PHYSICO-CHEMICAL INVESTIGATIONS ON COPPER SMELTING

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Synopsis

Equilibria between liquid copper and CO-CO_2 gas mixtures, and effects of sulphur and tin on the equilibria were investigated. In result we could confirm: activity coefficients of dissolved oxygen in liquid copper are considerably diminished by oxygen itself and by sulphur. Tin has also the same but very slight effect.

Introduction

The activities of oxygen and sulphur are two of the most important thermodynamic quantities to explain copper smelting reactions. There have been published many investigations in regard to the chemical behaviors of sulphur in liquid copper, but no remarkable differences among their results. As for oxygen, there is, so far as we know, little literature, and there are so great discrepancies that the explanation can not be sought only in experimental errors.

In general, the obvious method for determining the activity of component in solution is to measure its vapor pressure and compare it with that of standard state. But this method can not be applied for oxygen in liquid copper by reason that partial pressure of oxygen is not high enough to measure when its concentration is low. Thus, the activity of oxygen has been determined by studies of chemical equilibrium between liquid copper and CO-CO_2 gas mixtures.

Present works are divided into three parts as follows:

Part I: Study of equilibrium between liquid copper and CO-CO_2 gas mixtures.

Part II: Study of equilibria between liquid copper and CO-CO_2-SO_2 gas mixtures. Such equilibrium reactions are very closely connected with the copper smelting process. It is furthermore interesting to compare these equilibrium relations with a number of data on the solubilities of sulphur dioxide in liquid copper.

Part III: Study of equilibrium between liquid copper containing tin and CO-CO_2 gas mixtures.

PART I. STUDY OF EQUILIBRIUM BETWEEN LIQUID COPPER AND CO-CO_2 GAS MIXTURES

The equilibrium between liquid copper and CO-CO_2 gas mixtures was studied by Giradi and Siebert[1] but with uncertain results in respect to the activity coefficient of dissolved oxygen in liquid copper. Allen and Hewitt[2] investigated the equilibrium between liquid copper and H_2-H_2O gas mixtures up to the high oxygen

content.   Their results may be considered to be unreliable for the value of equilibrium constant obtained.

The purpose of this work is to study the equilibrium relation between liquid copper and CO-CO₂ gas mixtures as well as the activity coefficient of oxygen dissolved in liquid copper.

Experiment

The method of attack was to melt pure copper, usually with an initial charge of copper-oxygen alloy, in alumina crucibles under a circulating atmosphere of CO and CO₂ in the reaction system, and hold it at a desired temperature until the equilibrium was established.   The experimental melts were sampled and subsequently analysed for oxygen.   The P_{CO_2}/P_{CO} ratio of the equilibrium gas mixtures was determined by gas analyses.   The equilibrium ratio for the reaction,

$$\underline{O}(\text{in } l - \text{Cu}) + \text{CO} = \text{CO}_2 \qquad\qquad\qquad \text{(I-1)}$$

is represented as ;

$$K_0' = \frac{P_{CO_2}}{P_{CO} \cdot [O\%]} \qquad\qquad\qquad \text{(I-2)}$$

Apparatus and Procedure

Fig. I-1 is a schematic diagram of the apparatus for the equilibrium reaction. Electrolytic copper (99.98% Cu) was weighed and charged, usually with an initial percentage of oxygen in the form of cupric oxide or oxygen-master alloy prepared by pre-melting under a nitrogen stream in alumina crucibles.   The charge of 45 g was held in alumina crucibles (A), with alumina covers (B) so as to avoid any spattering of bubbling melts.   The charge and crucible were then placed on alumina supports (D) at the bottom of silica tube (H).   The furnace was evacuated to 10^{-4} mm mercury at a temperature up to 600° C.   The carbon monoxide gas was prepared by dripping formic acid on hot sulphuric acid and purified by bubbling through a 30 pct aqueous solution of potassium hydroxide and dried by passing through phosphorus pentoxide.   The carbon dioxide gas was prepared by thermal decomposition of magnesium carbonate at 550° C in vacuum and dried by passing through phosphorus pentoxide.

The gas mixtures, of which P_{CO_2}/P_{CO} ratio was controlled so as to roughly equilibrate with an initial oxygen content in charge, were led into the reaction system. After these procedures were ready, the current was increased and the charge was brought quickly to the desired temperature.   The gas mixtures were circulated in the reaction system by the mercury circulation pump (N).   Thus the liquid metal was bubbled, the rate of gas flow being 100 to 150 ml per minute.   Using such a circulation method, following effects may be expected ; 1—uniformalizing the temperature and concentration of metals. 2—accelerating the reaction between metals and gas mixtures due to increasing of the contact area, and 3—saving the time for the equilibrium to be quickened by both approaches of the oxygen concentration in liquid metal and the oxygen potential of the gas mixtures.

At the end of experimental run, all the taps were shut, the reaction tube was cut off from reaction system at $(a\text{-}a)$, and the melt was then sucked up in the
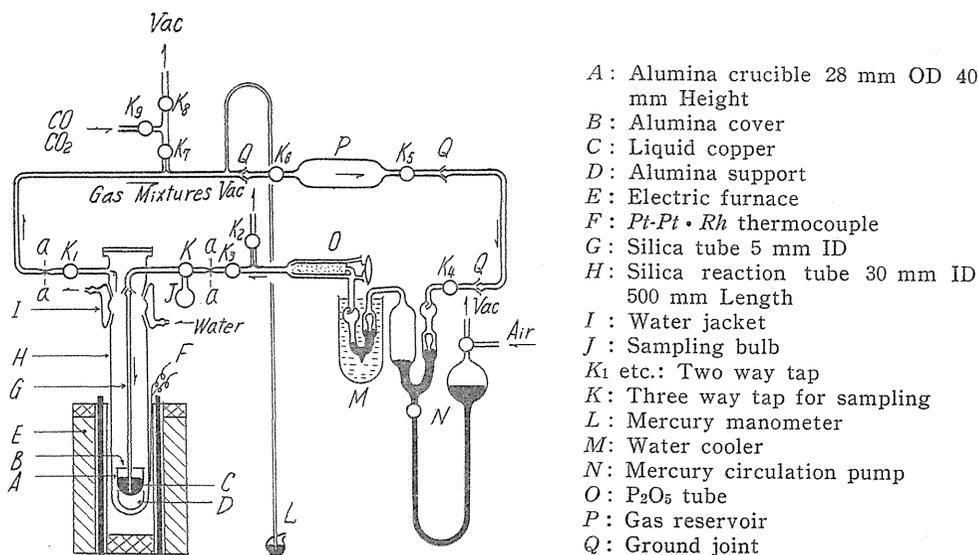
A : Alumina crucible 28 mm OD 40
    mm Height
B : Alumina cover
C : Liquid copper
D : Alumina support
E : Electric furnace
F : Pt-$Pt \cdot Rh$ thermocouple
G : Silica tube 5 mm ID
H : Silica reaction tube 30 mm ID
    500 mm Length
I : Water jacket
J : Sampling bulb
K_1 etc.: Two way tap
K : Three way tap for sampling
L : Mercury manometer
M : Water cooler
N : Mercury circulation pump
O : P_2O_5 tube
P : Gas reservoir
Q : Ground joint

FIG. I-1. Experimental apparatus for equilibrium reaction between liquid copper and CO-CO_2 gas mixtures.

central bubbling tube (G) by turning the three way tap (K) to sampling bulb (J). As soon as the melt was sampled, the reaction tube was quenched in water.   In this way, the satisfactory samples for oxygen analyses were taken.

Preliminary runs at 1,200° C indicated that a period of 2 hrs was sufficient for the establishment of the equilibrium from both directions of the reduction and oxidation.   In the equilibrium runs, the melts were held for the period of 3.5 hrs at 1,150° C, 3 hrs at 1,200° C and 2.5 hrs at 1,250° C, respectively.   The temperature of the melt was measured outside of the reaction tube with a Pt-$Pt \cdot Rh$ thermocouple.   It was checked frequently against a standard thermocouple immersed in the melt in the same condition as the experimental runs.   The furnace was held within $\pm 2°$ C of the desired temperature for all runs.   The temperature of most of the runs was much closer than the deviation mentioned above.

The water vapor based on the hydrogen released from the charge was eliminated by the phosphorus pentoxide tube (O).   The total pressure of gas mixtures in the reaction system was measured by the mercury manometer (L) which was served also as a safety trap.   The mercury vapor from the circulation pump was caught by a water cooler (M).

Gas Analyses

As the equilibrium gas composition was very low in CO, for example 0.1% CO, 99.9% CO_2, 'manometric method at fixed volume' was proved satisfactory for the present purpose.   The apparatus is shown in Fig. I-2.   The gas reservoir (P) with two taps and a ground joint was replaced to this apparatus from the reaction system in Fig. I-1.   After the apparatus was evacuated to 10^{-4} mm mercury, suitable quantities of gas mixtures were sampled in the bulb (A), next, liquid air baths (B), (F) and (H) were placed around the respective traps.   Then CO_2 in bulb (A) was condensed in the liquid air trap (B), uncondensable CO was oxidized to CO_2 with cupric

A : Gas sampling bulb
B, F, H : Liquid air trap
C, G : Mercury manometer
D : Oxidizing furnace with CuO
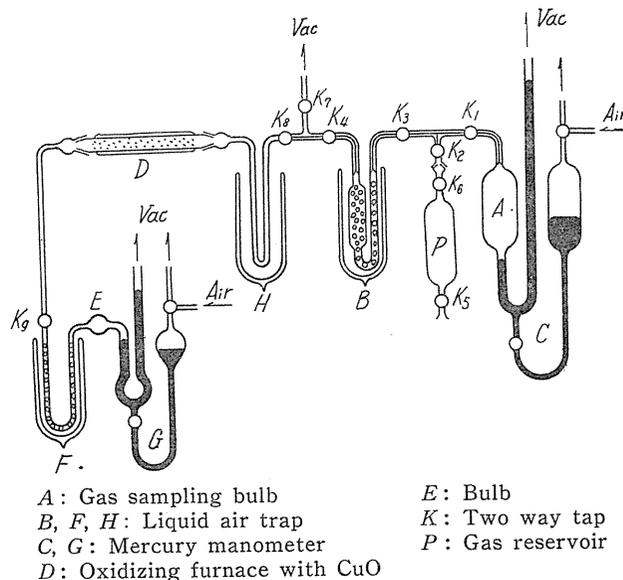
E : Bulb
K : Two way tap
P : Gas reservoir

FIG. I-2. Apparatus for gas analyses of CO-CO₂ gas mixtures.

oxide furnace and finally condensed in the trap (F).   After vaporizing, the pressures of CO_2 in the bulb (A) and CO_2 in the bulb (E) were measured, respectively. The volume of bulb (A) which comprised the spaces among taps (K_1), (K_2), (K_3) and (K_4), was approximately ten times that of bulb (E) which comprised the spaces from tap (K_9) to bulb (E), so that the accuracy of the pressure measurements of CO were ten times higher than that of CO_2.   By the careful tests, it was confirmed that the relative errors in the P_{CO_2}/P_{CO} ratio were estimated to within ± 1 pct over the entire range of gas compositions used in the present study.

Oxygen Analyses

Oxygen analyses were made by the hydrogen reduction method considerably improved.   Fig. I-3 is a schematic diagram of the apparatus.   The sample in the form of the solid rods 4 to 5 mm in diameter was thoroughly polished with an emery paper and cleaned with ether immediately before the determination.   The sample and boat were placed in the silica reduction tube (B).   Evacuating all the apparatus, the hydrogen gas was led to the reduction system.   After the liquid air bath (E) was fitted, the sample was heated to the reduction temperature, the hydrogen gas was circulated with the circulation pump (F), and resulting water vapor was condensed in the trap (E).   At the end of reduction, hydrogen was separated from condensed water by the evacuation and subsequently vaporized in bulb (H) with the known volume.   The volume of the water vapor V cc ($S.T.P.$) was determined by the measurement of its pressure, the weight of oxygen was computed as follows:

$$\text{grams of oxygen} = 0.000714 \times V$$

In Fig. I-3, a platinized asbestos furnace (D) was fitted with a view to mini-
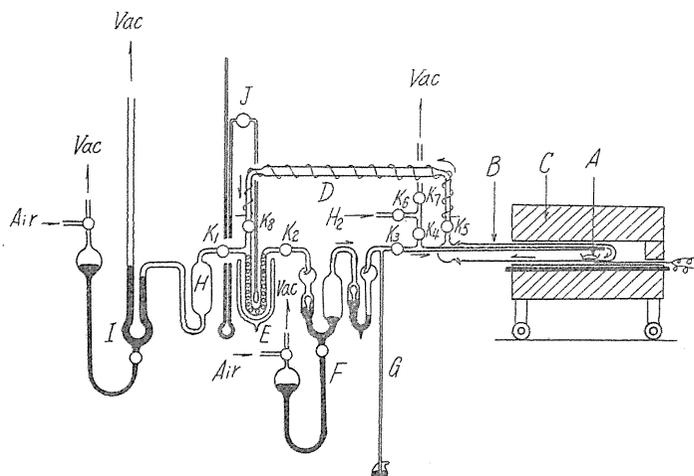
A : Sample
B : Silica reduction tube
C : Electric furnace
D : *Pt*-Asbestos furnace
E : Liquid air trap
F : Mercury circulation pump

G : Mercury manometer
H : Bulb
I : Mercury manometer
J : CO₂-Vapor pressure thermo-
    meter
K : Two way tap

FIG. I-3. Apparatus for oxygen analyses.

mizing an absorption of the water vapor with a glass wall and moreover to com-
pleting a reducing reaction of sulphur dioxide with hydrogen in the case of oxygen
determination of the samples containing sulphur from the equilibrium melts with
CO-CO_2-SO_2 gas mixtures. A vapor pressure thermometer with carbon dioxide (J)
was placed to measure the temperature at a petroleum ether trap where hydrogen
sulphide was separated from condensed water vapor.

In Table I-1 some results are compared by exchange of samples with various
methods. Results were reproducible to within about 0.0005 pct for very low oxygen
content and about 0.01 pct for very high content.

TABLE I-1. Oxygen Analyses by Various Methods

Method	Reduction temperature (°C) × time (min)	Analyses (%)		
		Sample-1	Sample-2	Sample-3
Present work	$1,050 \times 50 + 1,150 \times 50$	0.0488	0.0268	0.111
Vacuum fusion {A	$1,400 \times 15$	0.0485	—	—
{B	$1,760 \times 15$	—	0.0275	—
Al-reduction	$1,100 \times 60$	—	—	0.108

Experimental Results

Experimental runs were carried out at the temperatures of 1,155°, 1,206° and
1,256° C. The detailed studies were made at 1,206° C in order to determine the
effect of oxygen concentration on the equilibrium constant. Several runs were

TABLE I-2. Summarized Equilibrium Data

Run No.	P_{CO_2}/P_{CO}	[O%]	K'_O	Run No.	P_{CO_2}/P_{CO}	[O%]	K'_O
	1,206° C			53	822	0.403	2,040
				55	904	0.435	2,080
28	26.41	0.0120	2,200	57	825	0.487	1,690
41	26.52	0.0132	2,010	35	872	0.519	1,680
40	33.28	0.0151	2,200	58	832	0.531	1,570
48	36.72	0.0178	2,060	56	1,030	0.583	1,770
46[R]	43.25	0.0202	2,140	54	1,041	0.649	1,600
43	68.4	0.0303	2,260	70	1,080	0.759	1,420
45[R]	83.8	0.0389	2,150		1,155° C		
49	88.9	0.0403	2,210				
44	108.3	0.0488	2,220	59	36.78	0.0099	3,720
42[R]	244	0.111	2,200	61[R]	47.01	0.0140	3,360
47	240	0.119	2 020	60	67.6	0.0167	4,050
50	305	0.133	2,290	62[R]	70.9	0.0178	3,980
29	441	0.210	2,100	71	231	0.0562	4,110
51	441	0.212	2,080		1,256° C		
67	381	0.217	1,760				
31	466	0.254	1,830	65[R]	22.63	0.0172	1,320
52	620	0.295	2,100	64	20.27	0.0175	1,160
32	646	0.340	1,900	63	23.57	0.0182	1,300
68	732	0.366	2,000	66[R]	70.8	0.0604	1,170
69	677	0.398	1,700				

R: Start from higher oxygen content.

practised at 1,155° and 1,256° C at the levels of low oxygen concentration in order to establish the relation between equilibrium constant and temperature.

The equilibrium data are summarized in Table I-2. In this table, the runs marked R indicate the melts approached to equilibrium from the higher oxygen content than the oxygen potential corresponding to initial CO-CO₂ gas mixtures, and the remaining are the melts from the lower oxygen content. As may be seen in the column 4 of Table I-2, the equilibrium ratio $K'_O = P_{CO_2}/P_{CO} \cdot [O\%]$ is not a true constant but decreases with increasing oxygen content.

Fig. I-4 (*a*) shows the relation between the ratio P_{CO_2}/P_{CO} and oxygen content [O%] at three temperatures. A magnified view of this relation in low oxygen part is shown in Fig. I-4 (*b*). From the curvature of these lines, it is evident that the activity of oxygen is not proportional to its concentration. In Fig. I-4, also are included the results of Giradi and Siebert[1] and of Allen and Hewitt.[2]
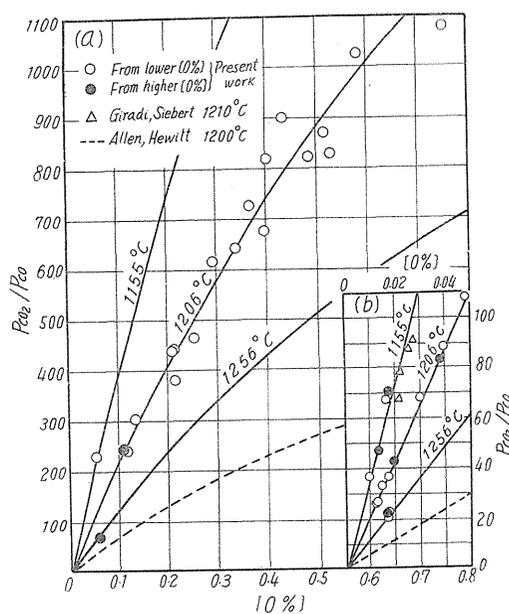

FIG. I-4. (*a*) Relation between P_{CO_2}/P_{CO} and oxygen content. (*b*) Magnification of low oxygen part.

In the study of Giradi and Siebert, the charge was melted without stirring. As oxygen in liquid copper solution is presumably regarded as a surface active element as well as sulphur,[3] it is always possible that the oxygen concentration of the surface of the equilibrium melts is somewhat higher than that of inner part. From this ground, it is expected that their results of the equilibrium ratio may be too high.

The marked discrepancy between the result of Allen and Hewitt and the present data is too great to be ascribed only to experimental errors and the explanation must be sought in another cause.

Effect of Carbon on the Activity of Oxygen

The data on the solubility of carbon in liquid copper that has been studied by a number of investigators, are not in considerable agreement. In the present work, dissolved carbon in the equilibrium melts has not determined, but it is possible that liquid copper contacted with CO-CO$_2$ gas mixtures dissolves the corresponding amounts of carbon to its potential of gas mixtures. The amounts of dissolved carbon may be calculated by considering thermal data together with the equilibrium measurement.

Taking that $P_{CO_2}/P_{CO} = 10$, $P_{CO} + P_{CO_2} = 1$ atm, and assuming that carbon solubility in liquid copper is 10^{-3} pct at $1,200°$ C, and further that a Cu-C solution obeys to Raoult's law, the amounts of dissolved carbon are roughly estimated as 10^{-8} pct. This value, of course, decreases with increasing the P_{CO_2}/P_{CO} ratio. It is hardly expected that such a minute amount of carbon has any effect on the activity of oxygen in liquid copper. Nevertheless, in the study of the solubility of sulphur dioxide in liquid copper, Floe and Chipman[4] found that the equilibrium relations are considerably affected by the traces of carbon. The investigation of this problem requires more sensitive techniques than have been available in the present work.

Thermodynamic Considerations

Determination of Equilibrium Constant and Oxygen Activity

The true equilibrium constant and oxygen activity are represented as,

$$K_O = \frac{P_{CO_2}}{P_{CO} \cdot a_O} \qquad (I\text{-}3)$$

$$a_O = f'_O \cdot [O\%] \qquad (I\text{-}4)$$

where the symbol f'_O designates the activity coefficient of oxygen in the binary Cu-O solution, the standard state for dissolved oxygen is defined as an infinitely dilute solution where the activity is equal to weight percentage. From the equations (I-2), (I-3) and (I-4), the following is given;

$$\log K'_O = \log K_O + \log f'_O \qquad (I\text{-}5)$$

Fig. I-5 shows the relation between $\log K'_O$ and oxygen content at three temperatures. The line at $1,206°$ C may be represented by the equation,

$$\log K'_O = 3.346 - 0.2105 \cdot [O\%] \qquad (I\text{-}6)$$

The first and second terms of the right side of this equation are equal to $\log K_O$

and $\log f'_O$ at $1{,}206°$ C, respectively. The relation between $\log f'_O$ and temperature can not be established from the present work. In general, the activity coefficient should be a function of temperature as well as composition in non-ideal solutions. Now assuming that $\log f'_O$ for a given oxygen content is proportional to a reciprocal of absolute temperature, the following is yielded;

$$\log f'_O = \frac{\varphi_O^O}{T} \cdot [O\%] \tag{I-7}$$

where φ_O^O corresponds to an interaction energy between oxygen atom pairs in liquid copper. Combination of the equation (I-7) with the value of $\log f'_O$ at $1{,}206°$ C yields $\varphi_O^O = -311.3$. The column 3 of Table I-3 gives $\log f'_O$ at various temperatures computed from the equation (I-7) and the value of φ_O^O.
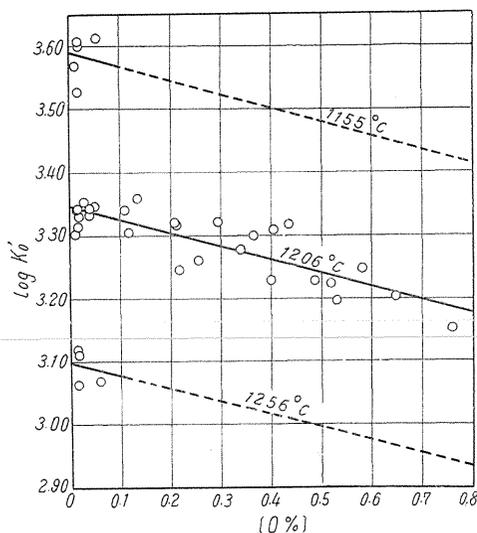
FIG. I-5. Relation between $\log K'_O$ and oxygen content.
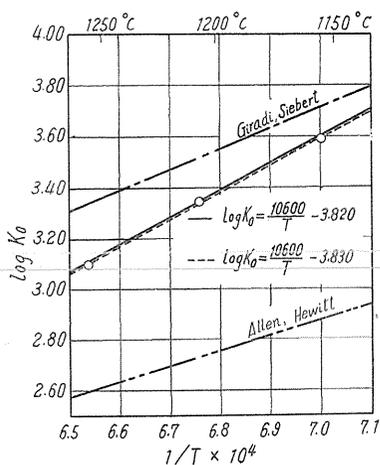
FIG. I-6. Relation between $\log K_O$ and reciprocal of absolute temperature.

TABLE I-3. Determined Values of $\log f'_O$ and $\log K_O$ at Various Temperatures

Temperature ($°$ K)	φ_O^O	$\log f'_O = \dfrac{\varphi_O^O}{T}[O\%]$	$\log K_O$
1,428		$-0.2180 \cdot [O\%]$	3.589
1,479	-311.3	$-0.2105 \cdot [O\%]$	3.346
1,529		$-0.2036 \cdot [O\%]$	3.098

The values of $\log K_O$ at $1{,}155°$ C and $1{,}256°$ C can be determined from $\log K'_O$ and $\log f'_O$ at each temperature and concentration. These results are shown in the last column of Table I-3. The broken line in Fig. I-6 shows the crude relation between $\log K_O$ and a reciprocal of absolute temperature which is expressed by the following equation;

$$\log K_O = \frac{10,600}{T} - 3.830 \tag{I-8}$$

As the value of $\log K_O$ at $1,206°$ C is more reliable than the others, it is preferable to adjust the equation (I-8) so as to conform to the value at $1,206°$ C, thus resulting equation is as follows:

$$\log K_O = \frac{10,600}{T} - 3.820 \tag{I-9}$$

The solid line in Fig. I-6 corresponds to the equation (I-9).

Also are included the results of Giradi and Siebert and of Allen and Hewitt. The former is given by apparent equilibrium constant, since their study has been made only in the limited range of low oxygen content and the true equilibrium constant can not be determined. The latter shows the equilibrium value converted from their data based on the equilibrium with H_2-H_2O gas mixtures. The present data seem to be between both results.

If the results by Allen and Hewitt are reliable, it must be considered that the discrepancy between both results may be due to the difference between both effects of hydrogen and carbon on the activity of oxygen in liquid copper. Their results, however, seem to be too low, considering the calculated value of partial pressure of oxygen on the liquid copper saturated with oxygen and considering the results of the statistical thermodynamical analyses on their equilibrium data by Yagihashi.[5] The more accurate investigations on this problem are needed in view of the elucidation of the effect of carbon on the activity of oxygen.

From above mentioned results, the following equilibrium relations are summarized:

$$\log K_O' = \frac{10,600}{T} - 3.820 - \frac{311.3}{T} \cdot [O\%] \tag{I-10}$$

$$\log a_O = \log [O\%] - \frac{311.3}{T} \cdot [O\%] \tag{I-11}$$

$$\log f_O' = - \frac{311.3}{T} \cdot [O\%] \tag{I-12}$$

The curves in Fig. I-4 which represents the experimental values at three temperatures have been drawn by using the equation (I-10). As shown in Fig. I-7, the equation (I-12) gives the relation between the activity and concentration of oxygen at three temperatures.

Estimation of Partial Pressure of Oxygen on Liquid Copper Saturated with Oxygen

The partial pressure of oxygen on the liquid copper can be estimated by combining the equation (I-10) with the
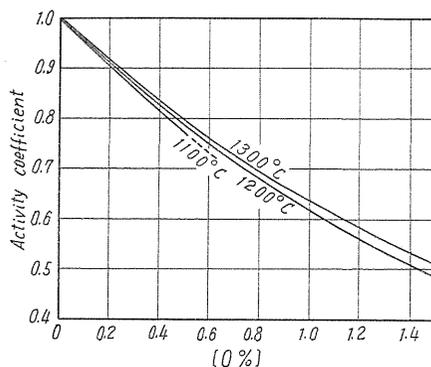

FIG. I-7. Relation between activity coefficient and concentration of oxygen in liquid copper.

thermal data. The equilibrium constant for the dissociation of carbon dioxide, i.e., $CO_2 = CO + 1/2\,O_2$, is calculated by the following equation;[6]

$$\log K = -\frac{14{,}550}{T} + 4.403 \tag{I-13}$$
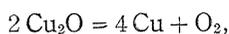
Combination of the equations (I-10) and (I-13) yields the following;

$$\underline{O}(\text{in } l-Cu) = \frac{1}{2}\,O_2,$$

$$\log \frac{P_{O_2}^{1/2}}{[O\%]} = -\frac{3{,}950}{T} + 0.584 - \frac{311.3}{T} \cdot [O\%] \tag{I-14}$$

TABLE I-4. Partial Pressure of Oxygen on Liquid
Copper Saturated with Oxygen

Temperature (°K)	Solubility of oxygen (%)	P_{O_2} (atm)
1,423	1.06	1.59×10^{-5}
1,473	1.50	3.28×10^{-5}
1,523	1.6	5.45×10^{-5}

Assuming that the equation (I-14) is available up to the solubility limit of oxygen, and using the solubility data of the equilibrium diagram by Hansen,[7] the partial pressures of oxygen on the liquid copper saturated with oxygen are estimated as shown in Table I-4. Fig. I-8 shows the comparison of these values with those of literature. The curve of Roberts and Smyth[8] is based on the experimental results. The value of Allen and Hewitt, which is far lower than the others, has been calculated from the equilibrium data of Cu-H_2-H_2O system. The curves of Lange,[9] Ruddle[10] and Kelley[11] are drawn respectively by using their equilibrium relations which have been calculated from thermal data. Accordingly the dissociation pressures have been computed from the following equation by assuming that $a_{Cu} = N_{Cu}$, $a_{Cu_2O} = 1$:

FIG. I-8. Relation between $\log P_{O_2}$ and reciprocal of absolute temperature.

$$2\,Cu_2O = 4\,Cu + O_2,$$

$$K = \frac{P_{O_2} \cdot a_{Cu}^4}{a_{Cu_2O}^2}$$

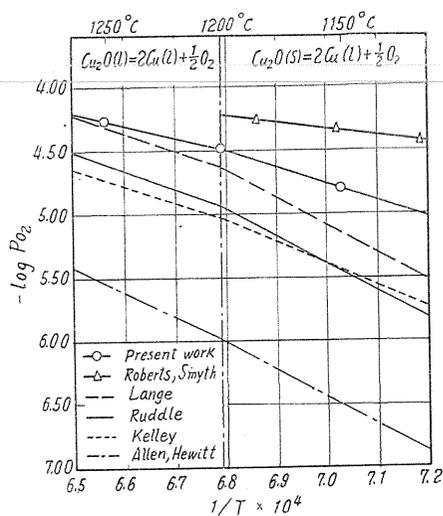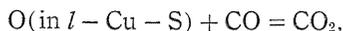The partial pressure of the present work can not be accepted with a high

reliability because of the far extrapolation to solubility limit and of the uncertainty of the solubility limit data. Nevertheless, the present data seem not to be far from the data of the literature.

PART II. STUDY OF EQUILIBRIA BETWEEN LIQUID COPPER AND CO-CO₂-SO₂ GAS MIXTURES
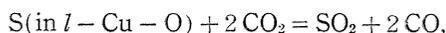
As previously stated, it was found that the solution of oxygen in liquid copper is non-ideal, but negative for Henry's law. Furthermore, it is significant and interesting in view of the underestanding of the fundamental copper smelting reactions to establish the activities of oxygen and sulphur in ternary Cu-O-S solution. According to several experimental results[12][13][14] on the equilibrium between liquid copper and H_2-H_2S gas mixtures, the solution of sulphur in copper is generally admitted as ideal. In the recent investigation by Yagihashi,[15] however, it was shown that this solution represents considerably negative deviation from Henry's law.

A number of investigations on the equilibrium between liquid copper and sulphur dioxide, for example those by Floe and Chipman[4] and by Johannsen and Kuxmann,[16] reached the general conclusion that the solubility of sulphur dioxide in liquid copper is out of proportion to a cube root of its pressure, namely, Sievert's law is not maintained between the both. From these results, it is to be expected that the solution of oxygen and sulphur in liquid copper may be non-ideal.
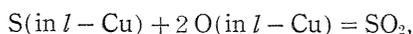
The purpose of the present work was to study the equilibria represented by the following relations;

$$\underline{O}(\text{in } l - Cu - S) + CO = CO_2,$$

$$K_O'' = \frac{P_{CO_2}}{P_{CO} \cdot [O\%]} \tag{II-1}$$

$$\underline{S}(\text{in } l - Cu - O) + 2 CO_2 = SO_2 + 2 CO,$$

$$K_S' = \frac{P_{SO_2} \cdot P_{CO}^2}{P_{CO_2}^2 \cdot [S\%]} \tag{II-2}$$

$$\underline{S}(\text{in } l - Cu) + 2 O(\text{in } l - Cu) = SO_2,$$

$$K_{O-s}' = \frac{P_{SO_2}}{[S\%] \cdot [O\%]^2} \tag{II-3}$$

Experiment

The method of attack was essentially the same as that previously described. The copper melts containing sulphur held in alumina crucibles were equilibrated with CO-CO₂-SO₂ gas mixtures at the desired temperature. The equilibrium melts were sampled and subsequently analysed for oxygen and sulphur. The compositions of the equilibrium gas mixtures were determined by gas analyses.

Possibility of Side Reaction in Equilibrium between Liquid Copper and CO-CO₂-SO₂ Gas Mixtures

When the gas mixtures consisted of CO, CO₂ and SO₂ is passed through the liquid metal or the reaction tube, the other species of gases may be formed by the

TABLE II-1. Limit of Formation of SO_3, SO, S_2, COS, CS_2

Product	Reaction	P_{SO_3}, $P_{CO_2}/P_{CO}=10$	
		1,200° C	800° C
SO_3	$SO_2+CO_2=SO_3+CO$	2×10^{-6}	6×10^{-9}
SO	$SO_2+CO=SO+CO_2$	3×10^{-2}	3×10^{-2}
S_2	$SO_2+2CO=\frac{1}{2}S_2+2CO_2$	$6\times10^{-1}\times P_{SO_2}$	$10^{5}\times P_{SO_2}$
COS	$SO_2+3CO=COS+2CO_2$	2×10^{-2}	10^{3}
CS_2	$2SO_2+6CO=CS_2+5CO_2$	$4\times10^{-5}\times P_{SO_2}$	$10^{3}\times P_{SO_2}$
CS	$SO_2+4CO=CS+3CO_2$	10^{-20}	4×10^{-23}
COS	$\frac{1}{2}S_2+CO=COS$	$2\times10^{-2}/\sqrt{P_{S_2}}$	$4\times10^{-1}/\sqrt{P_{S_2}}$
COS	$CS_2+CO_2=2COS$	$3/\sqrt{P_{CS_2}}$	$4/\sqrt{P_{CS_2}}$

side reaction. If any side reaction occurs, the equilibrium relations under consider-
ations do not hold good, hence it is necessary to check its possibility. In the case
of the existence of CO, CO_2 and SO_2, the formation of SO_3, SO, S_2, COS, CS and
CS_2 must be considered. Using the available thermal data, the limits of the for-
mation of these gases can be estimated as shown in Table II-1. Under the experi-
mental conditions, i.e., temperature 1,200° C, $P_{CO_2}/P_{CO} = 10 \sim 100$, $P_{SO_2} \leqq 0.01$ atm and
total pressure $= 1$ atm, the extent of the formation of every gas is less than $1/100$
of SO_2 or CO, and consequently considered to be neglegible in practice. As the
temperature falls, however, the quantities of S_2, COS and CS_2 should be considered.
Thus the composition of gas mixtures measured in a cold part comes to be quite
different from that of true equilibrium at the reaction temperature.

The comparison of stabilities among S_2, COS and CS_2 is also shown in the
lower part of Table II-1. In the experimental conditions that P_{SO_2} is less than 0.01
atm, both P_{S_2} and P_{CS_2} are naturally less than 0.01 atm. From the table, it is
therefore expected that the greater part of S_2 and CS_2 will be turned into COS with
decreasing temperature. Thus, if the side reaction may occur, it will do in the
part of lower temperature than that of melt, and resulting gas may be practically
COS. Accordingly, it is necessary to check at least the formation of COS in each
run of experiments, supposing that the side reaction may not proceed as calculated.

Charge

Suitable quantities of pure copper and sulphur-master alloy were weighed, and
placed in alumina crucibles. Sometimes it was convenient to add oxygen-master
alloy to usual charges. Sulphur-master alloy was prepared by pre-melting of pure
copper with cuprous sulphide in alumina crucibles under a nitrogen stream and
subsequently sampled in silica tubes 4 mm ID.

Equilibrium Measurements

In order to avoid any side reaction, sectional area of the gas passage from
melt to cold part was sufficiently reduced so as to maintain the rapid flow of the
equilibrium gas mixtures. Fig. II-1 shows three types of the reaction part. Appa-
ratus in Fig. II-1 (*a*), resembling to an original type, was unsuitable for a sampling

or CS by Reaction of SO_2 with $CO\text{-}CO_2$ Gas Mixtures

P_{SO}, P_{S_2}, P_{COS}, P_{CS_2} or P_{CS}/P_{SO_2}; total press $=1$ atm

	$P_{CO_2}/P_{CO}=100$		
400° C	1,200° C	800° C	400° C
3×10^{-14}	2×10^{-5}	6×10^{-8}	3×10^{-13}
2×10^{-2}	3×10^{-3}	3×10^{-3}	2×10^{-3}
$2\times10^{16}\times P_{SO_2}$	$6\times10^{-5}\times P_{SO_2}$	$10\times P_{SO_2}$	$2\times10^{12}\times P_{SO_2}$
3×10^{10}	2×10^{-5}	10^{-1}	3×10^{7}
$3\times10^{19}\times P_{SO_2}$	$4\times10^{-11}\times P_{SO_2}$	$10^{-3}\times P_{SO_2}$	$3\times10^{13}\times P_{SO_2}$
2×10^{-28}	10^{-24}	4×10^{-27}	2×10^{-32}

P_{COS}/P_{S_2} or P_{COS}/P_{CS_2}

$2\times10^{2}/\sqrt{P_{S_2}}$	$2\times10^{-3}/\sqrt{P_{S_2}}$	$4\times10^{-2}/\sqrt{P_{S_2}}$	$2\times10/\sqrt{P_{S_2}}$
$6/\sqrt{P_{CS_2}}$	$3/\sqrt{P_{CS_2}}$	$4/\sqrt{P_{CS_2}}$	$6/\sqrt{P_{CS_2}}$

A : Alumina crucible I : Gas outlet tube
B : Alumina cover J : Sampling bulb
C : Liquid copper K : Silica tube
D : Alumina support L : Liquid copper
G : Gas bubbling tube M: Silica vessel
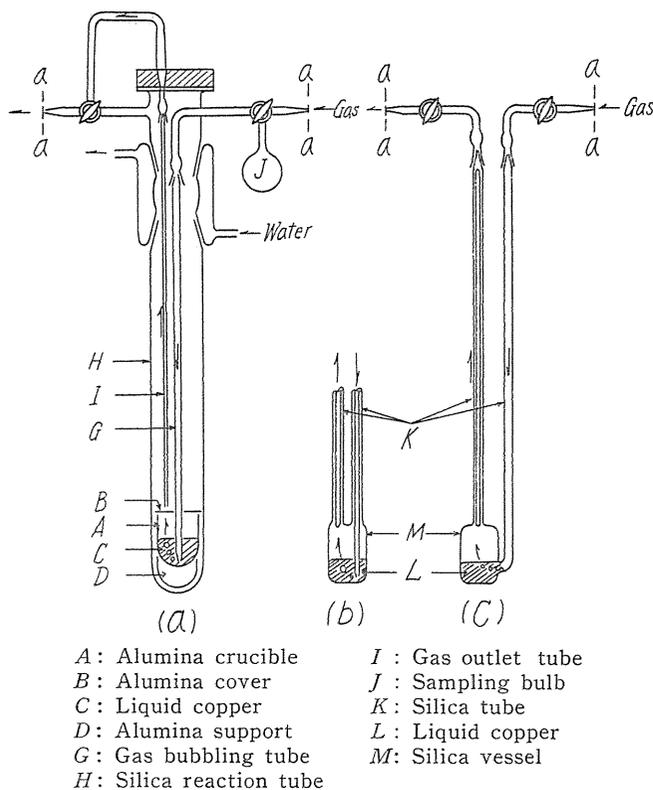H: Silica reaction tube

FIG. II-1. Apparatus of reaction part.

of equilibrium melts containing both oxygen and sulphur because they released sulphur dioxide from melts in a period of solidification. Then the reaction part in Fig. II-1 (b) or (c) was generally used. Connecting these parts with circulation system in Fig. I-1 at (a·a), the equilibrium reaction was carried out in the same

manner as previously described. After the attainment of equilibrium, two taps were shut, glass tubing was cut off at $(a\text{-}a)$, reaction part was then removed from furnace and immediately quenched in water. Thus the samples obtained were suitable for oxygen analyses. Preliminary tests at 1,200° C indicated that a period of 3 hrs was sufficient for the establishment of the equilibrium from both higher and lower oxygen content. In the equilibrium runs, the melts were held for 4 to 6 hrs at 1,200° C.

Gas Analyses

Equilibrium gas mixtures must be analysed for COS other than CO, CO_2 and SO_2. As the vapor pressure of COS[17] is a magnitude of 10^{-4} mm mercury at the temperature of liquid air, COS as well as CO_2 and SO_2, being evacuated to a vacuum of the order 10^{-3} mm mercury at this temperature, are to be separated from uncondensable CO. The separation of COS from SO_2 can be made by the differential method mentioned by Treadwell[18] as follows: while iodine in neutral solutions oxidizes only SO_2, bromine in alkaline solutions oxidizes both SO_2 and COS. Thus, the procedure of gas analyses is summarized in Fig. II-2.

Gas mixtures
| evacuating 10^{-3} mm
| through liquid air bath

CO CO_2, SO_2, COS
| oxidizing by | condensed in
| CuO furnace | liquid air trap,
CO_2 | vaporizing,
| condensed in | pressure measurement
| liquid air trap, | for fixed volume
| vaporizing, $P_2 \equiv CO_2 + SO_2 + COS$
| pressure measurement |
| for fixed volume | oxidizing with | oxidizing with
$P_1 \equiv CO$ | Iodine solution | Bromine solution $\rightarrow P_2 - P_4 \equiv CO_2$
                       H_2SO_4 H_2SO_4
                       $BaSO_4$ $BaSO_4$
                       $P_3 \equiv SO_2$ $P_4 \equiv SO_2 + COS$
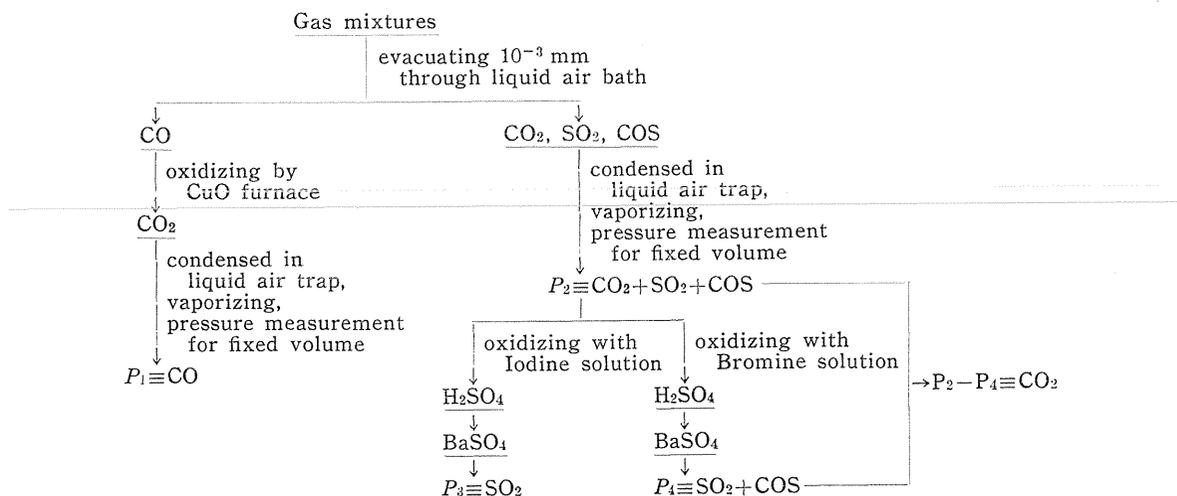
FIG II-2. Flow sheet of gas analyses.

The apparatus for gas analyses is shown in Fig. II-3. Evacuating all the apparatus, suitable quantities of gas mixtures were introduced in the sampling bulb (A) from gas reservoir (P). Liquid air baths (B), (H) and (F) were placed respectively around the traps. While CO_2, SO_2 and COS were condensed in the trap (B), uncondensable CO was pumped through (K_1), (K_3), (K_4), (K_7), oxidizing furnace (D) and (K_8), and finally condensed in the trap (F) as CO_2. Next, vaporizing each gas in the bulb (A) and (E), respectively, the pressure in the bulb (E) was measured by the mercury manometer (G) for a fixed volume, and converted to a corresponding value P_1 for the buld (A). Then, the pressure P_2 in the bulb (A) was also measured by the manometer (C). Next, the gas mixture in the bulb (A) were drawn through (K_1), (K_3), (K_4), (K_{10}) and condensed in the liquid air trap

A : Gas sampling bulb   E : Bulb
B, F, H, J : Liquid air trap   I : Absorption tube
C, G : Mercury manometer   K : Tap
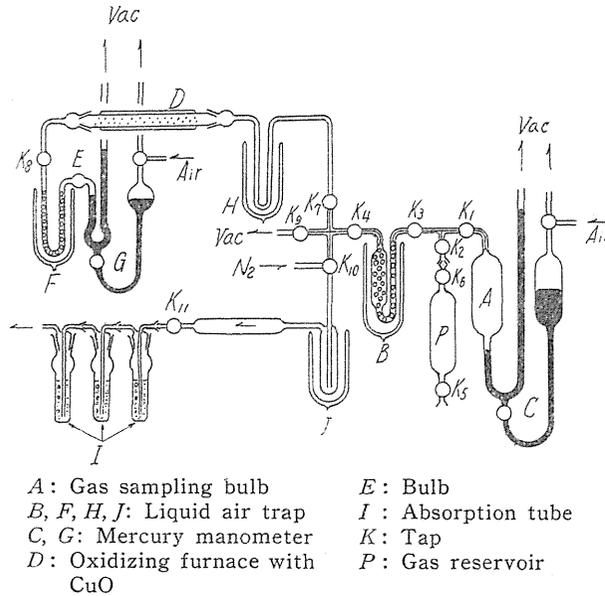D : Oxidizing furnace with   P : Gas reservoir
     CuO

FIG. II-3. Apparatus for gas analyses of CO-CO₂-SO₂(-COS) gas mixtures.

(J). After vaporizing, the gases were passed with a nitrogen stream from three-way tap (K_{10}) through three absorption tubes (I) which contained iodine solutions at first. Thus, SO_2 in gas mixtures was oxidized to sulphuric acid in absorption tubes and subsequently the pressure P_3 corresponding to the bulb (A) was determined. Secondary, the same quantities of gas mixtures as foregoing analyses were sampled in the bulb (A), P_1 and P_2 were determined in the same manner as mentioned above, then both COS and SO_2 were oxidized with bromine solutions and corresponding value P_4 was determined.

Now, let P be the total pressure which was measured in the equilibrium reaction, and the partial pressures of CO, CO_2, SO_2 and COS are determined respectively as follows :

$$P_{CO} = \frac{P_1}{P_1 + P_2} \cdot P, \qquad P_{CO_2} = \frac{P_2 - P_4}{P_1 + P_2} \cdot P,$$

$$P_{SO_2} = \frac{P_3}{P_1 + P_2} \cdot P, \qquad P_{COS} = \frac{P_4 - P_3}{P_1 + P_2} \cdot P$$

Furthermore, additional experiments were made for some gas mixtures which were low in CO and high in SO_2. Suitable amounts of these gases were sampled in the bulb (A), and then passed through (K_1), (K_3), (K_4), (K_{10}), (K_{11}) and the absorption tubes (I) with bromine solutions by passing nitrogen stream from the vacuum side of the manometer (C). Thus P_4 was determined. The difference between P_4 determined by such a procedure without liquid air baths and that by usual procedure, was found to be within experimental errors. It was therefore accepted that COS was fully condensed in the liquid air trap under the experimental

conditions used, and that presumably uncondensable SO had no existence in equilibrium gas mixtures.

Analyses of Oxygen and Sulphur

Oxygen analyses were made in the same principle as previously described. In the present case, however, not only water vapor but also hydrogen sulphide were formed by hydrogen reduction and both were condensed in the liquid air trap. The separation of hydrogen sulphide from water was carried out by replacing the liquid air bath to the petroleum ether bath $-105°$ C and subsequently evacuating hydrogen sulphide. While this procedure was confirmed to be sufficient for the quantitative separation by the preliminaly test, there was no comparison of analytical value with that of the vacuum fusion method which had some difficulties for oxygen analyses of the sample containing sulphur.

Sulphur in copper were determined by usual gravimetric method.

Experimental Results

Experimental runs were carried out only at 1,206° C. The equilibrium data are summarized in Table II-2. In this table, the runs marked R indicate the melts

TABLE II-2. Summarized Equilibrium Data at 1,206° C

Run No.	P_{CO_2}/P_{CO}	$P_{SO_2} \times 10^2$ (atm)	[O%]	[S%]	K''_O	$K'_S \times 10^5$	K'_{O-S}
4	51.3	0.996	0.0259	0.271	1,980	1.40	54.8
5	50.0	1.199	0.0259	0.314	1,930	1.53	56.9
6	60.2	2.301	0.0336	0.485	1,790	1.31	42.0
16	91.2	0.712	0.0422	0.054	2,160	1.59	74.0
17	84.3	0.594	0.0388	0.054	2,170	1.55	73.1
18	91.3	1.052	0.0427	0.075	2,140	1.68	77.0
24	44.50	0.637	0.0210	0.173	2,120	1.86	83.5
27	54.6	0.169	0.0238	0.029	2,290	1.96	103.0
28	47.02	0.111	0.0224	0.034	2,100	1.48	64.9
29	68.1	0.436	0.0334	0.043	2,040	2.19	90.8
30	59.3	0.573	0.0276	0.078	2,150	2.09	96.5
31	77.6	1.027	0.0369	0.075	2,100	2.27	100.6
32	64.3	1.204	0.0315	0.158	2,040	1.84	76.8
36	32.32	0.273	0.0160	0.096	2,020	2.72	111.0
41	43.72	0.829	0.0252	0.358	1,740	1.21	36.5
42	28.31	0.285	0.0141	0.155	2,010	2.30	92.5
43^R	50.6	0.902	0.0253	0.268	2,000	1.32	52.6
44^R	75.4	1.217	0.0366	0.149	2,060	1.44	61.0
46	15.91	0.317	0.0087	0.657	1,830	1.91	63.8
47	13.68	0.208	0.0091	1.141	1,500	0.98	22.0
48	25.25	0.335	0.0121	0.301	2,090	1.75	76.0
50	45.09	1.471	0.0275	0.617	1,640	1.17	31.5
51	15.67	0.335	0.0098	0.780	1,600	1.75	44.7
53	52.2	3.015	0.0301	0.614	1,730	1.80	54.2
54	53.7	2.137	0.0273	0.409	1,970	1.81	70.1
55	73.8	2.585	0.0357	0.235	2,070	2.02	86.3
57	17.07	0.349	0.0112	0.850	1,520	1.41	32.7
19*	35.36	1.223	—	0.761	—	1.29	—
25*	21.53	0.486	—	0.942	—	1.11	—
34*	47.15	3.124	—	1.051	—	1.34	—

R: Start from higher oxygen content.
* : Unsuitable sample for oxygen analyses.

approached to equilibrium from higher oxygen content, and the remaining are the melts from the lower oxygen content. The runs with asterisk were analysed only for sulphur because samples taken were unsuitable for oxygen analyses. The sulphur analyses of these runs seem to be somewhat reliable by reason that sulphur content is extremely higher than oxygen and consequently there are no appreciable losses of sulphur due to release of sulphur dioxide.

In all runs, it was confirmed by the differential gas analyses that there was no existence of COS under the experimental conditions used in this investigation.

As may be shown in the column 6 of Table II-2, the equilibrium ratio K_O'' for the reaction (II-1) is not a true constant. From Fig. II-4 which shows the relation between K_O'' and sulphur content, it may be seen that K_O'' decreases with increasing sulphur. Though K_O'' is, of course, affected by oxygen content as shown previously, the marked decline of the curve may be considered to be mainly due to influences of sulphur.
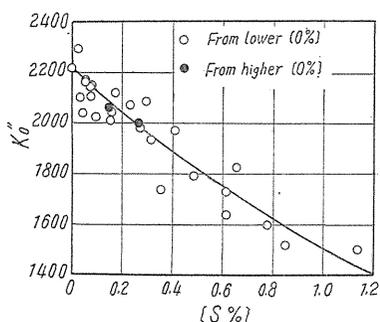
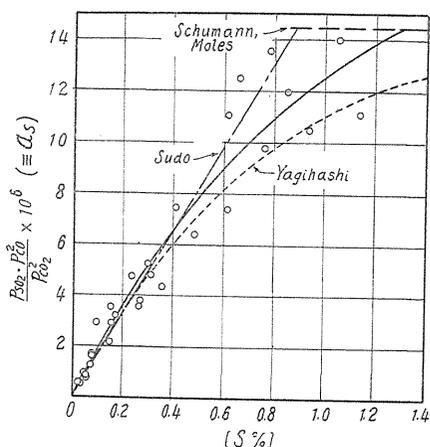FIG. II-4. Relation between K_O'' and sulphur content at 1,206° C.

FIG. II-5. Relation between $P_{CO}^2 \cdot P_{SO_2}/P_{CO_2}^2$ and sulphur content at 1,206° C.

From the column 7 of the table, it may be seen that equilibrium ratio K_S' for the reaction (II-2) is not a constant. Fig. II-5 shows the plot of the ratio $P_{CO}^2 \cdot P_{SO_2}/P_{CO_2}^2$, corresponding to the activity of sulphur in liquid copper, against sulphur content. Though the scattering of the points is large above 0.6 pct sulphur, it will be seen that the solution of sulphur in liquid copper is non-ideal but negative for Henry's law. The equilibrium $\underline{S}(\text{in } l - \text{Cu}) + H_2 = H_2S$ was investigated by many investigators. The equilibrium gas ratio P_{H_2S}/P_{H_2} can be converted to the present equilibrium gas ratio $P_{CO}^2 \cdot P_{SO_2}/P_{CO_2}^2$ by using the available thermal data. In Fig. II-5, also are shown the results converted from the equilibrium data by Sudo[13] and by Yagihashi[15] at 1,200° C. It is shown that three sets of plots are in good agreement within the range of 0.4 pct sulphur. For liquid copper in equilibrium with liquid cuprous sulphide, Schumann and Moles[19] have found P_{H_2S}/P_{H_2} ratio equal to 4.2×10^{-3} at 1,200° C. Accordingly to Fig. II-5, this should correspond to a maximum solubility of about 1.3 pct sulphur in liquid copper.

It must be noted that the comparison of the results based on the equilibrium data of Cu-H₂-H₂S system with the present data partly influenced by oxygen is not valid for detailed considerations.

Thermodynamic Considerations

The equilibrium relations for the reactions (II-1), (II-2) and (II-3) can be determined from the data in Table II-2 in the same manner as previously described.

$O + CO = CO_2$ *Equilibrium*

The equilibrium constant and oxygen activity for this reaction may be represented as follows:

$$K_O = \frac{P_{CO_2}}{P_{CO} \cdot a_O} \tag{II-4}$$

$$a_O = f'_O \cdot f^S_O \cdot [O\%] \tag{II-5}$$

where the symbol f'_O represents the activity coefficient of oxygen in binary Cu-O solution and the symbol f^S_O represents the ratio of the actual activity coefficient in ternary Cu-O-S solution to f'_O in binary solution. The standard state for oxygen is defined as an infinitely dilute solution, where activity is equal to weight percentage.

Combination of the equations (II-1), (II-4) and (II-5) gives the following;

$$\log K''_O - \log f'_O = \log K_O + \log f^S_O \tag{II-6}$$

From the equation (II-6), (I-12) which represents $\log f'_O$, and the values of K''_O in the column 6 of Table II-2, the plot of $\log K''_O - \log f'_O$ against sulphur content is given as shown in Fig. II-6. Extrapolated value of $\log K''_O - \log f'_O$ at zero sulphur content represents the constant $\log K_O$ and the slope corresponds to the value of $\log f^S_O/[S\%]$. Accordingly, these values at 1,206° C are as follows:

$$\log K_O = 3.345, \quad \log f^S_O = -0.1640 \cdot [S\%]$$

FIG. II-6. Relation between $\log K''_O - \log f'_O$ and sulphur content at 1,206° C.

There is a fairly good agreement between this value of $\log K_O$ and that from the equation (I-9), i.e., $\log K_O = 3.346$; it is quite possible, therefore, that the $\log K_O$-temperature relation for the reaction (II-1) is represented by the equation (I-9).

Next, assuming that $\log f^S_O$ for a given sulphur content is proportional to a reciprocal of absolute temperature, the following equation may be obtained;

$$\log f^S = -\frac{242.6}{T} \cdot [S\%] \tag{II-7}$$

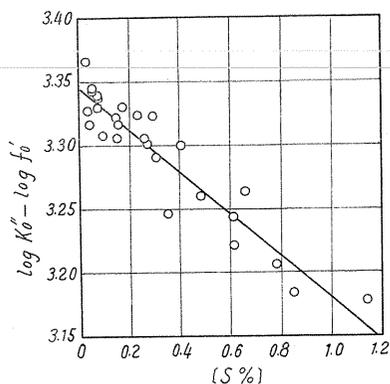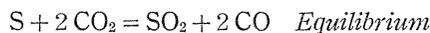Proper combinations among the equations (II-5), (II-6), (II-7), (I-9) and (I-13) yield the following equations:

$$\log K_0'' = \frac{10,600}{T} - 3.820 - \frac{311.3}{T} \cdot [\mathrm{O}\%] - \frac{242.6}{T} \cdot [\mathrm{S}\%] \qquad \text{(II-8)}$$

$$\log a_0 = \log [\mathrm{O}\%] - \frac{311.3}{T} \cdot [\mathrm{O}\%] - \frac{242.6}{T} \cdot [\mathrm{S}\%] \qquad \text{(II-9)}$$

$\mathrm{S} + 2\,\mathrm{CO_2} = \mathrm{SO_2} + 2\,\mathrm{CO}$ *Equilibrium*

The equilibrium constant and activity of sulphur for this reaction may be represented as follows:

$$K_\mathrm{S} = \frac{P_{\mathrm{SO_2}} \cdot P_{\mathrm{CO}}^2}{P_{\mathrm{CO_2}}^2 \cdot a_\mathrm{S}} \qquad \text{(II-10)}$$

$$a_\mathrm{S} = f_\mathrm{S}' \cdot f_\mathrm{S}^0 \cdot [\mathrm{S}\%] \qquad \text{(II-11)}$$

where f_S' represents the activity coefficient of sulphur in binary Cu-S solution. Interaction coefficient f_S^0 which represents the effect of oxygen on the activity coefficient of sulphur, can be calculated from the equation (II-7) by using a relation derived by Wagner,[20] which in this instance takes the form:

$$\frac{\partial \log f_\mathrm{S}}{\partial [\mathrm{O}\%]} = \frac{32}{16} \cdot \left(- \frac{242.6}{T} \right) \qquad \text{(II-12)}$$

which on integration gives,

$$\log f_\mathrm{S}^0 = \log f_\mathrm{S} - \log f_\mathrm{S}' = - \frac{485.2}{T} \cdot [\mathrm{O}\%] \qquad \text{(II-13)}$$

where f_S represents the actual activity coefficient of sulphur in ternary Cu-O-S solution.

From each value of $\log K_\mathrm{S}'$ and $\log f_\mathrm{S}^0$ in experimental data, the plot of the value $\log K_\mathrm{S}' - \log f_\mathrm{S}^0 = \log K_\mathrm{S} + \log f_\mathrm{S}'$ and sulphur content can be made as shown in Fig. II-7. Though the scattering of the points is large by reason that the experimental methods used in the present study are not suited for purpose of the determining sulphur activity, it will be seen that there is the downward tendency of the curve with increasing sulphur content. Assuming the curve to be linear, $\log K_\mathrm{S}$ and $\log f_\mathrm{S}'$ at 1,206° C may be determined as follows:

$$\log K_\mathrm{S} = - 4.709, \qquad \log f_\mathrm{S}' = - 0.1904 \cdot [\mathrm{S}\%]$$

The result by Yagihashi[15] is also shown in Fig. II-7. There is good agreement between both results. Assuming $\log f_\mathrm{S}'$ for a given sulphur content to be proportional to $1/T$, the following is derived,

$$\log f_\mathrm{S}' = - \frac{281.6}{T} \cdot [\mathrm{S}\%] \qquad \text{(II-14)}$$

The $\log K_\mathrm{S}$-temperature relation for the reaction (II-2) can not be established directly from the present results, but it may be calculated by considering other equilibrium data together with the present data. The equilibrium $\mathrm{S}(\mathrm{in}\ l-\mathrm{Cu}) + \mathrm{H_2} = \mathrm{H_2S}$ has been investigated by Umezu,[12] by Sudo,[13] by Hirakoso and Tanaka[14]
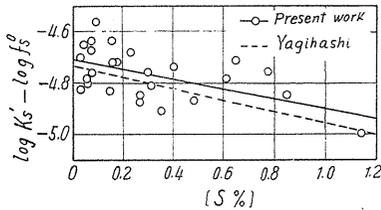
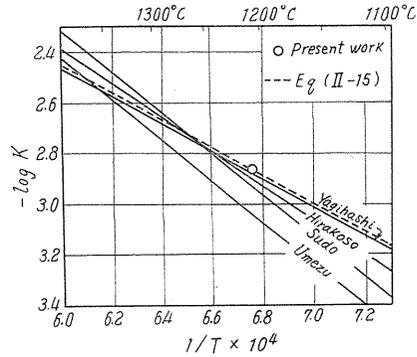FIG. II-7. Relation between $\log K'_S - \log f^O_S$ and sulphur content at 1,206° C.

FIG. II-8. Relation between $\log K$ and reciprocal of absolute temperature, $S(\text{in } l-\text{Cu}) = 1/2 \, S_2(g)$; $K = P^{1/2}_{S_2}/a_S$.

and by Yagihashi,[15] respectively. In Fig. II-8, the plots of $\log K = \log (P^{1/2}_{S_2}/a)$ against $1/T$ are summarized, and an open circle shows the result calculated from $\log K_S = -4.709$ and equilibrium data for the reactions, $1/2 \, S_2(g) + O_2 = SO_2$[21] and $CO + 1/2 \, O_2 = CO_2$.[6] As may be seen in Fig. II-8, there are some discrepancies among these results. Here, adopting the temperature function of $\log K$ of Yagihashi by reason that there is a good agreement between values of $\log f'_S$ and $\log K$ by authors and by Yagihashi, and furthermore adjusting this relation so as to conform to the value of $\log K$ of the present work, the following equation results;

$$S(\text{in } l - Cu) = \frac{1}{2} S_2(g),$$

$$\log K = \log \frac{P^{1/2}_{S_2}}{a_S} = -\frac{5,430}{T} + 0.815 \qquad (\text{II-15})$$

The broken line in Fig. II-8 is drawn by using the equation (II-15). Combining the equation (II-15) with thermal data for sulphur dioxide and carbon dioxide, the following equation is derived;

$$\log K_S = -\frac{15,600}{T} + 5.839 \qquad (\text{II-16})$$

Proper combinations among the equation (II-2), (II-10), (II-11), (II-13), (II-14) and (II-16) yield the following, which represent the equilibrium relation between sulphur in liquid copper and $CO-CO_2-SO_2$ gas mixtures, and the sulphur activity:

$$\log K'_S = -\frac{15,600}{T} + 5.839 - \frac{485.2}{T} \cdot [O\%] - \frac{281.6}{T} \cdot [S\%] \qquad (\text{II-17})$$

$$\log a_S = \log [S\%] - \frac{485.2}{T} \cdot [O\%] - \frac{281.6}{T} \cdot [S\%] \qquad (\text{II-18})$$

$\underline{S} + 2\,\underline{O} = SO_2$ *Equilibrium*

The $\log K_{O-S}$-temperature relation is derived by combination of the equation (I-9) and (II-16) as follows:

$$\log K_{O-S} = 2 \log K_0 + \log K_S = \frac{5,600}{T} - 1.801 \tag{II-19}$$

Introduction of the activities of oxygen and sulphur in ternary Cu-O-S solution into the equation (II-19) yields the following;

$$\log K'_{O-S} = \frac{5,600}{T} - 1.801 - \frac{1,107.8}{T} \cdot [O\%] - \frac{766.8}{T} \cdot [S\%] \tag{II-20}$$

In the absorption equilibrium of sulphur dioxide in pure liquid copper, as $[O\%]$ is equal to $[S\%]$, the following is derived;

$$\log K''_{O-S} = \frac{5,600}{T} - 1.801 - \frac{1,874.6}{T} \cdot [O\% \text{ or } S\%] \tag{II-21}$$

The equation (II-20) or (II-21) is empirical that derived from equilibrium data in the range, $P_{SO_2} < 0.03$ atm, $[O\%] = 0.01\text{-}0.04\%$ and $[S\%] = 0.03\text{-}1.1\%$; and it must be noted that equilibrium measurements have been made in the presence of CO-CO₂ gas mixtures.

It is interesting to compare these equations with other results which have been measured by a number of investigators. The relation between $\log K''_{O-S}$ and oxygen or sulphur content at 1,200° C is shown in Fig. II-9, in which the results of Floe and Chipman[4][22] and of Johannsen and Kuxmann[16] are included. As shown in Fig. II-9, the equation (II-21) agrees at low concentration with the result based on very recent experimental data of Johannsen and Kuxmann and agrees at high concentration with the later revised data of Floe and Chipman.[4] The latter considered that the abnormality of earlier data[22] at low concentration was due to the effect of the traces of carbon remained in liquid copper, and re-examined[4] similar equilibrium by using thoroughly decarburized copper. It is uncertain at this stage whether the discrepancy at low concentration between the equation (II-21) and later data of Floe and Chipman is due to the effect of carbon or not.
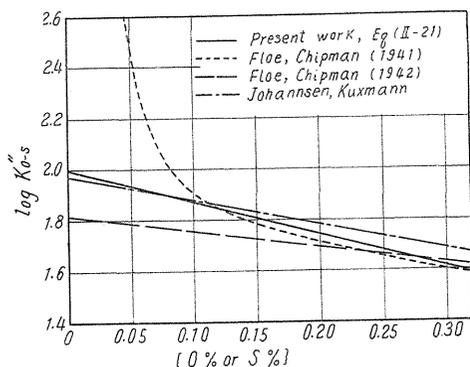

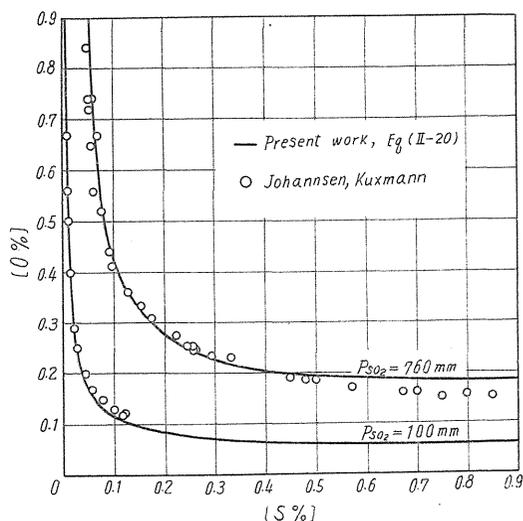FIG. II-9. Relation between $\log K''_{O-S}$ and oxygen or sulphur content.

FIG. II-10. Equilibrium relation between oxygen and sulphur in liquid copper at 1,150° C.

The equilibrium relation between oxygen and sulphur in liquid copper at 1,150° C is shown in Fig. II-10, in which the data of Johannsen and Kuxmann are also included. As may be seen in Fig. II-10, there is a fairly good agreement at low sulphur content. Some discrepancy above 0.4 pct sulphur at 1 atm sulphur dioxide is presumably ascribed to an uncertainty in the sulphur activity measurements at high concentration in the present work.

PART III. STUDY OF EQUILIBRIUM BETWEEN LIQUID COPPER CONTAINING TIN AND CO-CO₂ GAS MIXTURES

Although tin is one of the most important alloying elements in copper, there is, so far as we know, little literature to refer about the effect of tin on the chemical behaviors of oxygen in liquid copper. The purpose of this work is to study the equilibrium repersented the following reaction ;

$$\underline{O}(\text{in } l - \text{Sn}) + CO = CO_2,$$

$$K_0''' = \frac{P_{CO_2}}{P_{CO} \cdot [O\%]} \tag{III-1}$$
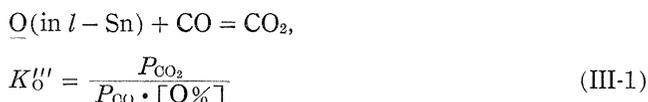
and furthermore to determine the activity of oxygen in ternary Cu-O-Sn solution.

Experiment

The experimental apparatus and procedure were the same as described in Part I. The Cu-Sn melts held in alumina crucibles, were equilibrated with CO-CO₂ gas mixtures circulated in the reaction system. After the attainment of equilibrium, the melts were sucked up in silica bubbling tubes and equilibrium gas mixtures were sampled in the gas reservoir, subsequently metals were analysed for oxygen and tin, and the ratio P_{CO_2}/P_{CO} were determined.

The charges consisted of pure electrolytic copper and tin-master alloy which had been pre-melted in alumina crucibles, sometimes, suitable amounts of cupric oxide were added to charges. It was confirmed by equilibrium runs from both higher and lower oxygen contents that a reaction period of 4 hrs was sufficient to establish the equilibrium. The reactions were carried out at the temperatures 1,155° C and 1,206° C, and in the range up to 10 pct tin, but the reaction at 1,250° C was omitted because of marked vaporization of tin. The gas mixtures were analysed in quite the same manner as described in part I. The oxygen analyses were made by the hydrogen reduction method as previously described, sometimes their results were checked by the vacuum fusion method. Tin in copper was determined by usual chemical analyses.

Experimental Results

Equilibrium data are summarized in Table III-1. The runs marked R represent the melts from higher oxygen content in initial charges, and the remaining are the melts from lower content. The runs marked S indicate the melts in the presence of oxide phases, where the equilibrium compositions of gas mixtures have constant values for given tin contents. Fig. III-1 shows the effect of tin on the

TABLE III-1. Summarized Equilibrium Data

Run No.	P_{CO_2}/P_{CO}	[O%]	[Sn%]	K_O'''
1,155° C				
107[S]	167.2	0.0406	1.97	4,120
108	135.3	0.0391	1.94	3,460
109	95.1	0.0260	4.94	3,660
110[S]	65.7	0.0193	9.35	3,400
111[S]	67.3	0.0204	9.35	3,300
112[S]	105.0	0.0271	5.04	3,870
113[S]	67.2	0.0190	9.83	3,540
114	230.7	0.0562	0.24	4,100
116	35.36	0.0088	5.27	4,020
117	32.73	0.0095	9.94	3,450
118	47.05	0.0114	5.04	4,130
134[R]	71.8	0.0196	7.63	3,660
135[R]	78.5	0.0229	5.09	3,430
1,206° C				
101	70.1	0.0327	1.97	2,140
102	56.1	0.0248	4.98	2,260
103	59.6	0.0284	9.98	2,100
104	116.9	0.0494	2.14	2,370
105	47.19	0.0244	5.05	1,930
120	52.1	0.0272	7.17	1,920
121[S]	107.7	0.0531	4.62	2,030
122	175.3	0.0845	1.61	2,070
123[S]	81.1	0.0406	6.90	2,000
124[S]	197.9	0.0956	1.41	2,070
125[S]	111.2	0.0521	4.22	2,130
126[S]	85.3	0.0420	6.95	2,030
127[S]	83.2	0.0402	6.78	2,070
128[S]	109.5	0.0532	4.16	2,060
129[S]	188.7	0.0869	1.51	2,170
131[R]	87.0	0.0391	6.19	2,220
132[R]	77.6	0.0418	7.16	1,860
133[R]	99.7	0.0540	4.75	1,850

R : Start from higher oxygen content.
S : Melt of oxygen saturation.

relation of the ratio P_{CO_2}/P_{CO} and oxygen content at 1,155° C and 1,206° C. From this illustration, it may be seen that the relation P_{CO_2}/P_{CO} − [O%] for each tin content is nearly linear, and for a given ratio P_{CO_2}/P_{CO}, oxygen content is slightly increased by tin, namely, activity of oxygen is diminished with increasing tin content. The limits of oxygen saturation are represented by broken lines, in the right field of which the oxide phases may appear.

FIG. III-1. Relation between P_{CO_2}/P_{CO} and oxygen content for various tin contents.

Thermodynamic Considerations

$\underline{O} + CO = CO_2$ *Equilibrium*
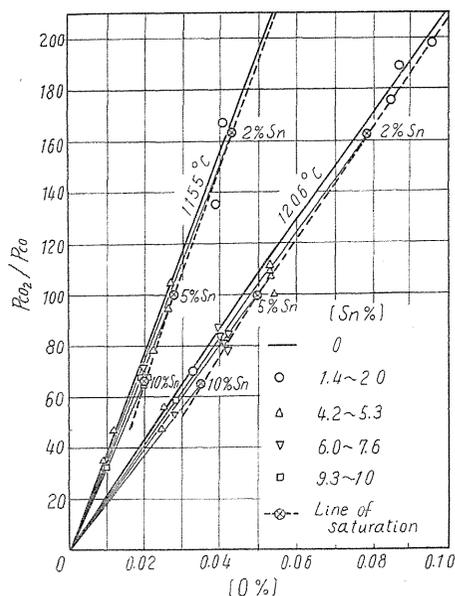
The equilibrium constant for the reaction (III-1) and the activity of oxygen in ternary Cu-O-Sn solution may be expressed as follows:

$$K_O = \frac{P_{CO_2}}{P_{CO} \cdot a_O} \tag{III-2}$$

$$a_O = f_O' \cdot f_O^{Sn} \cdot [O\%] \tag{III-3}$$

where the symbol f_O^{Sn} represents the interaction coefficient corresponding to the effect of tin on the activity of oxygen. Combination of the equation (III-1), (III-2) and (III-3) yields the following;

$$K_O''' = K_O \cdot f_O' \cdot f_O^{Sn} \tag{III-4}$$

Here, $\log f_O'$ has been found to be represented by the equation (I-12). From the values of K_O''' given in the column 5 of Table III-1 and $\log f_O'$ for each oxygen content, the values of $\log K_O''' - \log f_O' = \log K_O + \log f_O^{Sn}$ can be plotted against tin content at two temperatures as shown in Fig. III-2. From solid lines in Fig. III-2, $\log K_O$ and $\log f_O^{Sn}$ at two temperatures can be calculated as shown in the columns 2 and 4 of Table III-2, respectively.

The values of $\log K_O$ in the column 3 have been calculated from the equation (I-9). There is a good agreement between the results from the present work and from the equation (I-9), it is accordingly conceivable that the $\log K_O$-temperature relation may be represented by the equation (I-9).

Next, assuming $\log f_O^{Sn}$ for a given tin content to be proportional to $1/T$, the following is given;

$$\log f_O^{Sn} = \frac{\varphi_O^{Sn}}{T} \cdot [Sn\%] \tag{III-5}$$

FIG. III-2.   Relation between $\log K_O'''$ $-\log f_O'$ and tin content.

From the equation (III-5) and the values of $\log f_O^{Sn}$ in the column 4, the interaction parameter φ_O^{Sn} at two temperatures can be calculated as shown in the column 6.
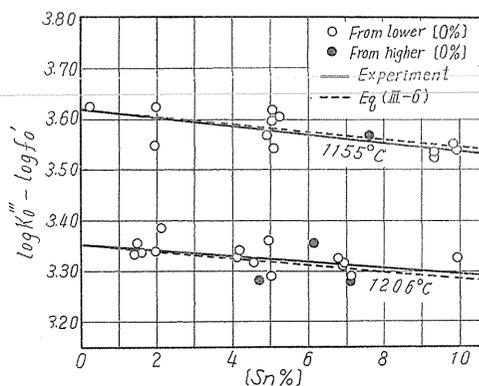
TABLE III-2.   Estimated Values of $\log K_O$ and $\log f_O^{Sn}$

Temperature ($^\circ$K)	$\log K_O$		$\log f_O^{Sn}/[Sn\%]$		φ_O^{Sn}	
	Present work	Eq. (I-9)	Present work	Eq. (III-6)	Present work	Average
1,428	3.618	3.603	−0.0078	−0.0067	−11.1	−9.6
1,479	3.352	3.346	−0.0055	−0.0065	− 8.1	

Some discrepancy between the results at 1,155° C and at 1,206° C may be ascribed to experimental errors. Thus, taking an average for both, i.e., $\varphi_O^{Sn} = -9.6$ as given in the last column, and combining it with the equation (III-5), the following is yielded;

$$\log f_O^{Sn} = -\frac{9.6}{T} \cdot [Sn\%] \qquad (III\text{-}6)$$

Two sets of broken lines in Fig. III-2 are represented by the equation (III-6).

Suitable combinations among the equations (III-3), (III-4), (III-6), (I-9) and (I-12) give the following equations;

$$\log K_O'' = \frac{10,600}{T} - 3.820 - \frac{311.3}{T} \cdot [O\%] - \frac{9.6}{T} \cdot [Sn\%] \qquad (III\text{-}7)$$

$$\log a_O = \log [O\%] - \frac{311.3}{T} \cdot [O\%] - \frac{9.6}{T} \cdot [Sn\%] \qquad (III\text{-}8)$$

The curves in Fig. III-1 which indicate the relation $P_{CO_2}/P_{CO} - [O\%]$ for each tin content have been drawn by the equation (III-7).

Deoxidation Equilibrium of Copper with Tin

As may be seen in Fig. III-1, the solubilities of oxygen in liquid copper alloy diminished with increasing tin. In the present work, the compositions of the oxide phases in equilibrium with Cu-Sn-O melts have not been established, it is therefore impossible to determine the accurate equilibrium relations for the deoxidation with tin. Now, in order to obtain approximate informations on the deoxidation equilibrium, taking the data on the compositions of liquid alloys in equilibrium with oxide phases, $\log [O\%]$ has been plotted against $\log [Sn\%]$ as shown in Fig. III-3. It may be seen that such plots give the two parallel lines, of which slope is approximately equal to $-1/2$. This indicates that the product $[Sn\%] \cdot [O\%]^2$ is approximately constant for tin content up to 10 pct. Table III-3 shows the values of apparent deoxidation constant K'_{Sn-O} at three temperatures. The value at 1,100° C
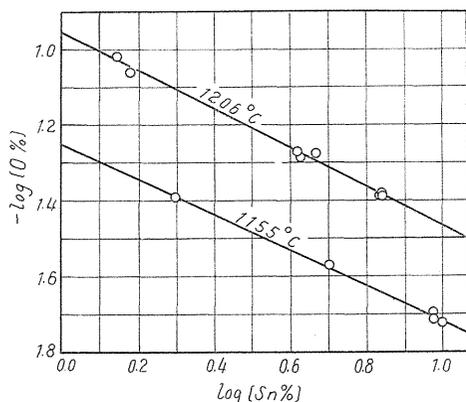

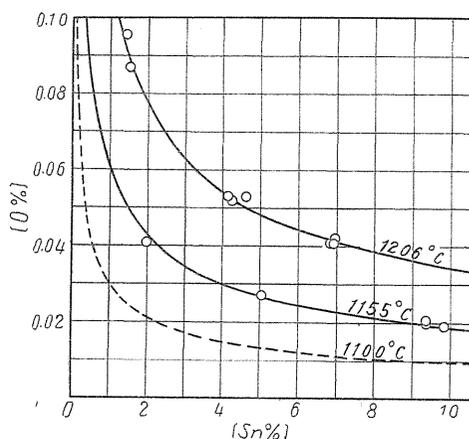FIG. III-3. Relation between log [O%] and log [Sn%] in oxygen saturated melts.

FIG. III-4. Equilibrium relation between oxygen and tin in liquid copper.

has been estimated from the data at other temperatures. Fig III-4 shows the relation between [O%] and [Sn%]. It is seen that experimental values may be fully expressed by these curves. The broken lines in Fig. III-1 have been drawn by such relations.

TABLE III-3. Estimated Values of K'_{Sn-O}

Temperature (°C)	$K'_{Sn-O} = [Sn\%] \cdot [O\%]^2$
1,100	0.0009
1,155	0.0036
1,206	0.012

In order to determine the true equilibrium constant for the deoxidation relations of liquid copper with tin, accurate data on the activity of tin in liquid copper and further detailed physico-chemical informations on the oxide phases composed of Cu_2O, SnO and SnO_2 are desired.

Conclusions

The equilibria between CO-CO_2 gas mixtures and liquid copper with and without sulphur or tin have been studied by the gas circulation method.

Equilibrium constant for the reaction,

$$\underline{O} + CO = CO_2$$

is represented as follows :

$$\log K_O = \log\left(\frac{P_{CO_2}}{P_{CO} \cdot a_O}\right) = \frac{10,600}{T} - 3.820$$

The activities of oxygen in binary Cu-O solution, ternary Cu-O-S solution and Cu-O-Sn solution are represented by the following relations, respectively ;

Cu-O solution : $\log a_O = \log[O\%] - \dfrac{311.3}{T} \cdot [O\%]$

Cu-O-S solution : $\log a_O = \log[O\%] - \dfrac{311.3}{T} \cdot [O\%] - \dfrac{242.6}{T} \cdot [S\%]$

Cu-O-Sn solution : $\log a_O = \log[O\%] - \dfrac{311.3}{T} \cdot [O\%] - \dfrac{9.6}{T} \cdot [Sn\%]$

Next, from the equilibrium measurements between liquid copper and CO-CO_2-SO_2 gas mixtures, the following relations are derived ;

$\underline{S} + 2CO_2 = SO_2 + 2CO,$
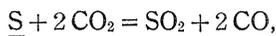
$\log K'_S = \log\left(\dfrac{P_{SO_2} \cdot P_{CO}^2}{P_{CO_2}^2 \cdot [S\%]}\right) = -\dfrac{15,600}{T} + 5.839 - \dfrac{485.2}{T} \cdot [O\%] - \dfrac{281.6}{T} \cdot [S\%]$

$\underline{S} + 2\underline{O} = SO_2$

$\log K'_{S-O} = \log\left(\dfrac{P_{SO_2}}{[S\%] \cdot [O\%]^2}\right) = \dfrac{5,600}{T} - 1.801 - \dfrac{1107.8}{T} \cdot [O\%] - \dfrac{766.8}{T} \cdot [S\%]$

Furthermore, apparent equilibrium constant for the deoxidation reaction of liquid copper with tin up to 10 pct is estimated as follows :

Temperature (°C)	$K'_{Sn-O} = [Sn\%] \cdot [O\%]^2$
1,155	0.0036
1,206	0.012

Further studies on the effects of the traces of carbon remained in copper are desired.

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