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# Thermodynamical studies of copper metallurgy. (Report I)

By

Tokiaki Tanaka

(1948, 12, 10)

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## I. Introduction

Investigating the contents of Copper metallurgy which has been performed up to the present, it still remains in the stage of describing the arts of metallurgy in detail which have been empirically transmitted since old times and we can find little results in it which have been obtained from scientific researches. Therefore we must go forward and investigate many empirical facts from the chemico-physical points of view and furthermore develop it up to the point where we can draw quantitative conclusions for the many rules-of-thumb methods. Especially if we assume various changes in the smelting conditions in the future, it is positively necessary for us to open a new theoretical field and to resolve these problems on the more scientific and definite ground in order to draw appropriate metallurgical conclusions in accordance with circumstances.

In consequence of remarkable development of chemical thermodynamics, it has also been applied to steel making and the time has arrived when the processes of steel making are studied from a chemical and thermodynamic viewpoint. But in the field of non-ferrous metallurgy no researches have yet been made up to this day.

In this sense, it is the aim of my research to investigate various phenomena in copper metallurgy thermodynamically and to contribute to the improvement and development of the operations in copper smelting.

## II. Determination of the chemical constant of sulphur vapour $S_2$ from the equilibrium between ferrous sulphide and hydrogen.

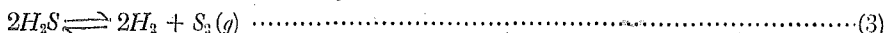
When we put forward the chemico-physical consideration on many chemical reactions occurring in the process of copper smelting, we must first of all calculate the affinity between copper and sulphur.

There are cuprous sulphide and cupric sulphide as the compounds of copper and sulphur. And these two compounds are very important, as they are the chief components in copper ores. As it is generally known that cupric sulphide dissociates in high temperatures and turns to cuprous sulphide, I shall consider only cuprous sulphide in the present paper.

In order to determine the equilibrium equation of  $2Cu_2S \rightleftharpoons 4Cu + S_2(g)$ , it is necessary to determine the chemical constant of sulphur vapour  $S_2$ . And so the author calculated the chemical constant of  $S_2$  gas from the reduction equilibrium of ferrous sulphide by hydrogen, as this has been investigated by comparatively many investigators.



In the reaction shown in the above equation, the dissociation pressure of ferrous sulphide is so small that we cannot measure it directly. Therefore we must calculate it indirectly from the reduction equilibrium of ferrous sulphide by hydrogen.



Now if we represent the equilibrium constant of equation (1), (2) and (3) as  $K_{PI}$ ,  $K_{PII}$ , and  $K_{PIII}$  respectively, we may denote as follows.

$$K_{PII} = \frac{p_{H_2S}}{p_{H_2}}$$

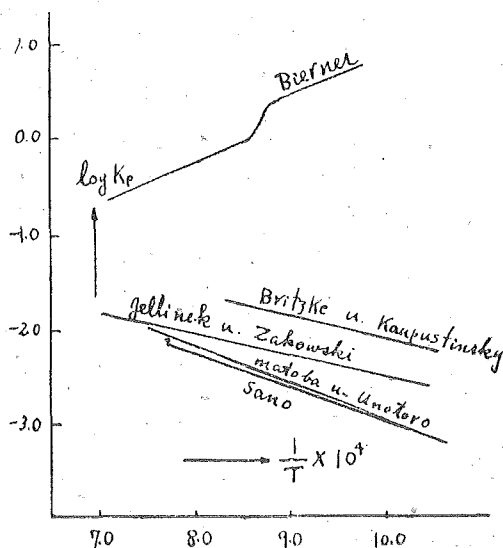
$$K_{PIII} = \frac{p_{H_2}^2 \cdot p_{S_2}}{p_{H_2S}^2}$$

Hence  $K_{PI} = p_{S_2} = K_{PII}^2 \cdot K_{PIII}$

or  $\log K_{PI} = 2\log K_{PII} + \log K_{PIII} \dots\dots (4)$

Though the reduction equilibrium of ferrous sulphide by hydrogen has been investigated by E. V. Britzke and A. F. kaupustinsky<sup>1)</sup>, L. Biener<sup>2)</sup>, K. Jellinek and Zakowski<sup>3)</sup>, K. Sano<sup>4)</sup> and S. Matoba and T. Unotoro<sup>5)</sup> hitherto, their results show large differences (see fig 1). But the values determined by Sano, which have been obtained by circulating Method and those of Matoba and Unotoro obtained by flow method coincide fairly with each other. Therefore by adopting Sano

Fig. 1



Matoba's values, we have the third column of the table I.

Table I.

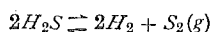
T° K	log $K_{PI}$	log $K_{PII}$	log $K_{PIII}$	investigators
976	-10.783	-3.126	-4.531	Matoba and Unotoro.
1062	- 9.304	-2.733	-3.738	Sano.
1073	- 9.037	-2.694	-3.649	Matoba and Unotoro.
1082	- 9.026	-2.725	-3.576	Sano.
1125	- 8.478	-2.615	-3.248	"
1129	- 8.364	-2.573	-3.218	Matoba and Unotoro.
1144	- 8.208	-2.549	-3.110	Sano.
1172	- 7.899	-2.492	-2.915	"
1173	- 7.839	-2.465	-2.909	Matoba and Unotoro.
1273	- 6.628	-2.174	-2.280	"

In regard to the dissociation equilibrium of (3), the following equation has been given by Lewis and Landall<sup>(5)</sup>,

$$\log K_{PIII} = -\frac{8400}{T} + 0.947 \log T + 0.722 \cdot 10^{-3}T - 1.62 \cdot 10^{-7}T^2 + 0.722 \dots\dots\dots(5)$$

The values calculated from this equation nicely coincide with the actual measurements as shown in the table II. Hence, if we adopt this equation and calculate the values of log  $K_{PIII}$ , we obtain the fourth column in the table I. By substituting these values in the equation (4), we can find the values of log  $K_{PI}$ . The values log  $K_{PI}$  shown in the second column of the Table I have been calculated in this way.

Table 2.



investigators	T° K	log $K_{PIII}$ (obs)	log $K_{PIII}$ (calc.)
preunner, Schupp.	1023	-4.050	-4.070.
" , "	1103	-3.420	-3.413
" , "	1215	-2.600	-2.613
" , "	1338	-1.928	-1.919
Randall, Bichowsky.	1362	-1.804	-1.794
Preunner, Schupp.	1405	-1.586	-1.581
Randall, Bichowsky.	1473	-1.286	-1.268
" , "	1537	-0.980	-0.998
" , "	1667	-0.514	-0.522

By Vant Hoff's equilibrium equation under constnt pressure, we have

$$\frac{d \log K_P}{dT} = \frac{\Delta H}{RT^2} \dots\dots\dots(6)$$

$\Delta H$  is a function of temperature; but we can regard  $\Delta H$  as constant over a small range of

temperature. If we represent the equilibrium constant at two different temperatures  $T_1$  and  $T_2$  as  $K_{P_1}$  and  $K_{P_2}$  respectively and assume that  $\Delta H$  is constant between these temperatures and then integrate the equation (6), we find

$$\Delta H = \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot 4.571 \log \frac{K_{P_2}}{K_{P_1}} \dots \dots \dots (7)$$

Now putting  $T_1 = 1062$  and  $T_2 = 1082$ , we see that the experimental value of  $\log K_{P_1}$  and  $\log K_{P_2}$  is  $-9.304$  and  $-9.026$  respectively from the second column in the table I.

Substituting these values the equation (7), we have

$$\Delta H_{1072} = 73024 \dots \dots \dots (8)$$

And from the reaction (1), the following formula is obtained.

$$\Delta H = \Delta H_0 + 2 \int C_{PF_e} dT + \int C_{P_S} dT - 2 \int C_{PF_{eS}} dT \dots \dots \dots (9)$$

Miething's table<sup>7)</sup> shows,

$$\int_0^{200} C_{PF_e} dT = 1007$$

Kelley<sup>8)</sup> gives the following equation as the heat capacity of iron.

$$\alpha: C_{PF_e(\alpha)} = 4.13 + 6.38 \cdot 10^{-3} T \quad (273 \sim 1041)$$

$$\alpha \rightarrow \beta: \Delta H_{1041} = 340$$

$$\beta: C_{PF_e(\beta)} = 6.12 + 3.36 \cdot 10^{-3} T \quad (1041 \sim 7911)$$

From these equations, we can calculate as follows.

$$\int_0^{1072} C_{PF_e} dT = 7937 \dots \dots \dots (10)$$

The heat capacity of ferrous sulphide  $F_eS$  at low temperature was determined by Anderson<sup>9)</sup> from  $57.9^\circ K$  to  $296.0^\circ K$ . As the heat capacity below  $100^\circ K$ , he also gave the following equation.

$$C_{PF_{eS}} = D\left(\frac{205}{T}\right) + E\left(\frac{370}{T}\right) \dots \dots \dots (11)$$

But  $D\left(\frac{205}{T}\right)$  represents Debyes' function and  $E\left(\frac{370}{T}\right)$  Einsteins' function. Above  $290^\circ$  Kelley gave the following equation.

$$\alpha: C_{PF_{eS}(\alpha)} = 2.03 + 39.0 \cdot 10^{-3} T \quad (273 \sim 411)$$

$$\alpha \rightarrow \beta: \Delta H_{411} = 1050$$

$$\beta: C_{PF_{eS}(\beta)} = 12.05 + 2.73 \cdot 10^{-3} T \quad (411 \sim 1468)$$

Accordingly, if we adopt equation (11) from  $0^\circ K$  to  $100^\circ K$  and above  $280^\circ K$  the above Kelley's equations and then calculate graphically from  $100^\circ K$  to  $280^\circ K$  using Anderson's data, the result is as follows,

$$\int_0^{1072} C_{PF_{eS}} dT = 14623 \dots \dots \dots (12)$$

Since we may consider that the heat capacity of diatomic sulphur  $S_2$  is equal to that of oxygen, if we apply the equation  $C_{P_{O_2}} = \frac{7}{2} R + R \cdot E\left(\frac{3600}{T}\right)$  to vapour  $S_2$ , which Eucken gave for the oxygen, we find,

$$\int_0^{1072} C_{P_S} dT = 7709 \dots\dots\dots(13)$$

If we calculate  $\Delta H_0$ , substituting (8), (10), (12) and (13) into the equation (9), we have

$$\Delta H_0 = 78697 \dots\dots\dots(14)$$

On the other hand, equilibrium equation of the chemical reaction (1) is represented by

$$\begin{aligned} \log K_{PI} = \log p_{S_2} = & -\frac{\Delta H_0}{4.571T} + 3.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \int R \cdot E \left( \frac{3600}{T} \right) dT \\ & + \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_e} dT - \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_{eS}} dT + J_P \end{aligned}$$

Finally, substituting the value (14) in the above equation, we have

$$\begin{aligned} \log K_{PI} = \log p_{S_2} = & -\frac{17216}{T} + 3.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \int R \cdot E \left( \frac{3600}{T} \right) dT \\ & + \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_e} dT - \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_{eS}} dT + J_P \dots\dots\dots(15) \end{aligned}$$

The results of the actual calculation of each term in the equation (15) at several different temperatures are shown in the table 3. The term  $\frac{1}{4.571} \int \frac{dT}{T^2} \int R \cdot E \left( \frac{3600}{T} \right) dT$  has been calculated from the table of Landolt-Börnstein<sup>10)</sup> and the term  $\frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_e} dT$  has been from Schenk's table<sup>11)</sup>. For the values of  $-\frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_{eS}} dT$  below 280°K, the author has taken the graphical method, plotting various absolute temperatures as abscissae against  $\frac{1}{T^2} \int C_{PF_{eS}} dT$  as ordinates. Above 280°K, Kelley's equations have been used.

Substituting the values of each term thus obtained into the equation (15) and calculating  $J_P$ , we get the eighth column in the table 3, where the average value of  $J_P$  is 2.45. From this, it follows that the chemical constant of vapour sulphur  $S_2$  is equal to 2.45 and the equilibrium equation of (1) is

$$\begin{aligned} \log K_{PI} = \log p_{S_2} = & -\frac{17216}{T} + 3.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \int R \cdot E \left( \frac{3600}{T} \right) dT \\ & + \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_e} dT - \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_{eS}} dT + 2.45 \dots\dots\dots(16) \end{aligned}$$

The seventh and the last column in the table 3. show the comparison of the experimental values with the calculated values from equation (16).

Now if reciprocals of absolute temperatures are plotted as abscissae and common logarithms of the equilibrium constants as ordinates, we have the Fig 2, in which we see that there is a linear relation between  $\log p_{S_2}$  and  $1/T$ .

Let us consider the free energy of the formation of ferrous sulphide.



If we denote the equilibrium constant of this equation by  $K'_{PI}$

$$K'_{PI} = \frac{1}{K_{PI}}$$

$$\therefore \log K'_{PI} = -\log K_{PI} = -\log p_S \dots\dots\dots(18)$$

The free energy for the reaction (17) is represented as the following equation

$$\begin{aligned} \Delta F^\circ &= -RT \log K'_{PI} \\ &= -4.571T \log K'_{PI} \dots\dots\dots(19) \end{aligned}$$

From equation (18) and (19) we have

$$\Delta F^\circ = 4.571T \log p_S \dots\dots\dots(20)$$

Substituting the values of the last column of the table 3 into equation (20) and calculating free energy  $\Delta F^\circ$ , we obtain the table 4.

Fig. 2

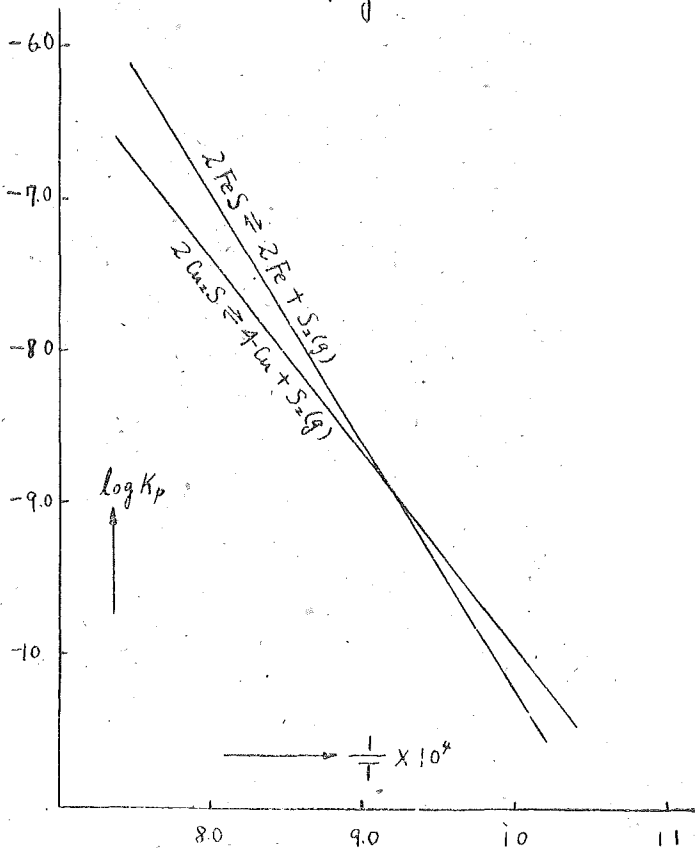
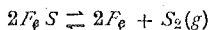


Table 3.



T°K	$-17216/T$	$3.5 \log T$	$\frac{1}{4.571} \int \frac{dT}{T^2} \int R \cdot E \left( \frac{3600}{T} \right) dT$	$\frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF, Fe} dT$	$-\frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF, S} dT$	$\log P_{S_2}(\text{obs})$	$J_P$	$\log p_{S_2}(\text{cal})$
973	-17.694	10.458	0.011	3.780	-9.674	-10.783	2.336	-10.664
1062	-16.211	10.591	0.015	4.065	-10.193	-9.304	2.429	-9.278

1073	-16.045	10.607	0.015	4.098	-10.261	-9.037	2.549	- 9.131
1082	-15.911	10.620	0.016	4.126	-10.304	-9.026	2.427	- 8.998
1125	-15.303	10.679	0.018	4.257	-10.538	-8.478	2.409	- 8.432
1129	-15.249	10.684	0.018	4.270	-10.564	-8.364	2.474	- 8.386
1144	-15.049	10.705	0.019	4.314	-10.648	-8.208	2.451	- 8.204
1172	-14.689	10.741	0.021	4.399	-10.787	-7.899	2.416	- 7.862
1173	-14.677	10.743	0.021	4.402	-10.787	-7.839	2.459	- 7.843
1273	-13.524	10.867	0.027	4.693	-11.288	-6.628	2.597	- 6.772
						aver	2.45	

Table 4.

T°K	973	1062	1073	1082	1125	1129	1144	1172	1173	1273
FD°	-47429	-45039	-44785	-44503	-43361	-43277	-42901	-42118	-42052	-39405

III. The theoretical calculation of dissociation pressures of cuprous sulphide in the reaction  $2C_{u_2}S \rightleftharpoons 4C_{u_2} + S_2(g)$



The dissociation pressure of cuprous sulphide is so small that we must determine it indirectly from the reduction equilibrium  $C_{u_2}S + H_2 \rightleftharpoons 2C_{u_2} + H_2S$  in the same manner as ferrous sulphide. But here the author calculates by using the chemical constant of sulphur vapour  $S_2$  which has been gained in the previous chapter.

Now if we represent the heat content of the reaction (21) as  $\Delta H$ , we see the following equation.

$$\Delta H = \Delta H_0 + 4 \int C_{P_{Cu_2}} dT + \int C_{P_{S_2}} dT - 2 \int C_{P_{Cu_2S}} dT \dots\dots\dots(22)$$

From the table of Miething, we see

$$\int_0^{298} C_{P_{Cu_2}} dT = 1180 \dots\dots\dots(23)$$

If we assume that the heat capacity of  $S_2$  is equal to that of oxygen and calculating from Eucken's equation  $C_P = \frac{7}{2} R + R \cdot E \left( \frac{3600}{T} \right)$ , the heat content of  $S_2$  is as follows.

$$\int_0^{298} C_{P_{S_2}} dT = 2071 \dots\dots\dots(24)$$

Concerning the heat capacity of cuprous sulphide at low temperatures, Anderson<sup>19)</sup> gave the following equation below 80°K.

$$C_P = D \left( \frac{92}{T} \right) + 2D \left( \frac{379}{T} \right)$$

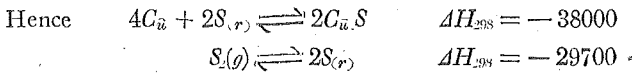
He also made actual measurements from 58°K to 292°K. Then up to 80°K we use the equation



$C_P = D \left( \frac{92}{T} \right) + 2D \left( \frac{379}{T} \right)$  and from 80°K to 298°K we calculate  $\int C_P dT$  graphically by using Anderson's data. The result is

$$\int_0^{298} C_{FeuS} dT = 3830 \dots\dots\dots (25)$$

Heat of reaction of  $2C_u + S_{(g)} \rightleftharpoons C_{u2}S$  has been determined by Wartenberg<sup>(33)</sup> who has obtained -1500 for  $\Delta H$  by direct method. While for the reaction  $S_2(g) \rightleftharpoons 2S_{(g)}$  Lewis and Landall<sup>(34)</sup> have given  $\Delta H_{298} = -29700$



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adding  $4C_u + S_2(g) \rightleftharpoons 2C_{u2}S \quad \Delta H_{298} = -67700$

Therefore in the reaction (21),  $\Delta H_{98}$  is equal to 67700.

$$\therefore \Delta H_{98} = 67700 \dots\dots\dots (26)$$

Substituting the equations (23), (24), (25) and (26) into the equation (22), we can calculate the value of  $\Delta H_0$ . The result is as follows.

$$\Delta H_0 = 68570 \dots\dots\dots (27)$$

Now if we denote the dissociation pressure of sulphur vapour  $S_2$  by  $p_{S_2}$ , the equilibrium equation of (21) is represented as

$$\log p_{S_2} = -\frac{\Delta H_0}{4.571T} + 3.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \left[ R \cdot E \left( \frac{3600}{T} \right) dT + \frac{4}{4.571} \int \frac{dT}{T^2} C_{Feu} dT - \frac{2}{4.571} \int \frac{dT}{T^2} C_{FeuS} dT + J_P \dots\dots\dots (28)$$

The value of  $\Delta H_0$  in the first term of this equation is given as 68570 from the equation (27) and the third term  $\frac{1}{4.571} \int \frac{dT}{T^2} \left[ R \cdot E \left( \frac{3600}{T} \right) dT \right]$  can be calculated from the table of Landolt-Börnstein. According to the table of Miething, the value of the fourth term is equal to 7.10 at 600°K.

$$\therefore \int_0^{600} \frac{dT}{T^2} C_{Feu} dT = 7.10$$

Above 600°K, we adopt the following equation by Kelley and  $\int_0^{600} C_{Feu} dT = 3012$  by Miething's table.

Finally let us consider the fifth and the sixth terms. Up to 298° we can calculate  $-\frac{2}{4.571} \int \frac{dT}{T^2} C_{FeuS} dT$  graphically from the experimental data of Anderson and over 298°K from the following equations which have been given by Kelley.

$$\begin{aligned} \alpha: C_{FeuS} &= 9.38 + 31.2 \cdot 10^{-5} T \\ \alpha \rightarrow \beta: \Delta H_{298} &= 1340 \\ \beta: C_{FeuS} &= 20.9 \end{aligned}$$

If we use the chemical constant  $J_{S_2} = 2.45$  obtained from the dissociation of ferrous sulphide and substitute it in the equation (28), we see the following equilibrium equation.

$$\log p_{S_2} = -\frac{15001}{T} + 3.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \left[ R \cdot E \left( \frac{3600}{T} \right) \right] nT + \frac{4}{4.571} \int \frac{dT}{T^2} \int C_{FeCu} dT - \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{FeCu:S} dT + 2.45 \dots \dots \dots (29)$$

Calculating each term of the equation (29), finally we have the results which are shown in the table 5. Substituting these values into the above equation and calculating the common logarithm of equilibrium constant  $\log K_P$ , we can determine the dissociation pressures of cuprous sulphide at different temperatures; The results are shown in the ninth column of the table 5.

Plotting the data of the second column as abscissae and the ninth column in the table 5. as ordinats, we see that the individual point falls beautifully upon a straight line as shown in the Fig. 2.

If we denote the equilibrium constant of the reaction  $4 C_{Cu} + S_2(g) \rightleftharpoons 2C_{Cu_2}S$  by  $K'_P$ , we have  $\log K' = -\log p_{S_2}$ .

Table 5.  
 $2C_{Cu_2}S \rightleftharpoons 4C_{Cu} + S_2(g)$

$T^\circ K$	$1/T$	$-15001/T'$	$3.5 \log$	$\frac{1}{4.571} \int \frac{dT}{T^2} \left[ R \cdot E \left( \frac{3600}{T} \right) \right] dT$	$\frac{4}{4.571} \int \frac{dT}{T^2} C_{FeCu} dT$	$-\frac{2}{4.571} \int \frac{dT}{T^2} \int C_{FeCu:S} dT$	$J_P$	$\log p_{S_2}$
1004	$9.960 \cdot 10^{-4}$	-14.941	10.506	0.012	8.624	-16.546	2.45	-9.895
1109	$9.017 \cdot 10^{-4}$	-13.527	10.657	0.017	9.120	-17.405	2.45	-8.688
1148	$8.711 \cdot 10^{-4}$	-13.067	10.710	0.019	9.295	-17.705	2.45	-8.298
1183	$8.453 \cdot 10^{-4}$	-12.680	10.755	0.021	9.448	-17.966	2.45	-7.972
1283	$7.794 \cdot 10^{-4}$	-11.692	10.879	0.027	9.867	-18.670	2.45	-7.139

Therefore the free energy of the reaction  $4C_{Cu} + S_2(g) \rightleftharpoons 2C_{Cu_2}S$  is represented by the following equation.

$$\Delta F^\circ = 4.571 T \log p_{S_2}$$

Substituting the values of the last column in the table 5 into the above equation, we obtain table 6.

Table 6.

$T^\circ K$	1004	1109	1148	1183	1283
$\Delta F^\circ$	-45411	-44042	-43544	-43109	-41867

As shown in the Fig 2, we see that the two lines of cuprous sulphide and ferrous sulphide cross each other. If we detrmine the temperature of the junction of these two lines, we find

$$T = 1090^\circ K \text{ or } 817^\circ C$$

Therefore it follows that the affinity of sulphur vapour  $S_2$  for iron is stronger than that of copper under  $81.7^\circ C$ , while above this temperature the affinity of copper for  $S_2$  becomes larger than that of iron conversely; in other words the affinity of copper and iron for sulphur vapour  $S_2$  is

related conversely with each other with 817°C as their turning point.

### IV. Dissociation equilibrium of hydrogen sulphide and determination of the chemical constant of hydrogen sulphide.



The equilibrium in the reaction  $2H_2S \rightleftharpoons 2H_2 + S_2(g)$  has been investigated by Preunner and Schupp<sup>15)</sup> and Randall and Bichowsky<sup>16)</sup> over a wide range of temperature. The values of  $\log K_P$  are given in the table 7.

Assuming that the heat capacity of diatomic sulphur is given by the same equation that Eucken has employed for oxygen, heat capacity of  $S_2$  is

$$C_P = \frac{7}{2} R + R \cdot E \left( \frac{3600}{T} \right)$$

For the heat capacity of hydrogen we take Eucken's formula

$$C_{PH} = \frac{7}{2} R + R \cdot E \left( \frac{5000}{T} \right)$$

For the heat capacity of hydrogen sulphide, we employ Meck's formula.

$$C_{PHS} = \frac{8}{2} R + R \cdot E \left( \frac{1690}{T} \right) + R \cdot E \left( \frac{3750}{T} \right) + R \cdot E \left( \frac{3850}{T} \right)$$

From the (30) equation, we obtain

Table 7.  
 $2H_2S \rightleftharpoons 2H_2 + S_2(g)$

investigator	temp $T^\circ K$	log $K$	investigator	temp $T^\circ K$	log $K$
Preunner, Schupp.	1023	-4.050	Preunner, Schupp.	1405	-1.586
" , "	1103	-3.420	Randall, Bichowsky.	1473	-1.286
" , "	1218	-2.610	" , "	1537	-0.980
" , "	1338	-1.928	" , "	1667	-0.514
Randall, Bichowsky.	1362	-1.804			

$$\begin{aligned} \Delta H &= \Delta H_0 + \int C_{PS} dT + 2 \int C_{H_2} dT - 2 \int C_{H_2S} dT \\ \therefore \Delta H &= \Delta H_0 + \frac{5}{2} RT + \int \left[ R \cdot E \left( \frac{3600}{T} \right) + 2R \cdot E \left( \frac{5000}{T} \right) - 2R \cdot E \left( \frac{1690}{T} \right) \right. \\ &\quad \left. - 2R \cdot E \left( \frac{3750}{T} \right) - 2R \cdot E \left( \frac{3850}{T} \right) \right] dT \dots\dots\dots(31) \end{aligned}$$

$\Delta H$  is a function of temperature, but over a small range, we may regard  $\Delta H$  as constant. Therefore we obtain the following formula as before.

$$\Delta H = \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot 4.571 \log \frac{K_{P2}}{K_{P1}}$$

With  $T_1 = 1023$  and  $T_2 = 1103$ , we obtain from the table 7  $\log K_{P_1} = -4.050$  and  $\log K_{P_2} = -3.420$ . Substituting these values into the above equation, we have

$$\Delta H_{1063} = 40620$$

Again substituting this value in the equation (31) and calculating  $\Delta H_0$ , the result is

$$\Delta H_0 = 37500$$

Accordingly the equilibrium equation of (30) is

$$\begin{aligned} \log K_P &= -\frac{37500}{4.571T} + 2.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \left[ R \cdot E \left( \frac{3600}{T} \right) + 2R \cdot T \left( \frac{5000}{T} \right) \right. \\ &\quad \left. - 2R \cdot E \left( \frac{1690}{T} \right) - 2R \cdot E \left( \frac{3750}{T} \right) - 2R \cdot E \left( \frac{3850}{T} \right) \right] dT + J_P \\ \therefore \log K_P &= -\frac{8204}{T} + 2.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \left[ R \cdot E \left( \frac{3600}{T} \right) + 2R \cdot E \left( \frac{5000}{T} \right) \right. \\ &\quad \left. - 2R \cdot E \left( \frac{1690}{T} \right) - 2R \cdot E \left( \frac{3750}{T} \right) - 2R \cdot E \left( \frac{3850}{T} \right) \right] dT + J_P \dots \dots \dots (32) \end{aligned}$$

In order to determine the value of  $J_P$  we substitute  $\log K_P$  shown in the table 8 into the equation (32) and then calculate each term of the above mentioned equation. The average value of  $J_P$  is as follows. (see Table 8.)

$$J_P = -3.26 \dots \dots \dots (33)$$

Table 8.  
 $2H_2S \rightleftharpoons 2H_2 + S_2(g)$

$T^\circ K$	$-8204/T$	$2.5 \log T$	$-\frac{1}{4.571} \int \frac{dT}{T^2} \int d\phi dT$	$\log K_P$	$J_P$
1023	-8.020	7.525	-0.208	-4.050	-3.347
1103	-7.438	7.606	-0.242	-3.420	-3.346
1218	-6.736	7.714	-0.291	-2.610	-3.297
1338	-6.132	7.816	-0.341	-1.928	-3.271
1362	-6.023	7.835	-0.349	-1.804	-3.267
1405	-5.839	7.869	-0.370	-1.586	-3.246
1473	-5.570	7.921	-0.400	-1.286	-3.237
1537	-5.338	7.967	-0.426	-0.980	-3.183
1667	-4.921	8.055	-0.481	-0.514	-3.167
					aver. -3.262

Hence we obtain following equation

$$\begin{aligned} \log K_P &= -\frac{8204}{T} + 2.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \left[ R \cdot E \left( \frac{3600}{T} \right) + 2R \cdot E \left( \frac{5000}{T} \right) - 2R \cdot E \left( \frac{1690}{T} \right) \right. \\ &\quad \left. - 2R \cdot E \left( \frac{3750}{T} \right) - 2R \cdot E \left( \frac{3850}{T} \right) \right] dT - 3.26 \dots \dots \dots (34) \end{aligned}$$

Let us now consider the value of the chemical constant of hydrogen sulphide. If we denote the chemical constant of vapour sulphur  $S_2$ , hydrogen and hydrogen sulphide by  $j_S$ ,  $j_{H_2}$  and  $j_{H_2S}$  respectively, the value of  $J_P$  in the equation (32) is



$$J_P = j_S + 2j_H - 2j_{HS} \dots\dots\dots(35)$$

The chemical constant of vapour sulphur  $S_2$  is equal to 2.45 as shown in the chapter II.

$$\therefore j_S = 2.45 \dots\dots\dots(36)$$

It is shown from the experiments that the chemical constant of hydrogen is

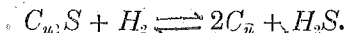
$$j_H = -3.685 \dots\dots\dots(37)$$

Substituting (33), (36) and (37) into the equation (37), we obtain

$$j_{HS} = -0.83$$

Therefore the chemical constant of hydrogen sulphide is equal to  $-0.83$ .

### V. Calculation of equilibrium constant of the reaction



Concerning the reduction equilibrium of cuprous sulphide by hydrogen, Jellinek and Zakouski<sup>(17)</sup> Britzke and Kaupustinsky<sup>(18)</sup> and Sano<sup>(19)</sup> have carried out this experiment. On the other hand, combining the dissociation equilibrium of cuprous sulphide and that of hydrogen sulphide, we can also determine the equilibrium constant of the reaction  $C_wS + H \rightleftharpoons 2C_u + HS$ . Therefore the author has compared the values thus obtained with the actual experimental data of Jellinek, Britzke and Sano.



adding  $2C_wS + 2H_2 \rightleftharpoons 4C_u + 2H_2S$



Then if we denote the equilibrium constant of (21), (30)<sup>1</sup> and (38) by  $K_{PI}$ ,  $K_{PII}$  and  $K_{PIII}$  respectively and represent the dissociation constant of the reaction (30), or  $2H_2S \rightleftharpoons 2H_2 + S_2(g)$  by  $K'_{PII}$ , we have

$$K_{PII} = \frac{1}{K'_{PII}}$$

$$\therefore K_{PI} \cdot K_{PII} = \frac{K_{PI}}{K'_{PII}} = K^2_{PIII}$$

Hence  $\log K_{PIII} = \frac{1}{2} (\log K_{PI} - \log K'_{PII}) \dots\dots\dots(39)$

Substituting the equation (29) and (34) in above formula, we find

$$\log K_{PIII} = -\frac{3399}{T} + \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{Pcu} dT - \frac{1}{4.571} \int \frac{dT}{T^2} \int C_{Pcu2S} + 0.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \left[ R \cdot E \left( \frac{1690}{T} \right) + R \cdot E \left( \frac{3750}{T} \right) + R \cdot E \left( \frac{3850}{T} \right) - R \cdot E \left( \frac{5000}{T} \right) \right] dT + 2.855 \dots(40)$$

Calculating the value of  $\log K_{PIII}$  by the use of this equation, the eighth column of the table 9 is obtained.

If we adopt the equation (5) instead of the equation (34) and calculate  $\log K_{PIII}$ , we have the

fifth column of the table 10. The table 10 and the Fig 3 show the comparison of the values thus calculated with the experimental data of Sano, Jellinek and Britzke. From the Fig 3.

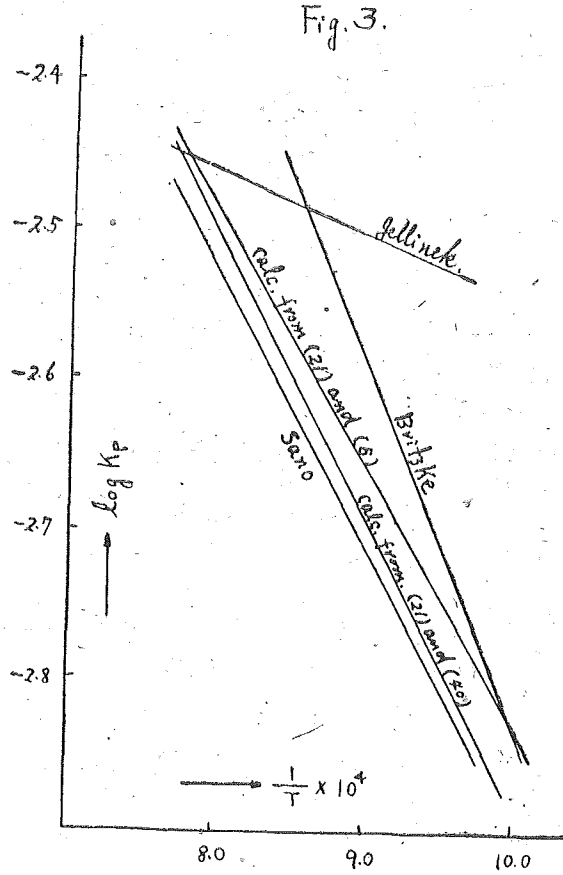


Table 9,



$T^\circ K$	$-3399/T$	$0.5 \log T$	$\frac{2}{4.571} \int \frac{dT}{T^2} \int C_{P_{Cu}} dT$	$-\frac{1}{4.571} \int \frac{dT}{T^2} \int C_{P_{Cu_2S}} dT$	$\frac{1}{4.571} \int \frac{dT}{T^2} \int \Delta \phi_{IT}$	$J_P$	$\log K_{III}$
1004	-3.385	1.501	4.312	-8.273	0.106	2.855	-2.884
1109	-3.065	1.522	4.560	-8.703	0.134	2.855	-2.697
1148	-2.961	1.530	4.648	-8.853	0.140	2.855	-2.641
1183	-2.873	1.536	4.724	-8.983	0.149	2.855	-2.592
1283	-2.649	1.554	4.934	-9.3351	0.173	2.855	-2.468

we see that Sano's values and those which have been calculated from the equation (40) coincide fairly with each other.

Table 10.



T°K	log $K_{PII}$ (Sano)	log $K_{PIII}$ (Britzke)	log $K_{PIII}$ (Jellenek)	log $K_{PIII}$ (calc from 5)	log $K_{PIII}$ (calc from 40)
1004	-2.890	-2.824	—	-2.828	-2.884
1109	-2.714	-2.602	—	-2.661	-2.697
1148	-2.660	-2.523	—	-2.608	-2.641
1183	-2.614	—	-2.482	-2.565	-2.592
1283	-2.496	—	-2.456	-2.458	-2.468

## VI. Conclusions.

I. From the dissociation pressures of ferrous sulphide, the chemical constant of diatomic sulphur has been determined. The result is

$$j_{S_2} = 2.45$$

And the equilibrium equation of the reaction  $2FeS \rightleftharpoons 2Fe + S_2(g)$  is represented as

$$\log p_{S_2} = -\frac{17216}{T} + 3.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \left\{ R \cdot E \left( \frac{3600}{T} \right) \right\} dT + \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{Fe} dT \\ - \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{FeS} dT + 2.45$$

II. Employing this chemical constant and the heat of formation of cuprous sulphide determined by Wartenberg, the dissociation pressures of cuprous sulphide at high temperatures have been theoretically calculated. The equilibrium equation of the reaction  $2Cu_2S \rightleftharpoons 4Cu + S_2(g)$  is

$$\log p_{S_2} = -\frac{15001}{T} + 3.5 \log T + \int \frac{dT}{T^2} \left\{ R \cdot E \left( \frac{3600}{T} \right) \right\} dT + \frac{4}{4.571} \int \frac{dT}{T^2} \int C_{Cu} dT \\ - \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{Cu_2S} dT + 2.45$$

In the dissociation of cuprous and ferrous sulphide, there is a linear relation between common logarithm of equilibrium constant and reciprocal of absolute temperature. And these two lines cross each other at  $T = 817^\circ C$

From this it follows that the affinity of copper for diatomic sulphur  $S_2$  is stronger than that of iron for  $S_2$  over  $817^\circ$ , while below this temperature, the affinity of iron for  $S_2$  is larger than that of copper for  $S_2$ .

III. The dissociation equilibrium of  $2H_2S \rightleftharpoons 2H_2 + S_2(g)$  is represented as

$$\log K_P = -\frac{8204}{T} + 2.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \left\{ R \cdot E \left( \frac{3600}{T} \right) + 2R \cdot E \left( \frac{5000}{T} \right) \right. \\ \left. - 2R \cdot E \left( \frac{1690}{T} \right) - 2R \cdot E \left( \frac{3750}{T} \right) - 2R \cdot E \left( \frac{3850}{T} \right) \right\} dT - 3.26$$

Adopting  $j_{S_2} = 2.45$  and  $j_{H_2} = -3.685$ , which have been determined from the experimental data and  $J_P = -3.26$ , we can calculate the chemical constant of hydrogen sulphide. The result is

$$j_{H_2S} = -0.83$$

IV. Combining the equation (21) with the equation (34) and with the (5) respectively, the values of  $\log K_P$  in the reaction  $Cu_2S + H_2 \rightleftharpoons 2Cu + H_2S$  can be determined. The following table shows the values thus obtained.

$T^\circ K$	1004	1109	1148	1183	1283	remark
$\log f_{H_2S}/f_{H_2}$	-2.828	-2.661	-2.608	-2.565	-2.458	calc. from (21) and (5)
	-2.884	-2.697	-2.641	-2.592	-2.468	" " (21) and (40)

### Literature.

- 1) E. V. Britzke and A. F. Kaupustinsky: Z anorg. allg. chem. 194 (1930). 333.
- 2) L. Biener: Trans. Amer. Soc. Metals, 25 (1937) 454.
- 3) K. Jellinek and J. Zakowsky: Z. anorg. allg. chem. 142 (1925). 1.
- 4) K. Sano: Jour. chem. Inst. Japan. vol (1939) 579.
- 5) S. Matoba and T. Unotoro: Jour. iron. steel. Inst. Japan. vol. 28 (1942). 653.
- 6) Lewis and Landall: Schenk; physik. chem. der Eisenhiitt. I. 265.
- 7) Miething: Tabellen zur Berechnung des gesamten und freien Wärmehalts fest Körper.
- 8) Kelley: Contribution to the data on theoretical metallurgy II. P. 27.
- 9) Anderson: Jour. Amer. chem. Soc. vol. 53 (1931) P. 482.
- 10) Landolt-Börnstein: Physikplische chemische tabellen I. Erg-Bd S 702~707.
- 11) Schenk: Physikalische chemie der Eisenhiittpro. I. S. 297.
- 12) Anderson: Jour. Amer. chem. Soc. vol. 54 (1932) P. 107.
- 13) Wartenberg: Z. physik. chem. 67. 446 (1909).
- 14) Lewis and Landall: Thermodynamics P.542.
- 15) Preunner and Schupp: Zeit. physik. chem. 68. 157 (1909).
- 16) Randall and Bichowsky: Jour. Amer. chem. Soc. 46. 368 (1918).
- 17) Jellinek and Zakowski: Z. anorg. allg. chem. Bd 142 (1925). S. 21.
- 18) Britzke and Kaupustinsky: Z. anorg. allg. chem. Bd. 204 (1932). S. 95.
- 19) Sano: Jour. Japan. Institute. Metals. vol. 3 (1939). P. 718.