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Physical Chemistry of Copper metallurgy (Report II)

Reduction equilibria of cuprous Sulphide and hydrogen

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1 Introduction.

On copper metallurgy, it is important to investigate the affinity between copper and sulphur. As the dissociation pressure of cuprous sulphide is very low, it is difficult to measure it directly. Therefore we measured it indirectly, reducing cuprous sulphide by hydrogen.

Though the reduction equilibrium of cuprous sulphide by hydrogen has been investigated by K. Jellinek and J. Zakowski¹⁾, E. V. Britzke and A. F. Kapustinski²⁾ and K. Sano³⁾ hitherto, their results are very different from each other, (See fig. 1).

Then, in order to examine their data, this experiment was made by flow method and further the results of this experiment were compared with ones which had previously been calculated theoretically⁴⁾, from the reduction equilibrium of iron sulphide by hydrogen.

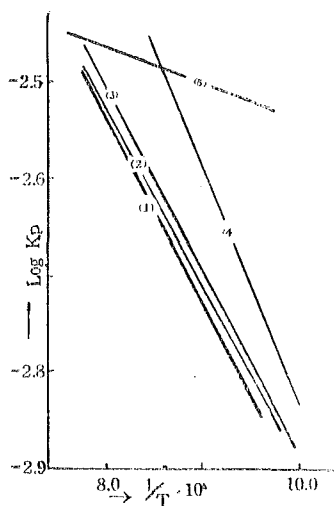


Fig. 1 Comparison of present results with results of previous investigators.

- (1) Authors (obs.) (2) K.Sano
(3) Authors.(calc.) (4) Britzke and Kapustinski (5) Jellinek and Zakowski

2. Preparation of the sample.

In previous experiments, cuprous sulphide used as the sample was made by the following method. Cupric sulphide was precipitated from cupric sulphate solution by passing hydrogen sulphide and heated in Rose crucible with powder of sulphur in the current of hydrogen.

But the precipitated cupric sulphide, obtained by this method, is rapidly oxidized to $CuS_2O_3 \cdot CuSO_4$ when it is contacted with air, and the oxidized salt is changed by hydrogen sulphide to colloidal cupric sulphide, which causes difficulties for filtration and decantation, as it passes through filter paper. And moreover, in case of simple reduction in Rose crucible, there remains many quantities of free sulphur.

Accordingly, in our experiment, cuprous sulphide was made by the following method.

40 gr of recrystallized cupric sulphate was dissolved in 300c.c. of water and heated up to its boiling point. On the other hand, 55 gr of crystallized sodium thiosulphate was dissolved in 100c.c. of water and the solution was slowly added, under stirring, to the previous hot cupric sulphate solution. The mixture was further heated, continued boiling, and then settled. After precipitation was completed, the precipitate was washed by decantation, until the precipitation of sulphate by barium chloride disappeared, and then filtered. The precipitate, dried first in air bath and then in desiccator, was black powder. This black precipitate was mixed with 12gr of sulphur which had been recrystallized by carbon bisulphide, charged in Rose crucible, and heated about 15 minutes in the current of hydrogen at first over a small flame and until finally the bottom of the crucible glowed faintly. Then, in order to drive off the excess sulphur, it was charged in a porcelain boat and reduced again about 1 hour at 650°C in the current of hydrogen. After cooling and breaking by a mortar, it was applied for the experiments. The analytical value of sulphur content of this sample was 20.12 %. (the theoretical value is 20.13%)

3. apparatus.

The apparatus used is shown diagrammatically in Fig. 2.

(a) The electrolytic cell.

Hydrogen was generated by electrolysis of 30 % caustic soda solution in the cell. The rate of passage of gas through the apparatus was controlled by a rheostat and hydrogen volume was measured indirectly by a precise amperemeter.

(b) The gas purifying apparatus.

Hydrogen gas was sufficiently purified and dried through the tubes filled with caustic potassium, phosphoric pentoxide, heated palladium asbestos, calcium chloride

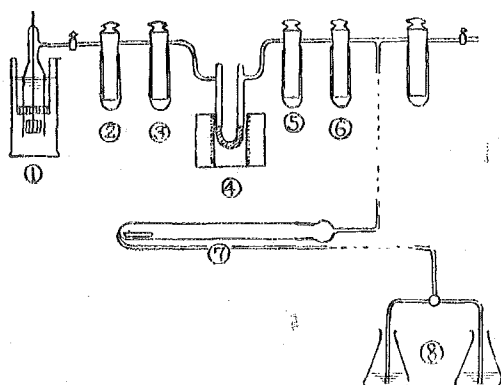


Fig. 2. Apparatus for studies of gas- Cu_2S equilibria.

- (1) Electrolytic cell.
- (2) Caustic Potassium
- (3) Phosphoric pentoxide
- (4) Palladium asbestos
- (5) Calcium chloride
- (6) Phosphoric pentoxide
- (7) Electric resistance furnace
- (8) Absorbent

and phosphoric pentoxide as shown in Fig. 2.

(c) The reaction tube.

The reaction tube was a porcelain tube of 3 cm in diameter and heated by nickel-chromium electric resistance furnace. Temperatures were determined precisely by a thermocouple in direct contact with the reaction tube.

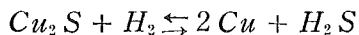
4. Experimental method.

After the sample had been placed in the center of the furnace and the air in the reaction tube had been perfectly replaced by hydrogen, electric furnace was switched on. Keeping electrolytic current constant, the system was brought

to the desired temperature. After keeping the furnace in that condition for a period of an hour, measurement was begun.

The absorbent was made from dissolving 40 gr of Zinc acetate and 10 gr of cadmium acetate in 100 cc of water, adding 30 cc of glacialacetic acid to them and finally diluting to 1000 cc with water. About 70 cc of this solution was taken into each absorption flask.

In the reaction tube, hydrogen sulphide was produced by the following reaction



When the gas was permitted to pass through the absorption flask for the definite period, the iodine solution of 1/100 N was added and zinc sulphide and cadmium sulphide precipitated in the flask were dissolved. After settling by 15 minutes, the excess of iodine was titrated by 1/100 N sodium thiosulphate, and then the volume of the hydrogen sulphide produced was determined.

In this measurement, 6 ~ 7 absorption flasks were used and the average value of them was taken. A period of absorption was 10 ~ 20 minutes and electrolytic current was limited to 1 Amp. at minimum in order to defend from the effect of thermal diffusion.

5. Experimental results.

The data obtained from this experiment are summarized in Table I and Fig. 3.

From this results it is evident that the ratio of hydrogen sulphide to hydrogen is in linear relation for the rate of passage at every temperature. Hence, we can calculate the equations of these straight lines by method of least squares. Then the ratios H_2S/H_2 in flowing velocity 0 are obtained by extrapolation. (see Fig. 3 and Table II.)

Now if reciprocals of absolute temperatures are plotted as abscissae and common logarithms of the equilibrium constants as ordinates, a linear relation is found, as is shown in Fig. 1. and the following equation is obtained by method of least squares.

$$\log K_p = -1941.504/T - 0.983 \dots \dots \dots (1)$$

Table I

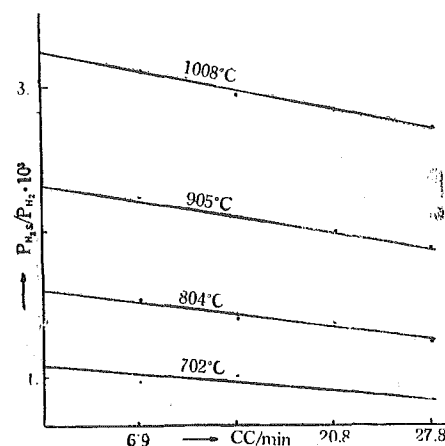
Temp. °C	Ampere	H_2S/H_2	Temp. °C	Ampere	H_2S/H_2
702	1	$0.978 \cdot 10^{-3}$	905	1	$2.237 \cdot 10^{-3}$
"	2	$1.019 \cdot "$	"	2	$2.004 \cdot "$
"	3	$0.813 \cdot "$	"	3	$1.997 \cdot "$
"	4	$0.827 \cdot "$	"	4	$1.875 \cdot "$
804	1	$1.533 \cdot "$	1008	1	$3.100 \cdot "$
"	2	$1.402 \cdot "$	"	2	$2.940 \cdot "$
"	3	$1.359 \cdot "$	"	3	$2.807 \cdot "$
"	4	$1.245 \cdot "$	"	4	$2.694 \cdot "$

$\log K_p$ in the fourth column of Table II, was calculated by the equation.

(1) The relation between the equilibrium constant and temperature is compared

Table II

Temp. °C	H_2S/H_2	$\log k_p(\text{obs.})$	$\log k_p(\text{calc.})$
702	$1.074 \cdot 10^{-3}$	-2.969	-2.975
804	$1.611 \cdot "$	-2.793	-2.787
905	$2.301 \cdot "$	-2.638	-2.632
1008	$3.223 \cdot "$	-2.492	-2.500

Fig. 3. P_{H_2S}/P_{H_2} as a function of cc/min.

with the previous results in Fig. 1. From this, it becomes clear that the result is very close to Sano's values obtained by a circulation method, but it is pretty lower than those of K. Jellinek and E. V. Britzke.

6. Comparison of the affinities of copper and of iron for Sulphur.

Now, comparing with affinities of copper and of iron for sulphur, we take K. Sano's) and S. Matoba & T. Uno's) data which obtained from the reduction equi-

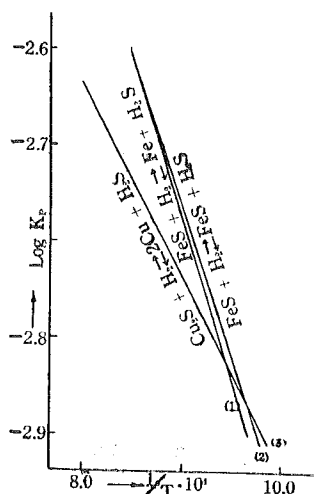


Fig. 4 Comparison of the affinities of copper and iron for sulphur.

- (1) S. Matoda and T. Uno
(2) K. Sano (3) Authors.

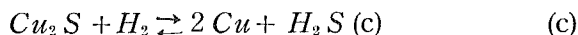
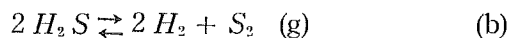
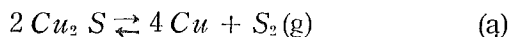
brium $FeS + H_2 \rightleftharpoons Fe + H_2S$ as shown in Fig. 4.

$$\log K_p = -3316.178/T + 0.3398 \dots \dots \text{K. Sano}$$

$$\log K_p = -3910.285/T + 0.887 \dots \dots \text{S. Matoba \& T. Uno.}$$

These two straight lines cross another one obtained from our experiment. The temperature at this cross point is 766°C from Sano and 780°C from Matoba. This fact shows that below these temperature iron sulphide is more stable than cuprous sulphide. In other words, affinities of iron and of copper for sulphur are related conversely with each other with 766 ~ 780°C as their turning point.

7. Dissociation pressure of cuprous sulphide



Representing the equilibrium constants of equation (a), (b), and (c) as K_{Pa} , K_{Pb} and K_{Pc} respectively, we can write as follows.

$$K_{Pa} = p_{S_2}$$

$$K_{Pb} = p_{S_2} \cdot p_{H_2}^2 / p_{H_2S}^2$$

$$K_{Pc} = p_{H_2S} / p_{H_2}$$

$$\therefore \log K_{Pa} = \log K_{Pb} + 2 \log K_{Pc} \quad (d)$$

As for the dissociation equilibrium of hydrogen sulphide, the following equation has been given by Lewis and Landall⁷⁾ and values calculated from this equation show a good coincidence with ones determined experimentally by Preunner⁸⁾ and Randall⁹⁾.

$$\log K_{pb} = -8400/T + 0.947 \log T + 0.722 \cdot 10^{-3} T - 1.62 \cdot 10^{-7} T^2 + 0.722$$

Substituting $\log K_{pb}$ calculated from this equation and $\log K_{Pc}$ obtained from our experiment into equation (d), we can find $\log K_{Pa}$. The 5th column of Table III. shows $\log K_{Pa}$ calculated in this way.

If reciprocals of absolute temperature are plotted as abscissae and common logarithms of equilibrium constants as ordinates, there is a linear relation between

Table III

Temp. °K	1/T	$\log K_{pb}$	$\log K_{Pc}$	$\log p_{S_2}(\text{obs.})$	$\log p_{S_2}(\text{calc.})$
975	$10.256 \cdot 10^{-4}$	-4.513	-2.969	-10.451	-10.466
1077	$9.285 \cdot 10^{-4}$	-3.617	-2.793	-9.213	-9.185
1178	$8.488 \cdot 10^{-4}$	-2.875	-2.638	-8.151	-8.136
1281	$7.806 \cdot 10^{-4}$	-2.234	-2.492	-7.218	-7.236

$\log p_{S_2}$ and $1/T$. Consequently, the next equation is obtained by method of least squares (See. Fig. 5.)

$$\log p_{S_2} = -13181.4/T + 3.053 \quad (2)$$

$\log p_{S_2}$ (calc.) shown in Table III are obtained from this equation.

8. Thermodynamic Treatment of Results.

For the data on the specific heats of cuprous sulphide, hydrogen, copper and hydrogen sulphide, we take following equations given by K.K. Kelley¹⁰).

$$Cu_2S (\alpha) \quad C_p = 9.38 + 31.2 \cdot 10^{-3}T \quad (3)$$

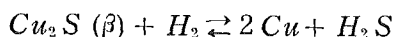
$$Cu_2S (\beta) \quad C_p = 20.9 \quad (4)$$

$$H_2 \quad C_p = 6.62 + 0.00081T \quad (5)$$

$$Cu \quad C_p = 5.44 + 1.462 \cdot 10^{-3}T \quad (6)$$

$$H_2S \quad C_p = 7.20 + 0.00360T \quad (7)$$

(i) Heat of reaction and standard free-energy change for the reaction



From equation (4), (5), (6) and (7) specific-heat change for this reaction is given as follows.

$$\Delta C_p = -9.44 + 0.005714T$$

Hence, heat of reaction is.

$$\Delta H = \Delta H_o - 9.44T + 0.002857 T^2 \quad (8)$$

On this basis, the standard free-energy equation for this reaction becomes

$$\Delta F^\circ = \Delta H_o + 9.44 T \ln T - 0.002857 T^2 + I T \quad (9)$$

From the equation $\Delta F^\circ = -RT \ln K_p$

$$\begin{aligned} \Sigma &= -4.571 \log K_p - 9.44 \ln T + 0.002857 T \\ &= \Delta H_o/T + I \end{aligned}$$

The value of Σ in every temperature can be determined by the experimental values $\log p_{H_2S}/p_{H_2}$ and so ΔH_o and I can be calculated by method of least squares. The results are

$$\Delta H_o = 15774, \quad I = -64.737$$

Substituting these values into equation (8) and (9), we obtain following equations.

$$\Delta H = 15774 - 9.44T + 0.002857T^2 \quad (10)$$

$$\Delta F^\circ = 15774 + 9.44T \ln T - 0.002857T^2 - 64.737T \quad (11)$$

From equation (10) and (11), we can find heat of reaction and free-energy change for the reaction $Cu_2S (\beta) + H_2 = 2Cu + H_2S$ at 25°C.

$$\Delta H_{298} = 13215 \quad \Delta F^\circ_{298} = 12249 \quad (12)$$

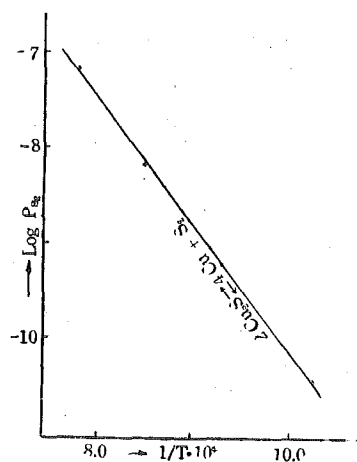


Fig. 5 Dissociation Pressures of cuprous sulphide.

(ii) Heat of reaction and standard free-energy change for $Cu_2S (\alpha) \rightleftharpoons Cu_2S (\beta)$

From equation (3) and (4) specific-heat change for this reaction becomes

$$\Delta C_p = 11.52 - 31.2 \cdot 10^{-3} T$$

$$\therefore \Delta H = \Delta H_o + 11.52T - 15.6 \cdot 10^{-3} T^2 \quad (13)$$

According to K. K. Kelley's data, $Cu_2S (\alpha)$ changes to $Cu_2S (\beta)$ by absorption 1340 cal at 376°K. Hence

$$\Delta H_{376} = 1340$$

Combining $\Delta H_{376} = 1340$ and equation (13), we obtain $\Delta H_o = -787$

$$\Delta H = -787 + 11.52T - 15.6 \cdot 10^{-3} T^2 \quad (14)$$

From equation (14) free-energy change for this reaction becomes

$$\Delta F^\circ = -787 - 11.52T \ln T + 15.6 \cdot 10^{-3} T^2 + IT \quad (15)$$

But, as free-energy change at transition point is zero, the integral constant I can be calculated by substituting $\Delta F^\circ_{376} = 0$ into equation (15)

$$I = 64.51$$

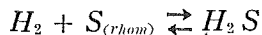
$$\Delta F^\circ = -787 - 11.52T \ln T + 15.6 \cdot 10^{-3} T^2 + 64.51T \quad (16)$$

Heat of reaction and free-energy change at 25°C become as follows from equation (14) and (15).

$$\Delta H_{298} = 1261, \quad \Delta F^\circ_{298} = 271 \quad (17)$$

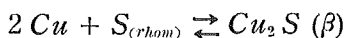
(iii) Heat of formation and free-energy change of cuprous sulphide.

As for heat of formation and free-energy change of hydrogen sulphide at 25°C, following equation was given by Lewis and Landall⁽¹¹⁾



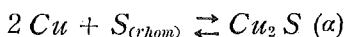
$$\Delta H_{298} = -4760, \quad \Delta F^\circ = -7840 \quad (18)$$

From equation (12) and (18), we find



$$\Delta H_{298} = -17975 \quad \Delta F^\circ_{298} = -20089 \quad (19)$$

Consequently, we obtain following results from equation (19) and (17)



$$\Delta H_{298} = -19236 \quad \Delta F^\circ_{298} = -20360$$

On the data of heat of formation of $Cu_2S (\alpha)$, following values have been reported by Wartenberg and Thomsen.

- 19000	Wartenberg.
- 18260	Thomsen
- 19236	Authors.

It is felt that Wartenberg's value for the heat of formation of cuprous sulphide favorably coincides with 19236 derived from the present equilibrium data.

(iv) Entropy of $Cu_2S (\alpha)$

As final check on the calculated value of free-energy and heat of formation of

cuprous sulphide, the entropy of cuprous sulphide may be calculated as follows. By combining $\Delta F^\circ = \Delta H - T \Delta S^\circ$, $\Delta F^\circ_{298} = -20360$ and $\Delta H_{298} = -19236$, we obtain

$$\Delta S^\circ_{298} = 3.77$$

Therefore, if we write the entropy of $S_{(rhom)}$, Cu , and Cu_2S (α) at $25^\circ C$ as S°_s , S°_{Cu} and $S^\circ_{Cu_2S}$, we find

$$S^\circ_{Cu_2S} - (2 S^\circ_{Cu} + S^\circ_s) = 3.77$$

K. K. Kalley¹³⁾ gives S°_{298} for $Cu = 7.97$ and for sulphur 7.64

$$\therefore S^\circ_s = 7.64 \quad S^\circ_{Cu} = 7.97$$

Consequently, S°_{298} for cuprous sulphide is calculated to 27.35 entropy units.

$$S^\circ_{Cu_2S} = 27.35 \text{ E. U.}$$

The value S°_{298} for Cu_2S (α) = 28.9 of low temperature specific-heat work carried out by Anderson¹³⁾, indicates this to be a desirable figure.

9. Conclusions.

(1) From the measurement of reduction equilibrium of cuprous sulphide by hydrogen, we obtained following equation by flow method.

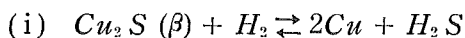
$$\log K_p = \log p_{H_2S} / p_{H_2} = -1941.504/T - 0.983$$

(2) Two straight lines, obtained from Sano and Matoba's data for the reaction $FeS + H_2 \rightleftharpoons Fe + H_2S$, and of authors for $Cu_2S + H_2 \rightleftharpoons 2Cu + H_2S$ cross at $766^\circ C$ and $780^\circ C$ respectively. From these results, it is presumed that affinities of copper and of iron for sulphur are related conversely with each other with $766^\circ C$ or $780^\circ C$ as their turning point.

(3) Employing above equation, we calculated dissociation pressure of cuprous sulphide

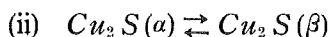
$$2 Cu_2S \rightleftharpoons 4 Cu + S_2 (g) \\ \log p_{S_2} = -13181.4/T + 3.053$$

(4) From conclusion (1), we calculated following thermodynamic values on cuprous sulphide.



$$\Delta H = 15774 - 9.44T + 0.002857T^2 \quad \Delta H_{298} = 13215$$

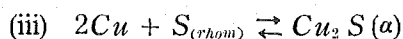
$$\Delta F^\circ = 15774 + 9.44T \ln T - 0.002857T^2 - 64.737T \quad \Delta F^\circ_{298} = 12249$$



$$\Delta H = -787 + 11.52T - 15.6 \cdot 10^{-3} T^2$$

$$\Delta F^\circ = -787 - 11.52T \ln T + 15.6 \cdot 10^{-3} T^2 + 64.51T$$

$$\Delta H_{298} = 1261 \quad \Delta F^\circ_{298} = 271$$



$$\Delta H_{298} = -19236, \quad \Delta F_{298}^{\circ} = -20360$$

(iv) Entropy of $Cu_2S(\alpha)$ at $25^{\circ}C$

$$S_{Cu_2S}^{\circ} = 27.35 \text{ E. U.}$$

(This research was aided financially by natural science grant made by ministry of education, of which we wish to express our appreciation).

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