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Thermodynamical studies of copper metallurgy. (Report I)

By

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(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.

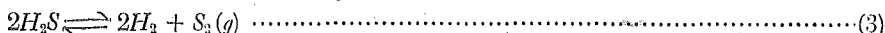
When we put forward the chemico-physical consideration on many chemical reactions occurring in the process of copper smelting, we must first of all calculate the affinity between copper and sulphur.

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.

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

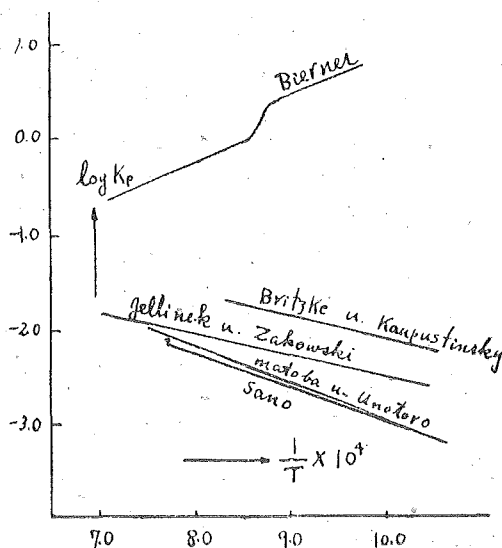
$$K_{PIII} = \frac{p_{H_2}^2 \cdot p_{S_2}}{p_{H_2S}^2}$$

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

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

Though the reduction equilibrium of ferrous sulphide by hydrogen has been investigated by E. V. Britzke and A. F. Kaupustinsky¹⁾, L. Biener²⁾, K. Jellinek and Zakowski³⁾, K. Sano⁴⁾ and S. Matoba and T. Unotoro⁵⁾ 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.

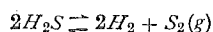
$T^{\circ} K$	$\log K_{PI}$	$\log K_{PII}$	$\log K_{PIII}$	investigators
976	-10.783	-3.126	-4.531	Matoba and Unotoro.
1062	- 9.304	-2.783	-3.738	Sano.
1073	- 9.037	-2.694	-3.649	Matoba and Unotoro.
1082	- 9.026	-2.725	-3.576	Sano.
1125	- 8.478	-2.615	-3.248	"
1129	- 8.364	-2.573	-3.218	Matoba and Unotoro.
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⁽⁵⁾,

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

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	$T^{\circ} K$	$\log K_{PIII}(\text{obs})$	$\log K_{PIII}(\text{calc.})$
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 constant pressure, we have

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

ΔH is a function of temperature, but we can regard ΔH 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 ΔH is constant between these temperatures and then integrate the equation (6), we find

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

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

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

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

$$\Delta H = \Delta H_0 + 2 \int C_{PF\epsilon} dT + \int C_{PS} dT - 2 \int C_{PF\epsilon S} dT \quad (9)$$

Miething's table⁷⁾ shows,

$$\int_0^{200} C_{PF\epsilon} dT = 1007$$

Kelley⁸⁾ gives the following equation as the heat capacity of iron.

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

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

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

From these equations, we can calculate as follows.

$$\int_0^{1072} C_{PF\epsilon} dT = 7937 \quad (10)$$

The heat capacity of ferrous sulphide $F\epsilon S$ at low temperature was determined by Anderson⁹⁾ from $57.9^\circ K$ to $296.0^\circ K$. As the heat capacity below $100^\circ K$, he also gave the following equation.

$$C_{PF\epsilon S} = D\left(\frac{205}{T}\right) + E\left(\frac{370}{T}\right) \quad (11)$$

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

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

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

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

Accordingly, if we adopt equation (11) from $0^\circ K$ to $100^\circ K$ and above $290^\circ K$ 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,

$$\int_0^{1072} C_{PF\epsilon S} dT = 14623 \quad (12)$$

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,

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

If we calculate ΔH , substituting (8), (10), (12) and (13) into the equation (9), we have

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

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

$$\begin{aligned} \log K_{PI} = \log p_{S_2} = & -\frac{\Delta H_0}{4.571T} + 3.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \int R \cdot E \left(\frac{3600}{T} \right) dT \\ & + \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_6} dT - \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_6S} dT + J_P \end{aligned}$$

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

$$\begin{aligned} \log K_{PI} = \log p_{S_2} = & -\frac{17216}{T} + 3.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \int R \cdot E \left(\frac{3600}{T} \right) dT \\ & + \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_6} dT - \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_6S} dT + J_P \quad \dots\dots\dots (15) \end{aligned}$$

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⁽¹⁰⁾ and the term $\frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_6} dT$ has been from Schenk's table⁽¹¹⁾. For the values of $-\frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_6S} dT$ below 280°K, the author has taken the graphical method, plotting various absolute temperatures as abscissae against $\frac{1}{T^2} \int C_{PF_6S} dT$ as ordinates. Above 280°K, Kelley's equations have been used.

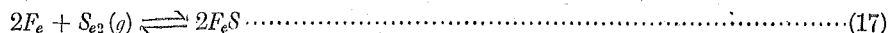
Substituting the values of each term thus obtained into the equation (15) and calculating J_P , we get the eighth column in the table 3, where the average value of J_P is 2.45. From this, it follows that the chemical constant of vapour sulphur S_2 is equal to 2.45 and the equilibrium equation of (1)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

$$\begin{aligned} \log K_{PI} = \log p_{S_2} = & -\frac{17216}{T} + 3.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \int R \cdot E \left(\frac{3600}{T} \right) dT \\ & + \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_6} dT - \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{PF_6S} dT + 2.45 \quad \dots\dots\dots (16) \end{aligned}$$

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}

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

$\therefore \log K'_{PI} = -\log K_{PI} = -\log p_{S_2} \dots\dots\dots(18)$

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

$$\Delta F^\circ = 4.571T \log p_{S_2} \dots\dots\dots(20)$$

Substituting the values of the last column of the table 3 into equation (20) and calculating free enrrgy ΔF° , we obtain the table 4.

Fig. 2

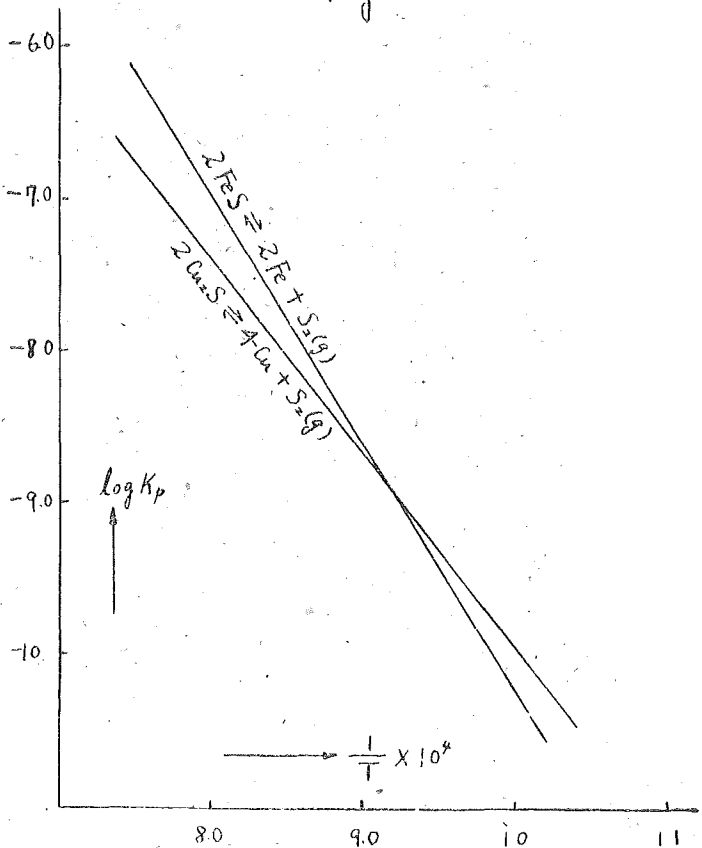


Table 3.
 $2FeS \rightleftharpoons 2Fe + S_2(g)$

$T^\circ K$	$-17216/T$	$3.5 \log T$	$\frac{1}{4.571} \int \frac{dT'}{T'^2} \int \frac{dT'}{T'} \cdot R \cdot E \left(\frac{3600}{T'} \right) dT'$	$\frac{2}{4.571} \int \frac{dT}{T^2} \int \frac{dT}{T} C_{PF, Fe} dT$	$-\frac{2}{4.571} \int \frac{dT}{T^2} \int \frac{dT}{T} C_{PF, S} dT$	$\log P_{S_2}(\text{obs})$	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
F ^o	-47429	-45039	-44785	-44503	-43361	-43277	-42901	-42118	-42052	-39405

III. The theoretical calculation of dissociation pressures of cuprous sulphide in the reaction $2C_{u2}S \rightleftharpoons 4C_u + S_2(g)$



The dissociation pressure of cuprous sulphide is so small that we must determine it indirectly from the reduction equilibrium $C_{u2}S + H_2 \rightleftharpoons 2C_u + H_2S$ 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 ΔH , we see the following equation.

$$\Delta H = \Delta H_0 + 4 \int C_{P_{Scu}} dT + \int C_{P_S} dT - 2 \int C_{P_{C_{u2}S}} dT \dots\dots\dots(22)$$

From the table of Miething, we see

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

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, Anderson¹²⁾ gave the following equation below 80°K.

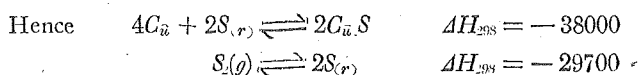
$$C_P = D\left(\frac{92}{T}\right) + 2D\left(\frac{379}{T}\right)$$

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

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

Heat of reaction of $2C_u + S_{(r)} \rightleftharpoons C_{u2}S$ has been determined by Wartenberg⁽¹³⁾ who has obtained -1500 for ΔH by direct method. While for the reaction $S_2(g) \rightleftharpoons 2S_{(r)}$ Lewis and Landall⁽¹⁴⁾ have given $\Delta H_{298} = -29700$



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

Therefore in the reaction (21), ΔH_{298} is equal to 67700.

$$\therefore \Delta H_{298} = 67700 \quad \dots\dots\dots (26)$$

Substituting the equations (23), (24), (25) and (26) into the equation (22), we can calculate the value of ΔH_0 . The result is as follows.

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

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

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

The value of ΔH_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.

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

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.

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

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.

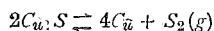
$$\log p_{S_2} = -\frac{15001}{T} + 3.5 \log T + \frac{1}{4.571} \int \frac{dT}{T^2} \int R \cdot E \left(\frac{3600}{T} \right) dT + \frac{4}{4.571} \int \frac{dT}{T^2} \int C_{Feu} dT - \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{Feu:S} dT + 2.45 \dots \dots \dots (29)$$

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 $4 C_u + S_2(g) \rightleftharpoons 2 C_{u_2}S$ by K'_P , we have $\log K' = -\log p_{S_2}$.

Table 5.



$T^\circ K$	$1/T$	$-15001/T$	$3.5 \log$	$\frac{1}{4.571} \int \frac{dT}{T^2} \int R \cdot E \left(\frac{3600}{T} \right) dT$	$\frac{4}{4.571} \int \frac{dT}{T^2} \int C_{Feu} dT$	$-\frac{2}{4.571} \int \frac{dT}{T^2} \int C_{Feu:S} dT$	J_P	$\log p_{S_2}$
1004	$9.960.10^{-4}$	-14.941	10.506	0.012	8.624	-16.546	2.45	-9.895
1109	$9.017.10^{-4}$	-13.527	10.657	0.017	9.120	-17.405	2.45	-8.688
1148	$8.711.10^{-4}$	-13.067	10.710	0.019	9.295	-17.705	2.45	-8.298
1183	$8.453.10^{-4}$	-12.680	10.755	0.021	9.448	-17.966	2.45	-7.972
1283	$7.794.10^{-4}$	-11.692	10.879	0.027	9.867	-18.670	2.45	-7.139

Therefore the free energy of the reaction $4C_u + S_2(g) \rightleftharpoons 2C_{u_2}S$ 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
ΔF°	-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 $817^\circ C$, 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 $2\text{H}_2\text{S} \rightleftharpoons 2\text{H}_2 + \text{S}_2(g)$ has been investigated by Preunmer and Schupp¹⁵⁾ and Randall and Bichowsky¹⁶⁾ 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

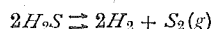
$$C_{PH} = \frac{7}{2} R + R \cdot E\left(\frac{5000}{T}\right)$$

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.



investigator	temp $T^{\circ}\text{K}$	$\log K$	investigator	temp $T^{\circ}\text{K}$	$\log K$
Preunmer, Schupp.	1023	-4.050	Preunmer, 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			

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

ΔH is a function of temperature, but over a small range, we may regard ΔH 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 ΔH_0 , the result is

$$\Delta H_0 = 37500$$

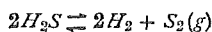
Accordingly the equilibrium equation of (30) is

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

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.



$T^\circ K$	$-8204/T$	$2.5 \log T$	$-\frac{1}{4.571} \int \frac{dT}{T^2} \int d\phi dT$	$\log K_P$	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

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

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_2} , j_{H_2} and j_{H_2S} respectively, the value of J_P in the equation (32) is



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

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

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

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

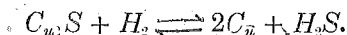
$$j_H = -3.685 \quad (37)$$

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

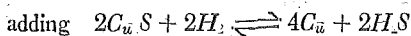
$$j_{HS} = -0.83$$

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⁽¹⁷⁾ Britzke and Kaupustinsky⁽¹⁸⁾ and Sano⁽¹⁹⁾ 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 $CuS + H \rightleftharpoons 2Cu + HS$. Therefore the author has compared the values thus obtained with the actual experimental data of Jellinek, Britzke and Sano.



Then if we denote the equilibrium constant of (21), (30)¹ 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

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

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

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

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

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

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.

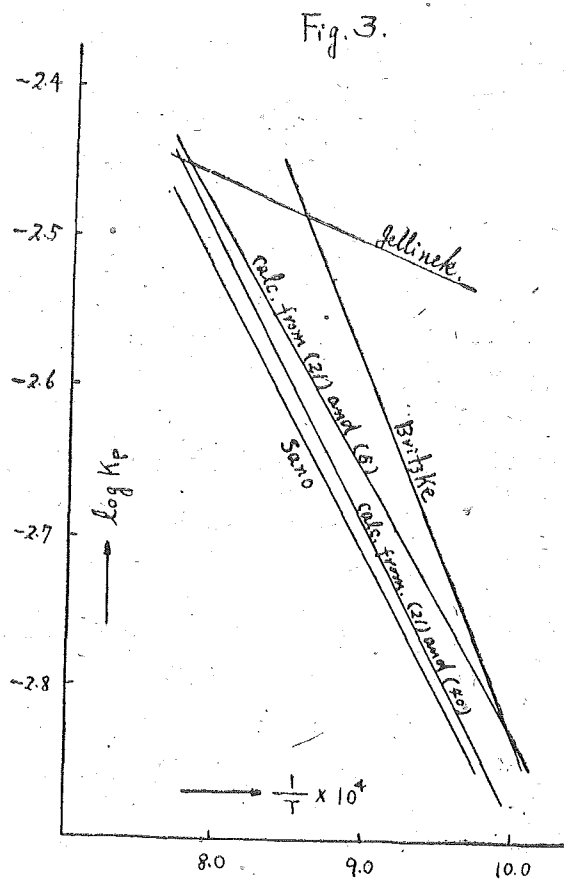


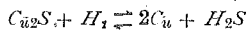
Table 9,



$T^{\circ}K$	$-3399/T$	$0.5 \log T$	$\frac{2}{4.571} \int \frac{dT}{T^2} \int \frac{C_{P_{Cu}} dT}{C_{P_{Cu_2S}} dT}$	$-\frac{1}{4.571} \int \frac{dT}{T^2} \int \frac{C_{P_{Cu_2S}} dT}{C_{P_{Cu}} dT}$	$\frac{1}{4.571} \int \frac{dT}{T^2} \int \frac{d\phi}{dT}$	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	-9.335	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} (Jelleneke)	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

$$\log p_{S_2} = -\frac{15001}{T} + 3.5 \log T + \int \frac{dT}{T^2} \left[R \cdot E \left(\frac{3600}{T} \right) \right] dT + \frac{4}{4.571} \int \frac{dT}{T^2} \int C_{Pcu} dT \\ - \frac{2}{4.571} \int \frac{dT}{T^2} \int C_{Pcu_2S} dT + 2.45$$

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° , 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

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

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 $C_uS + H_2 \rightleftharpoons 2Cu + H_2S$ 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)

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