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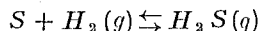
Physico-chemical Researches on Copper Metallurgy.

Report III: On the Equilibrium between Copper, Sulphur and Hydrogen in the [Sulphur-unsaturated] Region.

by Keinosuke HIRAKOSO, Tokiaki TANAKA
and Katsuya WATANABE.

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In order to establish some items essential information necessary for understanding copper pyrometallurgy, an experimental study has been made on the reaction of hydrogen with sulphur in molten copper at temperatures from 1145° to 1247°C.



The effect of temperature upon the equilibrium constant and the free energy change in the above reaction have been determined.

By combining the equilibrium measurements with the known free energy of hydrogen sulphide, the equilibrium sulphur pressure in molten copper is obtained.

It has long been recognized that sulphur plays a very important role in the copper smelting process. Especially in practice, various chemical reactions occurring when the material is in molten state must be considered. Therefore, if we would like to gain light on the mechanism of reactions occurring in the reverberatory furnace, the blast furnace and the converter, experimental work would be necessary to find the behaviour of sulphur.

However, most of the investigations on copper pyrometallurgical reactions have been made in relatively low temperature range and very little has been done in molten state.

Accordingly, the authors have made an experimental study in high temperatures on the equilibrium between hydrogen, sulphur and molten copper in sulphur-unsaturated region.

Materials, Apparatus and Procedure

Materials: The copper used was made by heating electrolytically refined copper at the temperatures of 1150°–1200°C in a current of hydrogen for about

two hours and removing all trace of oxygen. Cuprous sulphide used was prepared in the same manner as described in the previous report.¹⁾)

Bismuth sulphide which was used to prepare hydrogen and hydrogen sulphide gas mixtures was made as follows. Ten gr. of metallic bismuth and 2.5 gr. of sulphur powder that has been reprecipitated by carbon bisulphide were charged into a double bottomed Rose crucible and heated for about 20 minutes over a small flame.

After cooling and pulverizing, the above operation was repeated. Then, in order to drive off excess sulphur, it was charged in an alumina boat and reduced for about one hour at 300°C in a current of hydrogen.

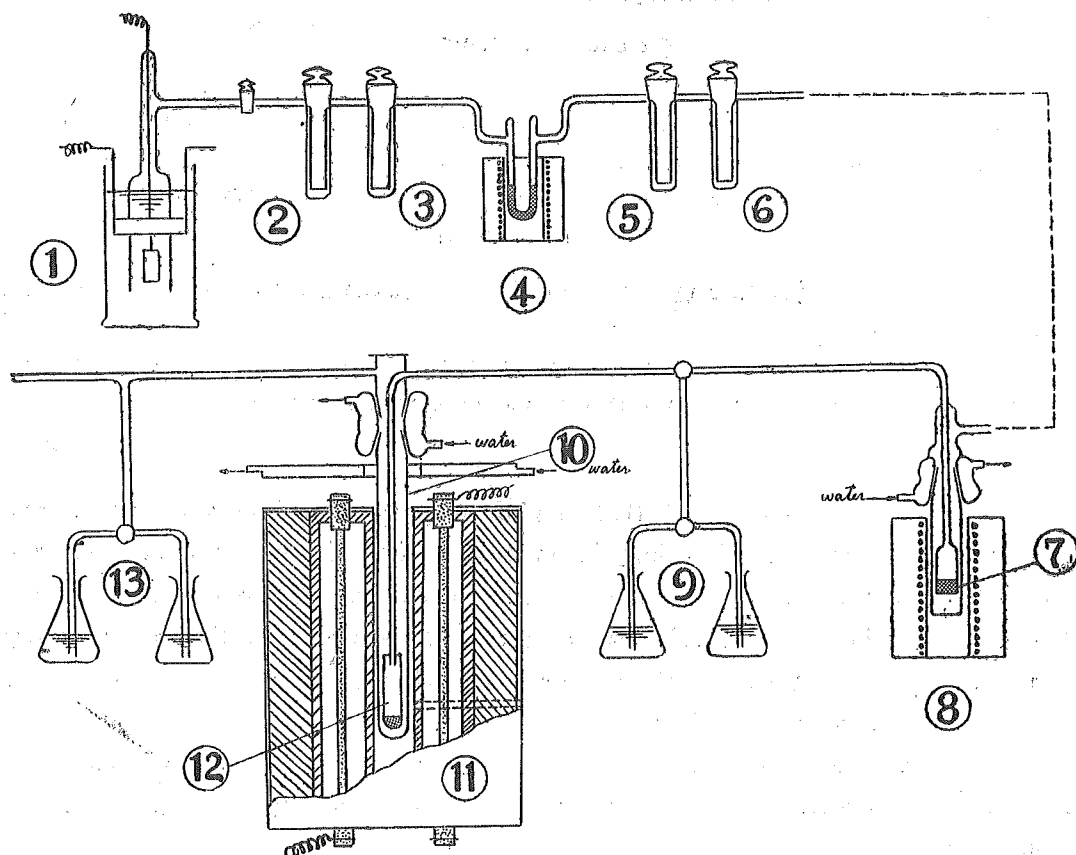


Fig. 1 Apparatus for the study of the equilibrium $S + H_2 \rightleftharpoons H_2S$

- | | |
|-------------------------|------------------------------|
| 1) Electrolytic cell. | 8) Bismuth sulphide furnace. |
| 2) KOH . | 9) Absorbent. |
| 3) P_2O_5 . | 10) Quartz tube. |
| 4) Platinized asbestos. | 11) Elema furnace. |
| 5) $CaCl_2$. | 12) Alumina crucible. |
| 6) P_2O_5 . | 13) Absorbent. |
| 7) Bismuth sulphide. | |

Apparatus: A schematic diagram of the apparatus is shown in fig. 1. Hydrogen

Judging from these microstructures, it was felt that the distribution of the $Cu-Cu_2S$ eutectic was very uniform in less than 10 gr., but increase of the melt weight over 10 gr. decreased the homogeneity of the sulphur distribution. Guided by the above results, the authors meteed 5 gr. of the alloy in each run.

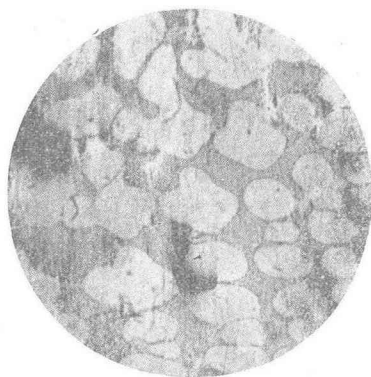


Photo. 3 (a) Tp.
Weight 2 gr, sulphur
content 0.3 %, temp
1196°C.



Photo. 3 (b) Centre.



Photo. 3 (c) Bottom.

Experimental results and Calculations

Runs were made at three different temperatures 1145°, 1196° and 1247°C. The results of these runs are recorded in tble 1. The hydrogen and hydrogen sulphide ratio in the outlet gas represents the composition just before the end of a run. Sulphur contents in the molten copper are given in weight per cent.

Fig. 2 shows the relationships of P_{H_2S}/P_{H_2} to weight per cent sulphur at 1145°C, 1196°C. and was plotted from the data in table. 1.

Table 1
Experimental Results

Inlet gas $\frac{P_{H_2S}}{P_{H_2}}$	Outlet gas $\frac{P_{H_2S}}{P_{H_2}}$	Sulphur wt. %	$\frac{P_{H_2S}}{P_{H_2} [S]} \%$
1145°C.			
$0.469 \cdot 10^{-3}$	$0.555 \cdot 10^{-3}$	0.110	$5.05 \cdot 10^{-3}$
$0.256 \cdot 10^{-3}$	$0.789 \cdot 10^{-3}$	0.180	$4.38 \cdot 10^{-3}$
$0.443 \cdot 10^{-3}$	$1.14 \cdot 10^{-3}$	0.264	$4.32 \cdot 10^{-3}$
$1.07 \cdot 10^{-3}$	$1.58 \cdot 10^{-3}$	0.364	$4.34 \cdot 10^{-3}$
$0.753 \cdot 10^{-3}$	$1.93 \cdot 10^{-3}$	0.427	$4.52 \cdot 10^{-3}$
1196°C.			
$0.360 \cdot 10^{-3}$	$0.355 \cdot 10^{-3}$	0.062	$5.73 \cdot 10^{-3}$
$0.452 \cdot 10^{-3}$	$0.546 \cdot 10^{-3}$	0.104	$5.25 \cdot 10^{-3}$
$1.00 \cdot 10^{-3}$	$1.05 \cdot 10^{-3}$	0.205	$5.12 \cdot 10^{-3}$
$1.40 \cdot 10^{-3}$	$1.43 \cdot 10^{-3}$	0.269	$5.32 \cdot 10^{-3}$
$1.93 \cdot 10^{-3}$	$2.09 \cdot 10^{-3}$	0.400	$5.23 \cdot 10^{-3}$
$2.05 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$	0.458	$4.91 \cdot 10^{-3}$
1247°C.			
$0.341 \cdot 10^{-3}$	$0.402 \cdot 10^{-3}$	0.051	$7.88 \cdot 10^{-3}$
$0.616 \cdot 10^{-3}$	$0.632 \cdot 10^{-3}$	0.097	$6.52 \cdot 10^{-3}$
$1.12 \cdot 10^{-3}$	$1.12 \cdot 10^{-3}$	0.217	$5.16 \cdot 10^{-3}$
$1.49 \cdot 10^{-3}$	$1.56 \cdot 10^{-3}$	0.296	$5.27 \cdot 10^{-3}$
$.92 \cdot 10^{-3}$	$2.42 \cdot 10^{-3}$	0.425	$5.69 \cdot 10^{-3}$

When the experimental values of $\log K_p$ at each temperature are plotted against the reciprocal of the absolute temperature, a linear relation is found as shown in fig 3. The equation of this line can be calculated by the method of least squares. The result is represented by the following equation.

$$\log K_p = -2056/T - 0.899$$

$$\Delta F^\circ = 9398 + 4.11T$$

Table 2
Equilibrium constant in the reaction of $S + H_2 (g) \rightleftharpoons H_2S (g)$

Temp. °C.	$1/T \cdot 10^4$	$K = \frac{P_{H_2S}}{P_{H_2} [S]} \%$	$\log K$ (obs.)	$\log K$ (calc.)
1145	7.052	$4.44 \cdot 10^{-3}$	-2.353	-2.349
1196	6.807	$5.10 \cdot 10^{-3}$	-2.292	-2.299
1247	6.579	$5.55 \cdot 10^{-3}$	-2.256	-2.252

From this expression the values of $\log K_p$ (calc.) are calculated for comparison with the experimental data. They are listed in the last column in table 2.

gas was generated electrolytically from 30 per cent solution of potassium hydroxide with pure nickel electrodes. To avoid overheating the electrolyte was cooled by glass tube carrying cold water. The volume of the gas can be controlled by a rheostat and measured indirectly by an amperemeter. Hydrogen gas thus obtained contains a small percentage of oxygen. It was therefore dried thoroughly with caustic potassium and phosphoric pentoxide and passed over platinised asbestos at 300°C, then over calcium chloride and through P_2O_5 to remove the traces of water vapour. The purified and dried gas was then introduced into a bismuth sulphide furnace. The rate of gas flow through the bismuth furnace and its temperature can be readily adjusted to give the desired hydrogen sulphide content in the gas mixture.

In the present work the effect of thermal diffusion may cause considerable errors. Therefore in order to avoid this source of error, electrolytic current was limited to 4 A. at minimum.

Finally, the H_2S/H_2 gas mixture was introduced into a reaction tube. It was a quartz tube, 300 mm. long $\times$ 30mm. inside dia. with one end closed. This tube was suspended vertically in an Elema furnace. The crucible holding the melt was made of pure alumina.

The hydrogen sulphide in the outgoing gas was absorbed in a zinc acetate solution. The amount of hydrogen sulphide was determined by iodometric titration.

Procedure: In making a run, reduced copper and cuprous sulphide prepared by the above method were mixed and placed in a pure alumina crucible, which was inserted into the reaction tube. After the air in the reaction tube had been perfectly replaced by hydrogen, the bismuth sulphide furnace was heated. The gas mixture from this furnace was analysed and hydrogen sulphide content was adjusted properly by the temperature of the furnace and rate of gas flow. The composition of the gas from the bismuth furnace should be precisely constant during a run, but, the constancy was satisfactory. Hydrogen and hydrogen sulphide mixture obtained in this way was introduced into the reaction tube and then the Elema furnace was started. Temperature of the melt was measured with Pt-Pt Rh thermocouple calibrated at the melting points of silver and copper, and it was controlled within $\pm 2^\circ\text{C}$. during a run by an adjustable transformer. After bringing the melt to the desired temperature, melting was continued to 3 to 4 hrs. Analysis was made on the outgoing gas periodically and direction to equilibrium was estimated by comparison with the composition of ingoing gas. Finally, the melt was quenched to room temperature by lowering the furnace and the reaction tube was taken out into the air. The sulphur content of the melt was analysed by weighing the sulphur as barium sulphate.

In carrying out an experiment on the equilibrium between melt and gas by using resistance type electric furnace, the agitation of the melt is impossible. In such a case there arise various problems regarding the homogeneity of the melt. If the amount of the melt were too much, the time needed for attaining equilibrium would prolong and analytical error due to segregation would occur. For this reason, to determine the suitable amount of the melt we made microscopic observations on many samples. The representative results are shown in photos. 1 to 3.

In photos 1 and 2, the eutectic network of copper and cuprous sulphide outlines the original copper grains; its distribution is very uniform. Therefore, satisfactory equilibrium values will be expected in these amounts.

On the other hand, in photo 3 we see the remarkable development of dendritic crystals and inhomogeneity of sulphur distribution.

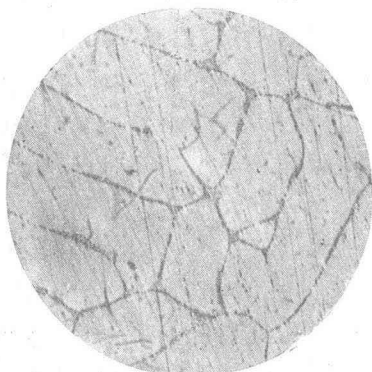


Photo. 1 (a) Outside.
Weight 5 gr, sulphur
content 0.1%, temp.
1145°C.

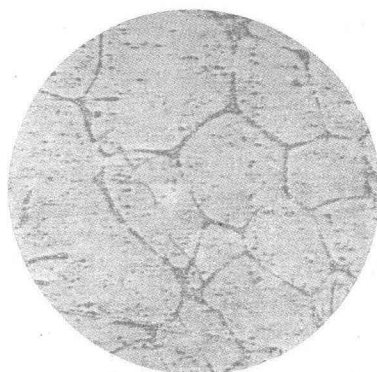


Photo. 1 (b) Inside.

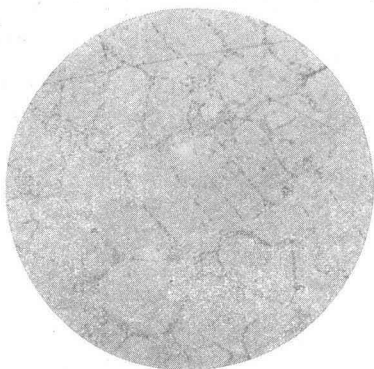


Photo. 2 (a) Outside.
Weight 10gr, sulphur
content 0.2%, temp.
1196°C.



Photo. 2 (b) Inside.

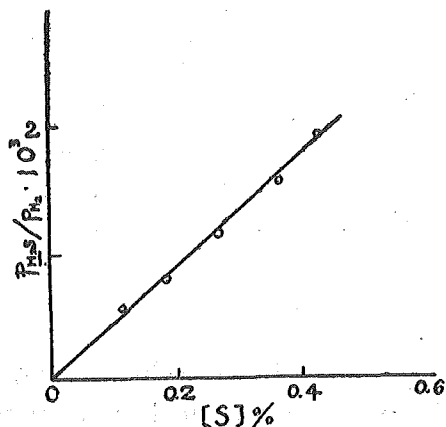


Fig. 2 a. Equilibrium at 1145°C.

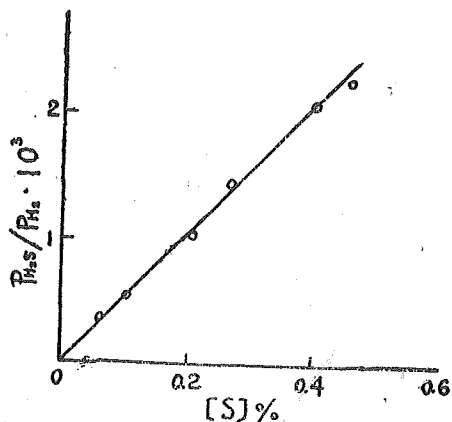


Fig. 2 b. Equilibrium at 1196°C.

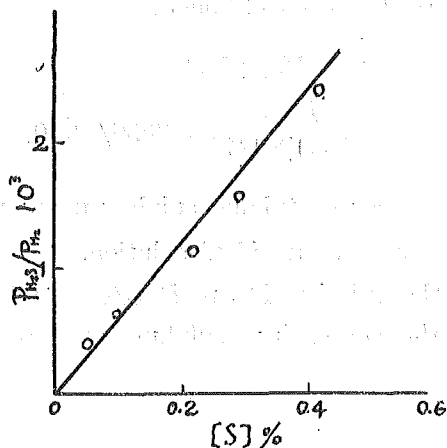


Fig. 2 c. Equilibrium at 1247°C.

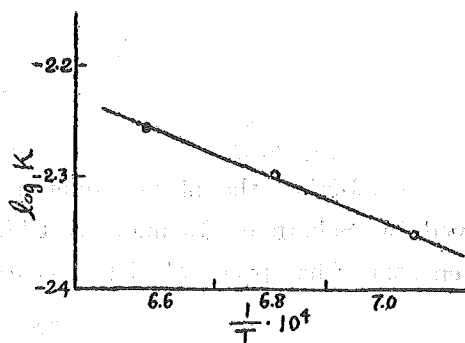
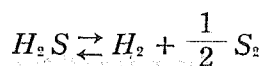


Fig. 3. Effect of temperature on equilibrium constant.

By combining the above equation with the relation of P_{S_2} to P_{H_2S}/P_{H_2} and T derived by Sherman, Elvander & Chipman²⁾, the relation of $P_{S_2}/[S]^2$ to T is obtained.



$$\log D_{H_2S} = -4740/T + 2.582$$

The result of the calculation is shown by the following equation

$$2S = S_2 (g)$$

$$\log P_{S_2}/[S]^2 = -13626/T + 3.388$$

$$\Delta F^\circ = 62284 - 15.49 T$$

Table 3
Equilibrium sulphur pressure in molten copper

Temp. °C	$1/T \cdot 10^4$	$2 \log K$	$2 \log D_{H_2S}$	$\log P_{S_2}/[S]^2$ (obs.)	$\log P_{S_2}/[S]^2$ (cala.)
1145	7.052	-4.706	-1.522	-6.228	-6.221
1196	6.807	-4.584	-1.290	-5.874	-5.887
1247	6.579	-4.512	-1.072	-5.584	-5.577

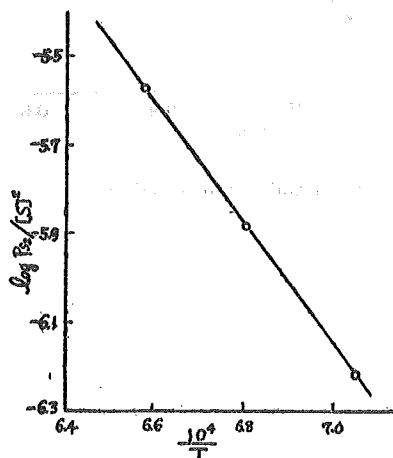
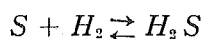


Fig. 4. The relation of $\log P_{S_2}/[S]^2$ to $1/T$.

Summary

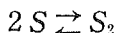
The equilibrium between molten copper, sulphur and hydrogen in the sulphur-unsaturated region has been determined by flow method at temperatures from 1145° to 1247 C. and the following equation has been obtained.



$$\log \frac{P_{H_2S}}{P_{H_2} [S]\%} = -2056/T - 0.899$$

Molten copper containing sulphur up to 0.5 % can be regarded as an ideal solution.

By combining the above equation with the relation P_{S_2} to P_{H_2S}/P_{H_2} and T derived by Scherman, Elvander & Chipman, the equilibrium sulphur pressure in molten copper has been calculated as follows.



$$\log \frac{P_{S_2}}{[S]^2} = -13626/T + 3.388$$

Acknowledgement

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Literature Cited

- 1) The memories of the faculty of engineering, Hokkaido University. vol. VIII. No. 3, p. 15, (1950).
- 2) Sherman, Elvander & Chipman: J. of Metals, vol. 188, p. 338 (1950)