Physico-chemical Researches on Copper Metallurgy

Report IV: Activity of Sulphur in Molten Copper

By

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In continuation of the previous reports, a study has been made of the equilibrium in the reaction of hydrogen with molten cuprous sulphide. The equation for this reaction was

$$Cu_2S\,(l) + H_2 = 2\,Cu\,(l) + H_2S$$

The equilibrium constant for this reaction was determined from 1145° to 1247°C by flow method and an experimental equation was obtained:

$$\text{Log } P_{H_2S} / P_{H_2} = -3341/T - 0.107$$

The corresponding equation for the sulphur pressure of the two-phase system was as follows:

$$\text{Log } P_{S_2} = -16195/T + 4.973$$

The solubility of sulphur in molten copper has also been discussed and the following relation has been obtained.

$$\text{Log } [S]_{max} = -2086/T + 1.45$$

By combining these data with the result of the previous report, activity of sulphur in higher range of concentration was estimated.

Introduction

In copper metallurgy, the thermodynamic properties of sulphur in melts have very important meaning for understanding of complicated reactions occurring in blast furnace, reverberatory furnace and converter.

Having these points in mind the authors reported the equilibria between hydrogen and molten copper containing 0.05~0.45% sulphur in the previous report.[1] But in higher range of sulphur content, very few studies have been carried out. The purpose of this investigation is to estimate the activity values for sulphur in higher concentration by a study of equilibrium in the region where two liquid phases, cuprous sulphide and copper, are present and by a determination of sulphur solubility in molten copper.

Equilibrium in the reaction of hydrogen with copper-saturated molten cuprous sulphide

Materials and Apparatus: Copper sulphide used was prepared in the following manner. Ten grs of pieces of electrolytically refined copper and 4 grs of sulphur powder that had been reprecipitated by carbon bisulfide were mixed in a Rose crucible and heated for about 15 minutes under an atmosphere of hyrogen sulphide. Then 6 grs of copper sulphide thus obtained and 4 grs of electrolytically refined copper were charged in an alumina crucible and melted at a temperature of 1200°C for two hours in a current of hydrogen.

The apparatus and procedure were essentially the same as those described in the previous report. The reaction tube was made of quartz, 300 mm in length and 30 mm in dia. inside, 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. The period of absorption was five minutes. The flow rate of hydrogen gas into the system was controlled by a rheostat and the amount was measured indirectly by an ampermeter. In the present work the effect of thermal diffusion may cause considerable errors. Therefore, in order to avoid this source of error, the electrolytic current was limited to 3 A at minimum and dead space in the reaction tube was reduced

TABLE 1
Experimental Results

Temp.°C	Flow rate cc/min.	$P_{H_2S}/P_{H_2}\cdot 10^3$
1145	20.88	2.82
1145	27.84	2.20
1145	34 80	2.17
1145	41.76	1.98
1196	20.88	3.27
1196	27.84	3.01
1196	34.80	2.85
1196	41.76	2.36
1247	20.88	3.96
1247	27.84	3.79
1247	34.80	3.68
1247	41.76	2.99

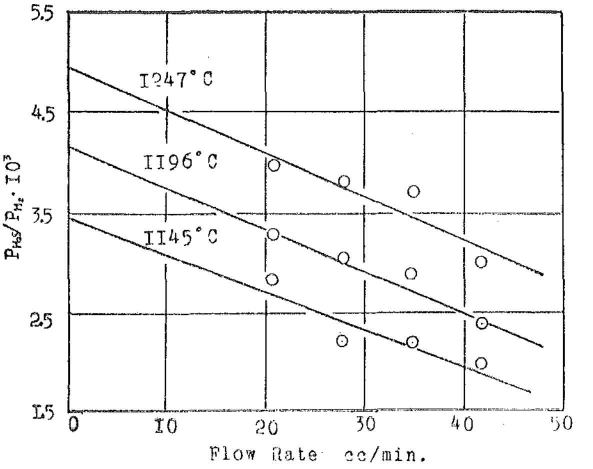

Fig. 1 Relation of P_{H_2S}/P_{H_2} to flow rate.

as much as possible. The temperature of the melt was measured with Pt-PtRh thermocouple calibrated at the melting points of aluminium, silver and copper and was controlled in general within ± 2°C during a run by a variable transformer.

Results and Calculations: Runs were made at three different temperatures, 1145°, 1196° and 1247°C. The results of these runs are recorded in Table 1 and the relation of gas ratio P_{H_2S}/P_{H_2} to flow rate is shown in Fig. 1.

From this figure, it will be seen that the gas ratio is a linear function of flow rate at every temperature. Hence, equilibrium constant K_P can be obtained by extrapolation to zero flow rate as shown in Fig. 1. In the fourth column of Table 2 the values of P_{H_2S}/P_{H_2} thus obtained are given.

TABLE 2 Equilibrium constant in the reaction of hydrogen with molten cuprous sulphide

Temperature			$K_P = P_{H_2S}/P_{H_2}$	Log K_P (obs.)	Log K_P (calc.)
°C	°K	1/T·10⁴			
1145	1418	7.052	$3.44 \cdot 10^{-3}$	− 2.463	− 2.463
1196	1469	6.807	$4.17 \cdot 10^{-3}$	− 2.380	− 2.381
1247	1520	6.579	$4.96 \cdot 10^{-3}$	− 2.305	− 2.305

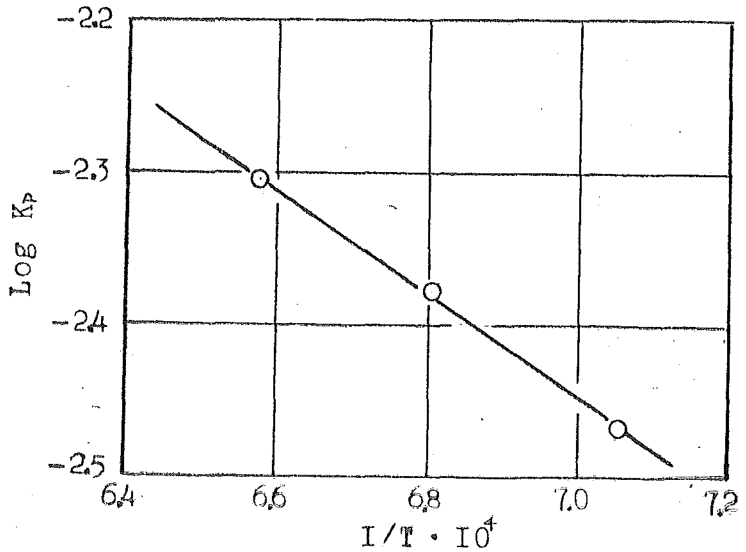

Fig. 2 Effect of temperature on equilibrium constant.

If 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. 2. The equation of this line can be computed by method of least squares. The result is represented by the following equation.

$$\mathrm{Log}\ K_P = -3341/T - 0.107$$

From this expression, Log K_P is calculated for comparison with the experimental data. The agreement is satisfactory.

By combining the above equation with the following relation of P_{S_2} to P_{H_2S}/P_{H_2} and T derived by Sherman Elvander & Chipman[2])

$$H_2S = H_2 + \frac{1}{2} S_2$$

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

the relation of P_{S_2} to T for sulphur-saturated melt is obtained. The result is as follows:

$$\mathrm{Log}\ P_{S_2} = -16195/T + 4.973$$

The values of Log P_{S_2} calculated from this equation are listed in Table 3.

TABLE 3 Equilibrium sulphur pressures for molten cuprous sulphide saturated with copper

Temp. °C	$1/T \cdot 10^4$	2 Log K_P	2 Log D_{H_2S}	Log P_{S_2} (obs.)	Log P_{S_2} (calc.)
1145	7.052	− 4.926	− 1.522	− 6.448	− 6.448
1196	6.807	− 4.760	− 1.290	− 6.050	− 6.051
1247	6.579	− 4.610	− 1.072	− 5.682	− 5.682

Consideration on sulphur activity in molten copper

On sulphur activity in molten copper it is evident from the previous peport that liquid copper containing sulphur up to 0.45% can be regarded as an ideal solution. But in higher range of sulphur content no study has been carried out. Activity of sulphur in higher range can be determined by the actual measurement of the equilibrium for the following reaction:

$$\underline{S} + H_2 = H_2S$$

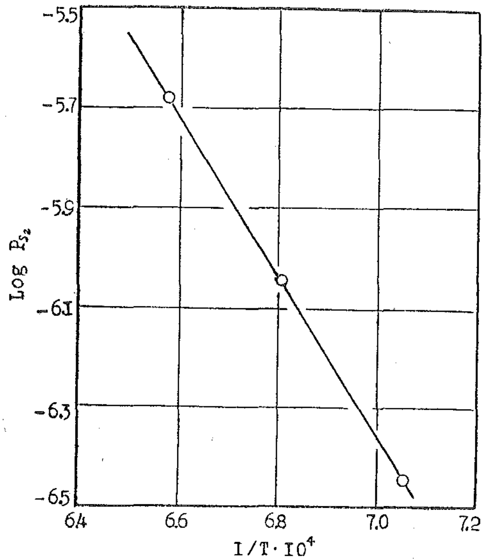

Fig. 3 Effect of temperature on equilibrium sulphur pressure of molten cuprous sulphide saturated with copper.

But when the sulphur solubility in molten copper and activity of sulphur in sulphur-saturated phase are known, activity in higher range can be derived.

The equilibrium diagram of the Cu–Cu_2S binary system is shown in Fig. 4.[3] It will be seen from this figure that a region of liquid immiscibility exists in the system and these immiscible phases are sulphur-saturated molten copper and the melt close to Cu_2S in composition.

Equilibrium system between copper, sulphur and hydrogen in the region of this immiscibility has three phases and three components. Hence, according to the *phase rule*, it has two degrees of freedom. Therefore, specification of temperature and pressure completely determines the state of the system at equilibrium. That is, in so far as two liquid phases are present, the equilibrium gas ratio is independent of the relational amount of the liquid phases. Moreover, the gas ratio P_{H_2S}/P_{H_2} is directly proportional to the chemical

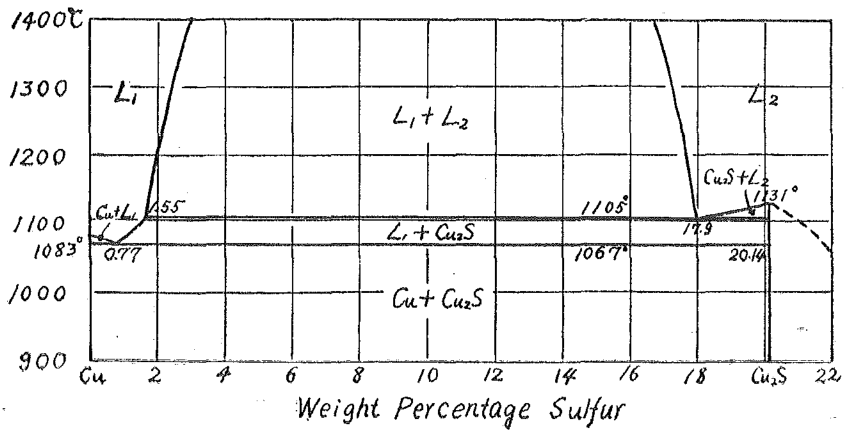

Fig. 4 Phase diagram of the system Cu–Cu_2S.

activity of sulphur in the condensed phase. Therefore, equilibrium values P_{H_2S}/P_{H_2} in the reaction $Cu_2S(l)+H_2=2Cu(l)+H_2S$ can be regarded as the gas ratio for sulphur-saturated molten copper.

From the experimental results of this research and of the previous report, assuming activity coefficient of sulphur in liquid copper to be less than unity and using the following equation, the relation between sulphur concentration and P_{H_2S}/P_{H_2} may be represented schematicaly by Fig. 5 at constant temperature.

$$\underline{S}+H_2=H_2S$$

$$K=\frac{P_{H_2S}}{P_{H_2}\cdot m\cdot[S]}$$

where m is activity coefficient of sulphur in molten copper
$[S]$ is sulphur concentration

In this figure, P′ is the saturation point of sulphur. In the region where the concentration of the solute is sufficiently low, the binary system Cu-S can be regarded as an ideal solution. Therefore, the activity coefficient m is equal to unity and so the relation between P_{H_2S}/P_{H_2} and $[S]$ may be represented by the straight line OA as shown in Fig. 5. But when the concentration increases over A′, the melt for this system shows deviation from the ideal solution. From the assumption, $m<1$, the value of P_{H_2S}/P_{H_2} at saturation point of sulphur must be less that PP′ obtained by the extrapolation of OA. As the result of this, the relation between P_{H_2S}/P_{H_2} and sulphur concentration may be illustrated by the curve AB. Further, when the concentration increases above P′, two liquid phases, sulphur-saturated molten copper and copper-saturated cuprous sulphide, appear. As mentioned previously, from the *phase rule*, it is evident that P_{H_2S}/P_{H_2} is constant and independent of the relational amount of liquid phases in the range P′Q′ at constant temperature. This constant value is represented by

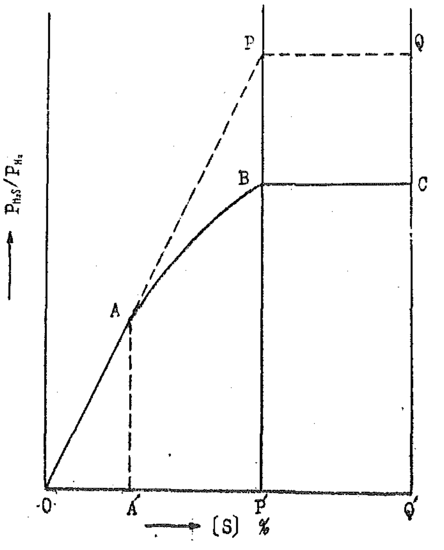

Fig. 5 Schematic P_{H_2S}/P_{H_2}—composition diagram.

the line BC.

The equilibrium values of P_{H_2S}/P_{H_2} on the dilute solution have been given in the previous report at temperatures 1145°, 1196° and 1247°C respectively. Equilibrium in the range of BC, has also been determined by the abovedescribed experiment. Therefore, if the solubility of sulphur in molten copper is given, activity of sulphur in higher concentration can be derived.

The boundary curves of the immiscible region were determined by Bornemann & Wagenmann. They obtained the solubility curves by the measurement of the electric resistance for the melt. The data on Cu-side are given in Table 4.

TABLE 4

Solubility of sulphur in molten copper given by Bornemann & Wagenmann

Temp. °C	Solubility of sulphur Wt. pct
1105	1.80
1140	1.93
1217	2.11
1280	2.42

On the other hand, if it be assumed that the melt can be regarded as an ideal solution up to the saturation point of sulphur, solubility of sulphur in molten copper can be calculated by combining the experimental result of this study with the relation from the previous report. The value thus obtained is about 0.8% at temperature 1145°C. Comparing this value with the above data by Bornemann & Wagenmann the difference between the two is seen to be too high.

Furthermore, by extrapolating the P_{H_2S}/P_{H_2} ratio in sulphur-unsaturated region to a maximum solubility of sulphur, P_{H_2S}/P_{H_2} for molten cuprous sulphide can be estimated. The value thus determined is about $8.5 \cdot 10^{-3}$, whereas the value observed from data obtained by the works is $3.44 \cdot 10^{-3}$. The former is about 2.5 times as great as the latter and the difference also seems to be too high.

From these two reasons, the genuineness of the solubility reported in the literature comes into question. Therefore, the authors actually analysed sulphur content in molten copper in equilibrium with molten cuprous sulphide. The method of determination was as follows: After abovedescribed equilibrium measurements, melt was quenched to room temperature by lowering the furnace and by taking out the reaction tube into the air. Then, sulphur in sulphur-saturated copper was analysed by gravimetric method. The results of these runs are listed in Table 5.

From this data sulphur solubility in molten copper may be computed as a function of temperature as follows,

$$\mathrm{Log}\,[S]_{max} = -2086/T + 1.45$$

where $[S]_{max}$ is sulphur solubility in wt. pct.

TABLE 5
Solubility of sulphur in molten copper

Temy. °C	Solubility of sulphur Wt. pct
1145	0.97
1196	1.06
1247	1.22

Referring to Table 5, it is seen that the values are about half the solubility reported by Bornemann & Wagenmann.

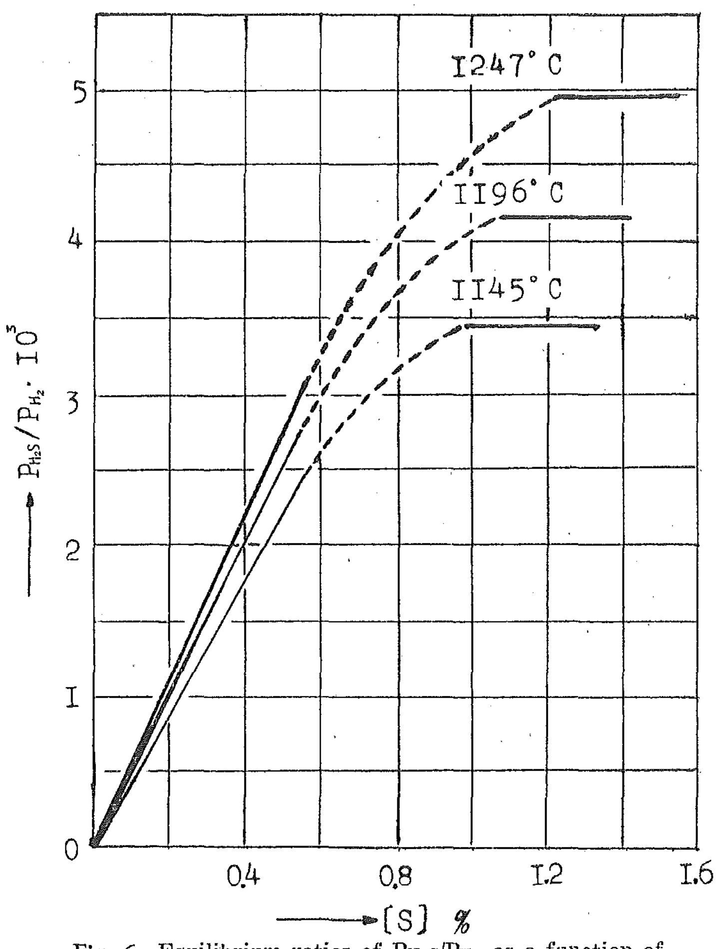

Fig. 6 Equilibrium ratios of P_{H_2S}/P_{H_2} as a function of sulphur concentration at 1145°; 1196° and 1247°C.

Finally, by combining the equilibrium data for the reaction $Cu_2S(l) + H_2 = 2Cu(l) + H_2S$ and solubility above-discussed with the result published in the previous report, the P_{H_2S}/P_{H_2} ratio in higher concentration has been estimated as shown in Fig. 6.

Summary

The equilibrium for the system containing hydrogen, copper-saturated molten cuprous sulphide and sulphur-saturated liquid copper has been determined at temperatures from 1145° to 1247°C by flow method and the following equation has been obtained:

$$\text{Log } K_P = -3341/T - 0.107$$

By combining the above equation with the data on dissociation of hydrogen sulphide given by Scherman, Elvander & Chipman, sulphur pressure of this two-phase system has been calculated as follows,

$$\text{Log } P_{S_2} = -16195/T + 4.973$$

Solubility of sulpur in molten copper has been determined. The results are 0.97, 1.06 and 1.22% at temperatures 1145°, 1196° and 1247°C respectively. These values are about half of those given by Bornemann & Wagenmann. They can be computed as a function of temperature as follows,

$$\text{Log } [S]_{max} = -2086/T + 1.45$$

By combining the experimental results of this study with the data of the previous report, the P_{H_2S}/P_{H_2} ratio in higher concentration has been estimated.

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