ON THE REDUCTION EQUILIBRIUM OF CUPROUS SULPHIDE BY HYDROGEN

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I. Introduction

In studying the reduction equilibrium of cuprous sulphide, Jellinek and Zakowski,[1] Britzke and Kapustinsky,[2] and Tanaka[3] adopted the flow method, while Cox, Bachelder, Nachtrieb, and Skapaki,[4] and one of the writers[5] the circulation method. The results of them, however, were not in good agreement each other. In the present study, the writers redetermined the equilibrium condition in the reaction of hydrogen with cuprous sulphide by a semi-dynamical method, keeping the temperature of the solid phases at a constant value and circulating its gaseous phase throughout the system.

II. Experiment

1. Apparatus

The general diagram of the apparatus employed in this investigation was shown in Fig. 1. In the follows the description of each part was made:

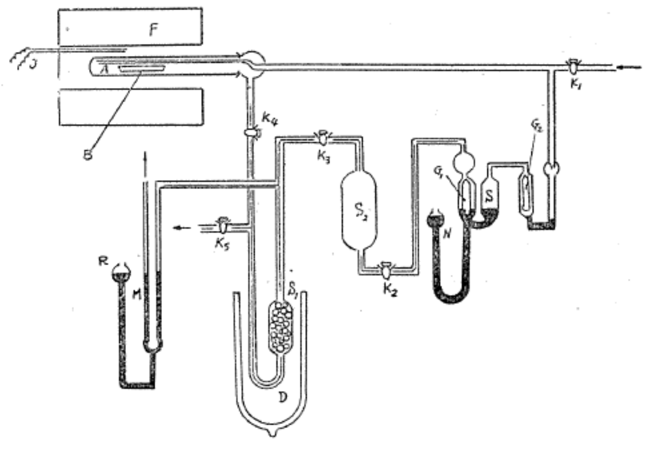

FIG. 1. Apparatus for equilibrium measurement.

a) Reaction System

A: a silica reaction tube (3.0×50 cm).

B: a silica boat ($1\times2\times5$ cm).

S_1, S_2: glass bulbs, the volumes of which are known accurately. For the purpose of enlargement of the inner surface area, the former bulb is filled with many glass beads.

D: a Dewar's vessel for cooling the bulbs S_1 with liquid nitrogen and solidifying hydrogen sulphide.

M: a mercury manometer for measuring the pressure in the bulb S_1.

F : a nichrome resistance furnace for heating the reaction tube, the range of effective part of the furnace being 15 cm with the uniformity of $\pm 1.0°$ at 600°C.

b) Circulation system

N : a mercury reservoir which is connected to the circulating pump with a rubber tube and movable.

G_1, G_2: special cocks for circulating the gas by raising and lowering N: in raising N, G_2 closes and the gas contained in S is sent to A through G_2, while in lowering, G_2 closes, G_1 opens and the gas is admitted into S from S_2.

2. *Materials*

a) Cuprous sulphide

Cuprous sulphide was prepared by passing the purified hydrogen sulphide gas into the cupric sulphate solution obtained from the cupric sulphate crystal recrystallized four times.

b) Hydrogen

Hydrogen gas was generated in Kipp's apparatus by the reaction of pure synthetic hydrochloric acid on electrolyzed zinc and purified by passing it through a series of purifiers containing the following substances respectively: potassium hydroxide, potassium permanganate, calcium chloride, Pt-asbestos, and also phosphorous pentaoxide.

3. *Experimental*

The silica boat B containing about 5 grams of cuprous sulphide was placed nearly in the middle of the reaction tube A and the purified hydrogen gas was admitted into the reaction tube through the cock K_1, and the cuprous sulphide was reduced partly at 850°$\sim$900°C, and then the whole system was evacuated for about two hours to remove the absorbed substances which might be present within the apparatus. When high vacuum was attained the purified hydrogen gas was admitted into the reaction system again. Then the circulation system was operated and the reaction tube A was heated to a desired temperature by the electric furnace F, whose temperature was controlled by means of potentiometric thermoregulator and kept constant within $\pm 1°$ at all experimental temperature.

It was found that the equilibrium between hydrogen gas and cuprous sulphide was attained in 30 minutes, but, to avoid any uncertainties, the majority of the experiments were continued for three hours. When the equilibrium condition was attained, the cocks K_2, K_4 were closed and the total pressure in the glass bulbs S_1, S_2 was measured, and then the bulb S_1 was cooled with liquid nitrogen contained in Dewar's vessel D and the bulbs were evacuated with sufficiently slow speed through the cock K_5. After high vacuum was obtained, the cocks K_5, K_3 were closed and Dewar's vessel D was removed and solid hydrogen sulphide in the bulb S_1 was vapourized and its partial pressure was measured with manometer M.

III. Results of Measurement

The equilibrium constant K_p of the reaction of $Cu_2S + H_2 = 2Cu + H_2S$ is equal to P_{H_2S}/P_{H_2}, where P_{H_2S} and P_{H_2} denote the partial pressure of hydrogen sulphide and hydrogen in the reaction chamber. By substituting the observed values of P_{H_2S} and P_{H_2} in the above relation, the constant was obtained as shown in the fourth column in Table 1. Hence the relation between K_p thus obtained and the temperature can be expressed as follows:

$$\log K_p = -1{,}429.45/T - 1.693 \tag{1}$$

TABLE 1. Results of Experimental Measurement

T °K	P_{H_2S} (mm)	P_{H_2} (mm)	$K_p \times 10^3$	$\log K_p$ (obs.)	$\log K_p$ (calc.)
1,265	1.265	729	1.734	−2.761	−2.819
1,228	1.002	721	1.837	−2.858	−2.857
1,196	0.873	695	1.256	−2.911	−2.898
1,129	0.772	742	1.040	−2.983	−2.961
1,103	0.691	721	0.959	−3.018	−2.989
1,074	0.613	724	0.846	−3.072	−3.024
1,039	0.635	695	0.913	−3.039	−3.069
992	0.572	772	0.747	−3.130	−3.134
966	0.522	710	0.735	−3.134	−3.162
941	0.452	749	0.603	−3.219	−3.212

The relation between $\log K_p$ and $1/T$ expressed in a straight line in the range of experimental temperatures was compared in Fig. 2 together with those of the other investigators. It is to be noticed that the results obtained at high temperatures such as 800°∼1,000°C are in good agreement with the values of K_p which was calculated by Kelley[6] thermodynamically, but, the data at 650°∼750°C approach nearly to those obtained by Cox, Bachelder, Nachtrieb, and Skapaki experimentally.

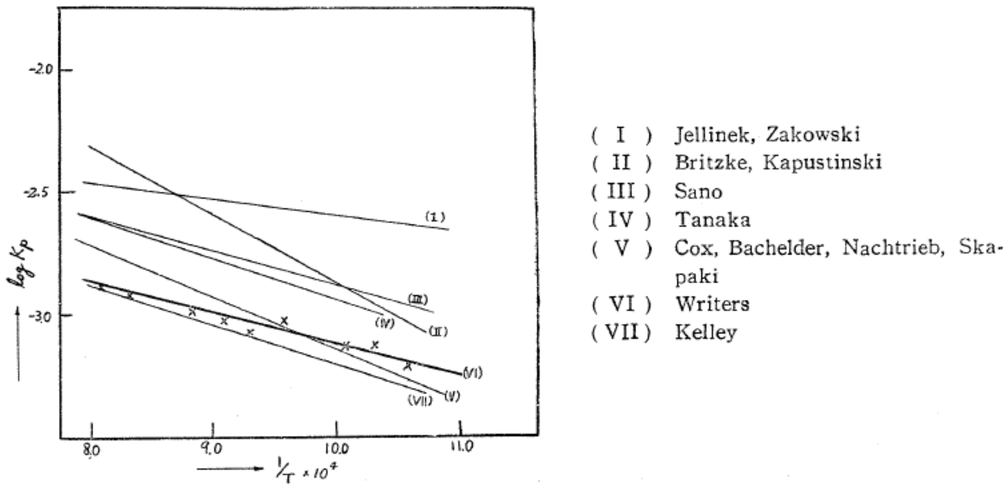

FIG. 2. Relation between $\log K_p$ and $1/T$.

IV. Summary

The reduction equilibrium of cuprous sulphide by hydrogen was studied by a circulation method at various temperatures ranging from 650° to 1,000°C and the following equation for the relation between the equilibrium constant K_p and the temperature T°K was obtained:

$$\log K_p = -1{,}429.45/T - 1.693$$

The values of K_p calculated from the above equation at 800°～1,000°C are in good agreement with those obtained from Kelley's equation, but the values at 650°～750°C approach nearly to the results obtained by Cox, Bachelder, Nachtrieb, and Skapaki experimentally.

References

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