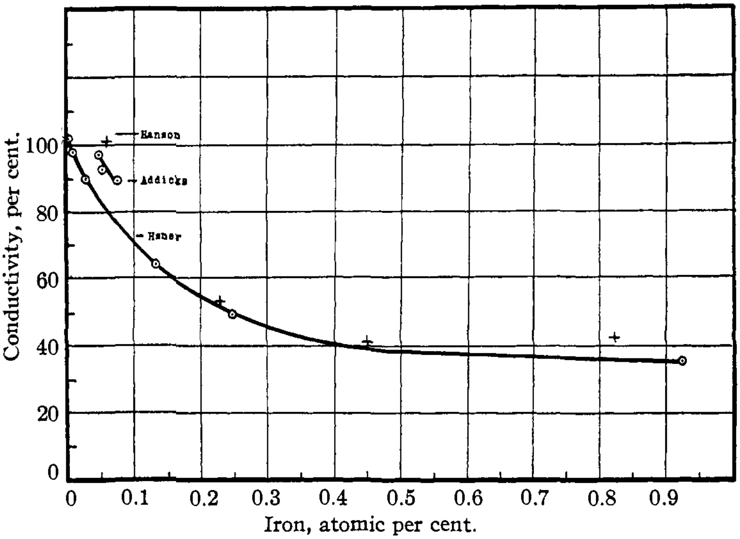

Fig. 4.—Effect of iron on conductivity of copper.

Table I

Data for Copper-Iron System

Melt no.	Copper, wt. %	Oxygen, wt. %	Sulfur, wt. %	Iron, wt. %	Iron, atomic %	Conductivity %
22	100.000	0.0002	0.0001	0.0002	0.0002	102.10
4	99.995	.0007	.0006	.0071	.0080	97.60
3	99.975	.0007	.0006	.0241	.0274	90.05
20	99.880	.0002	.0003	.1212	.1379	64.80
18	99.778	.0001	.0001	.2179	.2481	49.6
21	99.159	.0003	.0004	.814	.925	35.6

Addicks and Hanson are plotted. The displacement of their values at low iron concentration confirms the original premise of this paper that ferrous oxide is present in their alloys.

The effect of small additions of iron upon the conductivity is shown to be considerable. For the first 0.0071% of iron present, the conductivity is lowered 4.5%, a rate of 634% for 1% iron. This great depression tends toward agreement with Norbury's[9] generalization that solute elements far removed in the periodic system from the solvent metal cause the greater lowering in conductivity. Comparison, however, with Norbury's data for nickel solid solutions shows at once the more rapid lowering caused by iron. Norbury's idea seems to neglect the effect of the small solid solubility of iron.

The conductivity data confirm the expression of Hanson that the iron solid solubility at 750° is much less than the 3% originally reported by Ruer and Goerens.[10]

Hanson's suggestion that the solubility is less than 0.2% is not checked by the conductivity values. They seem to indicate between 0.3 and 0.4% as the limiting value.

Sample 22, the purest copper obtained in these experiments, had a conductivity of 102.1%. This can be compared with the values assembled by Wolff and Dellinger[11] for several samples of "pure" copper. Their highest value is 101.88%, obtained for electrolytic copper melted in a vacuum in an Acheson graphite crucible, drawn and tested as annealed wire. A piece of native Lake copper formed into wire without melting and tested in the annealed state yielded 101.87% conductivity. Their best value of several samples of electrolytic copper drawn to wire without melting and annealed is 101.60%. Meissner[12] observed 102.2% conductivity in a piece of electrolytically deposited wire which was carefully filed and ground to circular cross section and tested without drawing or annealing. This sample, however, cannot be regarded as statistically equivalent to the poly-crystalline aggregate obtained in wires which have been drawn and annealed. The electrolytic crystals may exhibit some preferred orientation and tend thereby to increase the conductivity toward the higher value of the copper single crystal.

The data for the binary system copper-cuprous oxide are assembled in Table II. The curve in Fig. 5 represents the relation of conductivity to volume per cent. of cuprous oxide calculated for a density of the oxide 6.0. Comparison is made to conductivity values calculated from the law of Le Chatelier, which requires that in systems whose components are

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[9] Norbury, *Trans. Faraday Soc.*, **16**, 570 (1921); *J. Inst. Metals*, **33**, 91 (1925).

[10] Ruer and Goerens, *Ferrum*, **14**, 49 (1917).

[11] Wolff and Dellinger, U. S. Bureau of Standards, *Sci. Paper*, **148**, 1910.

[12] Meissner, *Ann. Physik*, **47**, 1001 (1915).

insoluble in each other, the conductivity should be a linear function of the volume relationship. The observed conductivity is slightly lower than the calculated value, due to the occurrence of the cuprous oxide in the test wires as elongated, spherical globules. If the oxide were present as cylinders, extending in uniform cross section throughout the length of the wire sample, the calculated and observed values should coincide.

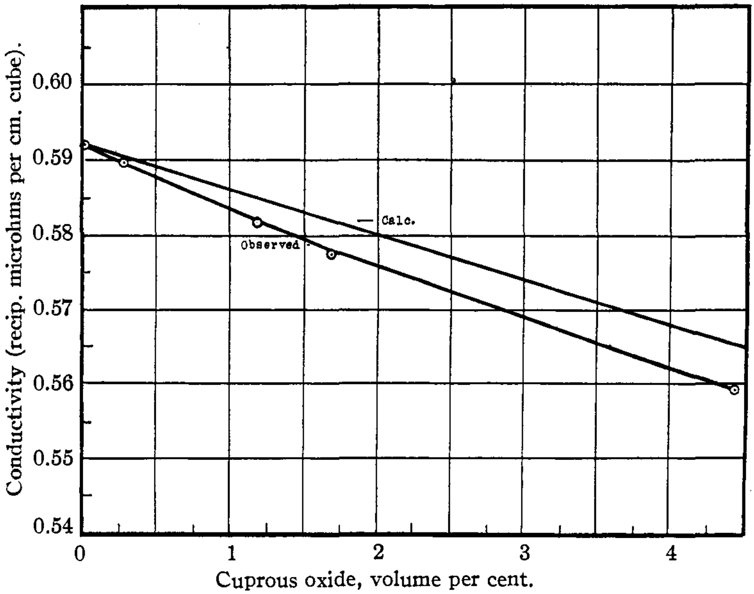

Fig. 5.—Effect of cuprous oxide on conductivity of copper.

TABLE II

DATA FOR BINARY SYSTEM COPPER-CUPROUS OXIDE

No.	Copper, wt. %	Oxygen, wt. %	Sulfur, wt. %	Iron, wt. %	Cuprous oxide Wt. % calcd.	Vol. % calcd.
22	100.00	0.0002	0.0001	0.0002	0.0018	0.003
7	99.980	.0201	.0002	.0003	.180	.267
6	99.912	.0889	.0004	.0003	.800	1.181
5	99.876	.1266	.0002	.0002	1.133	1.670
9	99.664	.3373	.0002	.0002	3.019	4.411

No.	Cond., %	Resistivity, ohms/meter-g.	Density calcd.	Cond. obs. recip. microhms per cm. cube	Cond. calcd. recip. microhms per cm. cube	Cond. obs. minus calcd. recip. microhms per cm. cube
22	102.1	0.15013	8.89	0.5921	0.5921	0.0000
7	101.8	.15057	8.881	.5898	.5905	− .0007
6	100.8	.15207	8.852	.5821	.5855	− .0034
5	100.25	.15292	8.834	.5777	.5822	− .0045
9	97.9	.15657	8.757	.5593	.5660	− .0067

In Fig. 6, the conductivity is plotted against weight per cent. of oxygen. Data of Hanson,[13] Antisell[14] and Addicks[3] are plotted for comparison. Antisell's figures seem to be the only ones capable of being reduced to a smooth curve. The curve indicated parallels closely the curve presented here, averaging perhaps 1.1% lower in conductivity. The lower conductivity is probably due to impurities other than oxygen in Antisell's metal.

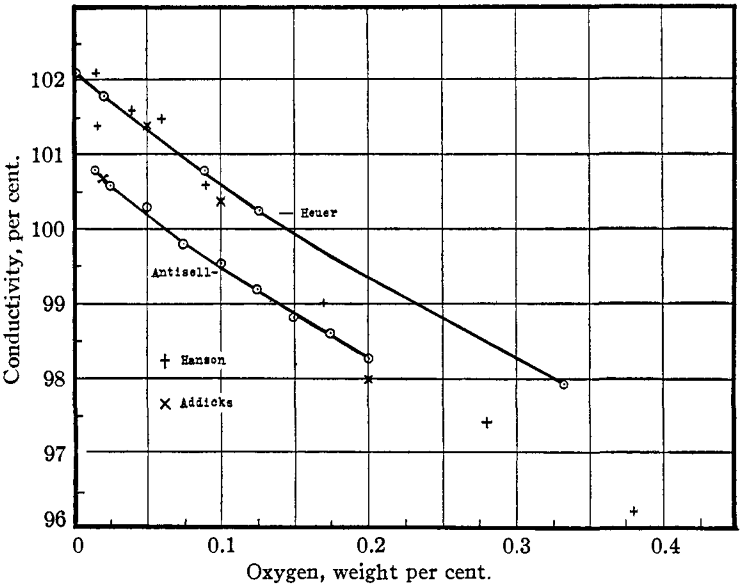

Fig. 6.—Effect of oxygen on conductivity of copper.

The data for the ternary melts are presented in Table III. The product mole fraction of iron × mole fraction of cuprous oxide of these melts evaluates the position of the equilibrium in the fused alloy, assuming that while cooling no further separation of ferrous oxide from the metal phase takes place. The line abc is sufficiently defined by the order of magnitude of this product. In the melts Nos. 14, 16 and 17, the close agreement is perhaps, fortuitous, as no such analytical accuracy is claimed.

Table III

Data for Ternary Melts

No.	Iron charged, %	Oxygen charged, %	Iron found, %	Oxygen found, %	Sulfur, %	Copper, %
14	0.13	0.02	0.0133	0.0035	0.0003	99.982
16	.11	.02	.0115	.0040	.0002	99.984
17	.05	.02	.0061	.0083	.0003	99.989
13	.10	.04	.0058	.0273	.0003	99.966

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[13] Hanson, *J. Inst. Metals*, **30**, 197 (1923).

[14] Antisell, *Trans. Am. Inst. Mining Met. Eng.*, **64**, 432 (1921).

TABLE III (*Concluded*)

No.	Mole fraction Fe × mole fraction Cu_2O	Cond. obs., %	Cond. calcd. from oxygen content (negl. Fe), %	Cond. lowering due to iron, %	Equiv. iron in solid sol., %	Micro-structure as cast
14	2.10×10^{-8}	101.80	102.05	0.25	0.0004	No eutectic
16	2.08×10^{-8}	101.85	102.05	.20	.0003	No eutectic
17	2.29×10^{-8}	102.0	102.0	.0	None	Copper plus eutectic
13	7.16×10^{-8}	101.85	101.7	− .15	None	Copper plus eutectic

The micro-structure of the alloys and the conductivity indicate the progress of the iron-copper oxide reaction at the eutectic temperature. Melts Nos. 14 and 16 contain copper, iron oxide and iron in solid solution of less than 0.0005%. No copper oxide eutectic remains. Melts Nos. 17 and 13 show residual copper oxide as eutectic. They contain iron in solid solution of the order of 0.0001%. These alloys indicate that the line TU is located on the diagram at such a low iron concentration as to practically coincide with the binary line of copper-oxygen. All alloys in the ternary system should react, therefore, at the eutectic temperature to form ferrous oxide. If the time be sufficient, the reaction will run either to complete oxidation of the iron or to the extinction of the cuprous oxide phase. Commercial copper containing the oxide eutectic should carry no iron in solid solution. The conductivity should be unaffected by the iron present.

The writer desires to express his appreciation of Dr. H. S. Lukens' kind interest in this work. To the U. S. Metals Refining Company and Mr. Sidney Rolle he is indebted for the conductivity measurements.

Summary

1. Thermodynamic calculations are advanced in this paper to question the validity of the existing data on the electrical conductivity of dilute solid solutions of iron in copper.

2. Revision of these data is made and iron is shown to reduce the conductivity of copper at the rate of 630% of the standard value for 1% iron.

3. The formation of ferrous oxide in alloys of copper, iron and oxygen is studied quantitatively. It is shown that iron can be completely oxidized in alloys containing cuprous oxide eutectic.

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