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Reduction Equilibria of Iron Oxides. II
Measurement of the Equilibrium of the Reaction, $FeO(l)+CO=Fe(s)+CO_2$*

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Synopsis

The author measured the equilibrium of the reaction, $FeO(l)+CO=Fe(s)+CO_2$, at the range from 1,370°C to 1,490°C, and the following equation was obtained as the temperature function of the equilibrium constant :

$$\log K_{CO\text{-}CO_2} = \log \frac{p_{CO}}{p_{CO_2}} = \frac{7,680}{T} - 5.37. \qquad \text{(a)}$$

Then, the author calculated the equilibrium constant of the reaction, $FeO(l)+H_2=Fe(s)+H_2O$, from equation (a) and the equilibrium constant of the water gas reaction and the following equation was obtained as the temperature function of log K:

$$\log K_{H_2\text{-}H_2O} = \log \frac{p_{H_2O}}{p_{H_2}} = \frac{6,390}{T} - 4.07. \qquad \text{(b)}$$

Finally the author calculated the dissociation pressure of molten FeO and the following equation was obtained as the temperature function of P_{O_2}:

$$\log P_{O_2}^{\frac{1}{2}} = -\frac{23,000}{T} + 10.39. \qquad \text{(c)}$$

I. Introduction

Many studies have been made on the equilibrium of this reaction at the temperature below 1,100°C.

Murphy, Wood and Jominy(1) measured the equilibrium of this reaction by passing the CO-CO_2 mixed gas of various ratio on the pure iron and detecting whether sample was oxidized or not at the temperature range from 1,093°C to 1,427°C.

But they performed two measurements only at the range of molten FeO, that is, 1,371°C and 1,427°C. Plotting log K against $1/T$ from their results, they calculated ΔH from the tangent of the straight line and heat of fusion of FeO:

$FeO(s)+CO=Fe(s)+CO_2$, $\Delta H=-4,600$ cal/g mol,

$FeO(l)+CO=Fe(s)+CO_2$, $\Delta H=-31,300$ cal/g mol,

Heat of fusion of $FeO=26,700$ cal/g mol.

Furthermore, Schenck(2) proposed the equation (1) and (2) as the temperature function of equilibrium constant from their result.

$FeO(s)+CO=Fe(s)+CO_2$ (1,093°C～1,360°C),

$$\log K = \log \frac{p_{CO_2}}{p_{CO}} = +\frac{4,600}{4,573T} - 1.19, \qquad (1)$$

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* The 12th report of the Research Institute of Mineral Dressing and Metallurgy.

(1) D. W. Murphy, W. P. Wood and W. E. Jominy, Trans. Am. Soc. Steel Treat., 19 (1932), 4.

(2) H. Schenck, *Physik. Chem. Eisenhüttenproz.*, 1 (1932) 141, 292.

$$\mathrm{FeO(l)} + \mathrm{CO} = \mathrm{Fe(s)} + \mathrm{CO_2} \quad (1{,}360^\circ\mathrm{C}\sim 1{,}427^\circ\mathrm{C}),$$

$$\log K = \log\frac{p_{\mathrm{CO_2}}}{p_{\mathrm{CO}}} = +\frac{31{,}300}{4.573T} - 4.57, \qquad (2)$$

Table 1. Calculated values of Schenck.

Equilibrium temp.		log K	CO %	
T°(K)	t°(C)			
1,600	1,327	−0.56	78.2	Fe(s) + Wüstit
1,643	1,370	−0.58	79.2	Fe(s) + Wüstit + FeO(l)
1,650	1,377	−0.60	80.0	Fe(s) + FeO(l)
1,700	1,427	−0.73	84.5	〃
1,750	1,477	−0.84	87.4	〃
1,792	1,519	−0.93	89.5	Fe(s) + Fe(l) + FeO(l)

where FeO does not mean the chemically pure compound but Wüstit, and changes its O_2 concentration along JD line of Fe-O diagram as shown in Fig. 1..

Table 1 gives calculated values of log K and CO% from the equation (1) and (2) at several temperatures.

As to O_2% of D in Fig. 1, 22.7% was obtained by Vogel and Martin(3) and 22.77% by Pfeil.(4) Also as to O_2% of δ-Fe at the melting point, 0.21% was obtained by Rosenhain, Tritton and Hanson.(5)

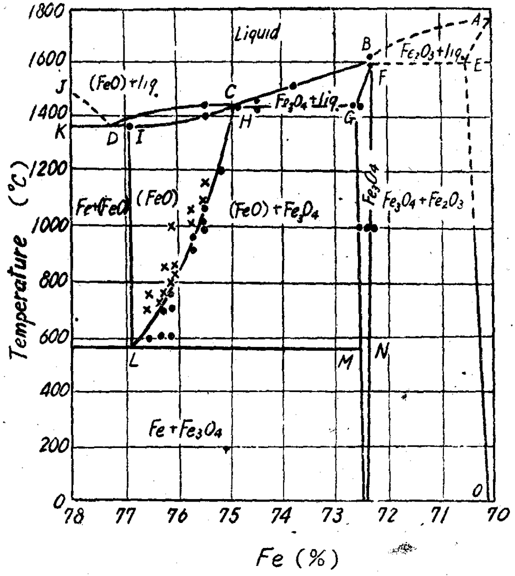

Fig. 1. Fe-O diagram

Furthermore, as to the melting point of Wüstit, coexist with δ-Fe, hitherto reported values are summerized as follows :

Authors	Melting point in °C
Vogel and Martin(3)	1,380
Pfeil(4)	1,370
Herty and co-workers(6)	1,355
Rosenhain, Tritton and Hanson(5)	1,370
Oberhoffer and Keil(7)	1,390
Murphy and co-workers(1)	1,360±10
Groebler and Oberhoffer(8)	1,377
Schönert(9)	1,380

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(3) R. Vogel and E. Martin, Arch. Eisenhüttenwes., 6 (1933), 237.

(4) Pfeil, J. Iron Steel Inst., 117 (1931), No. 1, 237.

(5) W. Rosenhain, F. S. Tritton and Hanson, J. Iron Steel Inst., 60 (1924) No. 1, 98.

(6) C. H. Herty and co-workers, Ind. Eng. Chem., 21 (1929), 52.

(7) P. Oberhoffer and O. von Keil, Stahl u. Eisen, 44 (1924), 220.

(8) H. Groebler & P. Oberhoffer, Stahl u. Eisen, 47 (1927), 1987.

(9) F. Schönert, Z. anorg. allgem. Chem., 154 (1926), 220.

The melting point of Fe, saturated with O_2, lowered at some degree and 1,517°C was reported by Rosenhain, Tritton and Hanson.(5) Therefore, the equilibrium of this reaction should be established from 1,370~1,380°C, melting point of Wüstit, to 1,517°C, melting point of Fe saturated with O_2. The author measured this equilibrium at the range from 1,360°C to 1,490°C by the statical method and checked the result of Murphy, Wood and Jominy.(1)

II. Experimental apparatus

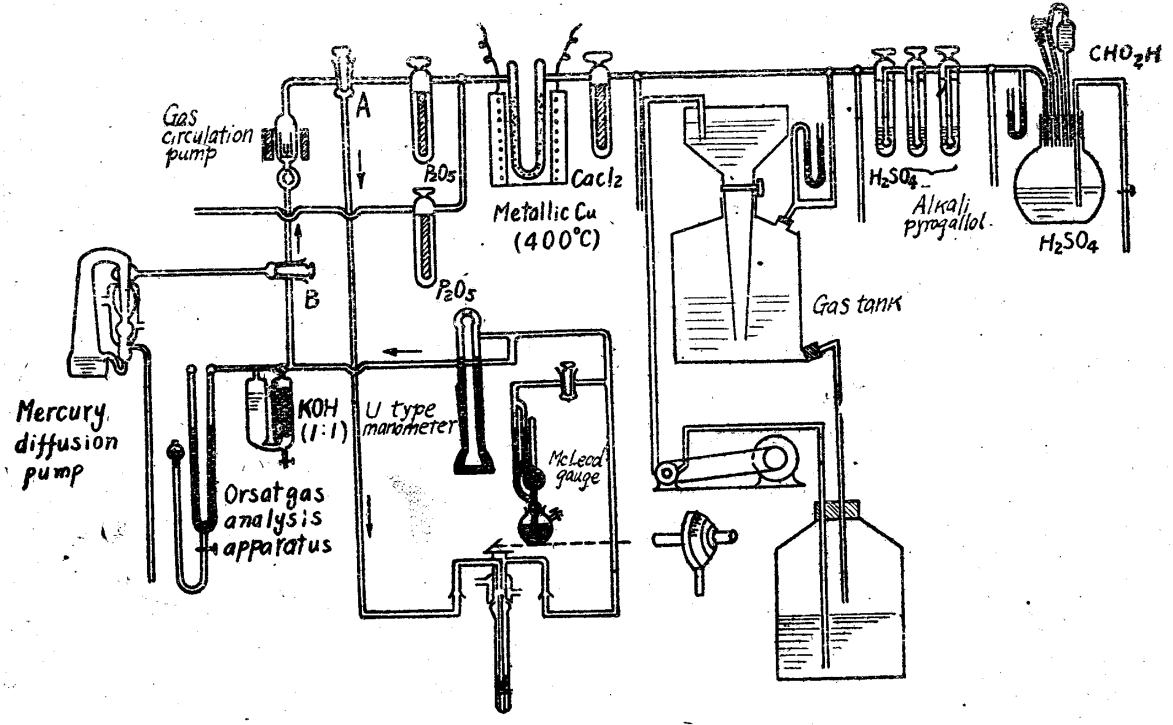

Fig. 2 Experimental apparatus.

Fig. 2 shows the outline of the experimental apparatus. CO gas, which was produced by dropping formic acid into H_2SO_4 heated at 100°~120°C, and O_2 contained in the gas was removed by the washing bottle filled with alkali pyrogallol solution. Then, it was reserved in a gas tank with the fluid paraffin.

Then CO gas in the tank was cleaned by passing it through towers with $CaCl_2$, metallic copper heated at 400°C and P_2O_5, and finally was introduced in the apparatus.

The sample of iron oxide charged into the iron crucible, protected by the tamman tube was set into the reaction tube of silica. Frequently iron oxide was mixed with the iron powder in order to decrease the temperature difference between the crucible and iron oxide.

The high frequency induction furnace was used for its heating and temperature was measured by the optical pyrometer. The optical pyrometer was corrected by comparing the temperature of molten FeO under N_2 atmosphere with the thermo-electric pyrometer with Pt-Pt·Rh couple.

The adhesive oil to the iron crucible when it was machined, as wwashed up with petroleum, alcohol and ether. At first blank iron crucible was set into the reaction tube and heated in vacuum. After cooling, 4~5 g of iron oxide, dried in the air bath at 120°C for 2 hr. previously, was charged and heated slowly to about 1,000°C in vacuum to remove the moisture and gas in the sample.

The degree of vacumm was measured by the McLeod gauge. When the apparatus attained the desired degree of vacuum, cock A was opened and filled with CO gas slowly to 730~740 mm Hg, measuring the U tube manometer. Then cook A was closed and sample was heated at a desired temperature, circulating CO gas in the apparatus to the direction shown in Fig. 2 by the piston gas circulating pump. Because the iron oxide and gas attained the equilibrium in about 3 hr., the sample was kept about 3~4 hr. at a constant temperature, then cooled rapidly.

The sample, attained the equilibrium with gas, was crushed under 200 mesh, and analysed after removing iron powder by magnet. Quantities of O_2 and metallic Fe were determined by the H_2 reduction method and mercury chloride method respectively, then quantity of total Fe was determined by $100-O_2\%$. CO% in gas was determined by the Orsat gas analysis method.

III. Sample

As the sample of iron oxide, the author used the pure Fe_2O_3 made by Merck or FeO prepared by decomposing the iron oxalate by heating in vacuum. The latter changed its O_2 concentration more or less whenever it was prepared, but it contained always about 20~22% O_2. Therefore small amount of Fe_2O_3 was added to FeO at first so that O_2 content of the sample might contain some excess than the equilibrium value.

Table 2. Compositions of FeO, prepared from ferrous oxalate.

No. of sample	Results of analysis		
	T Fe%	Metallic Fe%	O_2 %
1	78.48	9.49	20.00
2	79.48	9.88	21.04
3	79.26	8.41	21.11
4	79.95	9.98	20.25
5			20.33
6			22.86
8			21.43
9			22.22

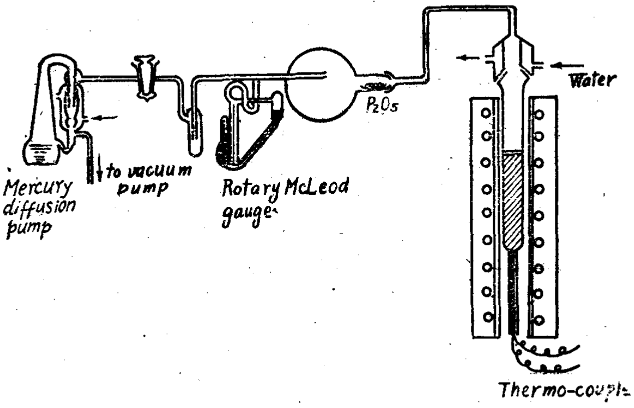

Fig. 3 Apparatus for preparation of FeO.

Fig. 3 shows the apparatus for preparation of FeO. At first 40~50 g of ferrous oxalate, made by Merck, was charged directly in the reaction tube covered with a small screen dish, then heated slowly in vacuum at the heating rate of 100°C/hr to 550°C and kept at 850°C for 2 hrs, finally quenched rapidly.

Compositions of iron oxide, prepared by this process, are shown in Table 2. Günther and Reheeg(10) reported already that they succeeded in obtaining FeO of

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(10) Günther, P. L. and H. Reheeg: Z. anorg. allgem. Chem., 243 (1939), 60.

99.98% purity. Although FeO, the author manufactured, was less pure than this for the reason of large amount preparation at a time, it could be used as the sample if its O_2 concentration was controlled before the experiment.

IV. Primary experiment

The temperature difference between iron crucible and sample in it could not be avoided during the experiment, because the iron crucible was used as a heating body in the high frequency induction furnace coil.

Especially this temperature difference was remarkable at the initial stage of experiment. In order to prevent this difference and to accelerate the reaction, small amount of reduced iron powder was mixed with the sample as previously mentioned, and the dimension of iron crucible was changed according to the experimental temperature.

Using so thicker iron crucible as to correspond to the increased temperature and placing it as shallow as possible in the protector of tamman tube, the author prevented the melting of iron crucible during the experiment.

Dimensions of crucibles used are shown in Fig. 4. As the preliminary experiment, the author investigated how much times were necessary to attain equilibrium when these crucibles were used.

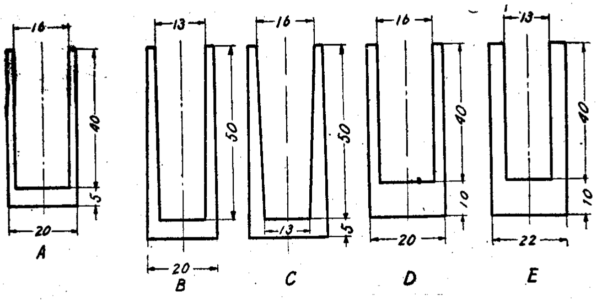

Fig. 4 Dimensions of used crucibles.

Table 3 gives relations between CO% in gas and the melting time when crucible A, B and C were used. From these results, all of experiments were kept constant temperature for 3∼4 hr.

Table 3. Time required to attain the equilibrium at each crucibles.

Classification of crucible	No. of experiment	Melting temp. °C	Sample	CO_2 %					
				30min	60 min	120min	180min	210min	240min
A	7 8. 9	1,413∼1,416	Fe_2O_3 3 g Iron powder 1 g	11.1	13.6	14.6	14.8		
B	10. 11	1,455	Fe_2O_3 4 g Iron powder 1 g		6.5	8.7	10.6		11.0
C	15	1,436	Fe_2O_3 3 g Iron powder 1 g		9.0	9.6	11.3		11.5
D	16	1,450	Fe_2O_3 3 g Iron powder 1 g			8.8		10.0	10.3

V. Results of experiment

(A) *Determination of the temperature function of the equilibrium constant.* Table 4 gives relations between gas compositions and equilibrium temperatures in the experiment. Plotting CO% in gas against temperature from experimental results, Fig. 5 was obtained. In Fig. 5 the calculated values from equation (2) are also shown for comparison.

Table 4. Experimental results.

No. of experiment	Sample	Classification of crucible	Equilibrium temp.		Time	Gas composition		$K=\frac{p_{CO_2}}{p_{CO}}$	log K	$\frac{1}{T}$
			t°C	°K	in min	CO_2%	CO%			
7	Fe_2O_3 3 g, Iron powder 1 g	A	1,414	1,687	180	14.8	85.2	0.174	−0.760	5.93
9	〃	A	1,413	1,686	180	14.6	85.4	0.171	−0.767	5.93
11	〃	B.	1,455	1,728	180	11.0	89.0	0.124	−0.970	5.79
15	〃	C	1,436	1,709	180	11.5	88.5	0.130	−0.886	5.85
16	〃	C	1,450	1,723	180	10.3	89.7	0.115	−0.939	5.80
17	〃	C	1,445	1,718	180	11.6	88.4	0.131	−1.883	5.82
18	〃	A	1,400	1,673	180	14.5	85.5	0.170	−0.770	5.98
21	〃	D	1,445	1,718	180	11.6	88.4	0.131	−0.883	5.82
23	〃	D	1,448	1,721	240	11.6	88.4	0.131	−0.883	5.82
25	FeO(Sample 6) 4 g Iron powder 1 g	D	1,470	1,743	240	10.3	89.7	0.115	−0.939	5.74
28	FeO(Sample 6) 3.5g Iron powder 0.5g	E	1,479	1,752	240	8.5	91.5	0.093	−1.032	5.71
29	FeO(Sample 8) 4 g Iron powder 0.5g	E	1,479	1,752	360	8.8	91.2	0.096	−1.018	5.71
30	FeO(Sample 8) 4 g Iron powder 0.5g	E	1,479	1,752	180	8.8	91.2	0.096	−1.016	5.71
31	〃	E	1,490	1,763	240	8.7	91.3	0.095	−1.021	5.67
32	〃	E	1,490	1,763	240	9.8	90.2	0.108	−0.964	5.67
35	FeO(Sample 9+10) 4 g Iron powder 0.5g	A	1,380	1,653	180	15.5	84.5	0.183	−0.737	6.05
36	〃	A	1,390	1,663	180	14.9	85.1	0.175	−0.757	6.01
38	Fe_2O_3 4 g, Iron powder 0 5 g	A	1,375	1,648	240	14.7	85.3	0.172	−0.764	6.07
39	〃	A	1,368	1,641	150	16.7	83.3	0.200	−0.698	6.09
40	〃	A	1,370	1,643	240	17.0	83.0	0.204	−0.689	6.09
41	〃	A	1,365	1,638	240	18.0	82.0	0.219	−0.659	6.11

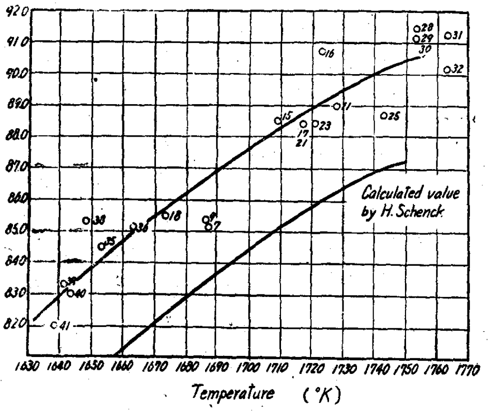

Fig. 5. Relation between CO% in gas and temperature.

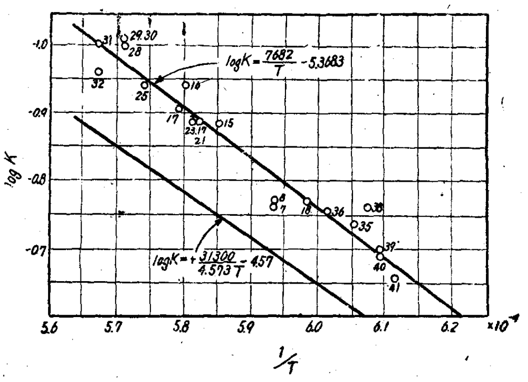

Fig. 6. Relation between Log K and $1/T$

The equilibrium constant of this reaction was given as follows:

$$K=\frac{p_{CO_2}}{p_{CO}}.$$

Now plotting log K against $1/T$, Fig. 6 was obtained and the temperature function of log K becomes as follows:

$$\log K=\log\frac{p_{CO_2}}{p_{CO}}=\frac{7{,}680}{T}-5.37, \tag{3}$$

$$\Delta F^{\circ}=24.6\,T-35{,}200. \tag{4}$$

Calculating values of K and CO% from the equation (3) at some temperatures, data in Table 5 were obtained showing good agreement with experimental results.

Table 5. Calculated values of K and CO% from equation (3).

Equilibrium temp.		log K	$K=\frac{CO_2}{CO}$	CO%
C°	°K			
1,360	1,633	−0.664,1	0.217	82.2
1 400	1,673	−0.776,5	0.167	85.7
1,440	1,713	−0.883,8	0.131	88.4
1,480	1,753	−0.986,1	0.103	90.6

(B) *Compositions of iron oxide.* Compositions of oxide which maintain the equilibrium with CO-CO_2 mixed gas at several temperatures are shown in Table 6. These oxides correspond to the oxide which coexist with δ-Fe saturated with O_2, and its O_2 concentration have been reported already by Rosenhain, Tritton and Hanson,(5) Vogel and Martin(3), Pfeil(4), but no one has ever investigated systematically.

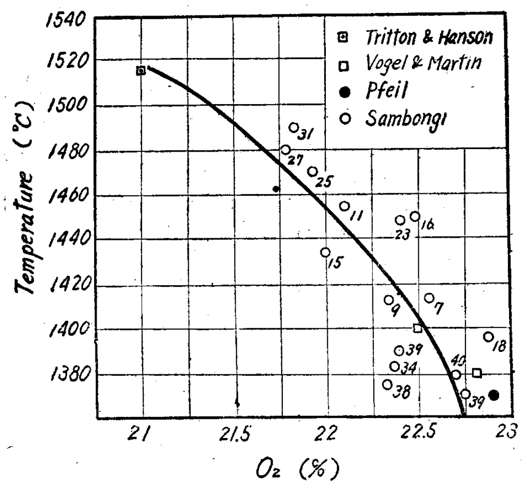

Fig. 7. Relation between O_2% in oxide and temperature.

Table 6. Compositions of iron oxide.

No. of experiment	Equilibrium temp. °C	Keeping time in min.	Analysis		
			Metallic Fe (%)	O_2 %	Total Fe (%)
7	1,414	180	0.29	22.58	77.42
9	1,414	180	0.31	22.35	77.65
11	1,455	180	0.46	22.11	77.89
15	1,436	180	0.43	22.00	78.00
16	1,450	240	0.69	22.50	77.50
18	1,400	180	0.29	22.77	77.23
24	1,448	240	0.23	22.43	77.57
25	1,470	240	0.34	21.95	78.05
29	1,479	360	0.51	21.82	78.18
31	1,490	240	0.32	22.00	78.00
32	1,490	240	0.32	21.84	78.16
34	1,383	130	0.15	22.39	77.61
36	1,390	180	0.31	22 40	77.60
38	1,375	240	0.24	22.30	77.70
39	1,368	150	0.34	22.74	77.26
40	1,370	240	0.30	22.69	77.31

In Fig. 7, experimental values of Tritton and Hanson(5), Vogel and Martin(3), Pfeil(4) were plotted also for comparison. From these results O_2 concentrations of oxide were higher than that of pure FeO at the lower temperature range than about 1,440°C and were lower at higher temperature.

IV. The equilibrium of the reaction, $FeO(l)+H_2=Fe(s)+H_2O$

Denoting the equilibrium constant of the reaction, $FeO(l)+CO = Fe(s)+CO_2$, and water gas reaction by K_{CO-CO_2} and K_w, and the equilibrium constant of this reaction, $FeO(l)+H_2=Fe(s)+H_2O$ by $K_{H_2O-H_2}$, $K_{H_2O-H_2}$ becomes as follows:

$$K_{H_2O\text{-}H_2}=\left(\frac{p_{H_2O}}{p_{H_2}}\right)=K_w\times K_{CO\text{-}CO_2}\cdot$$

Schenck(2) proposed the following equation as the temperature function of this reaction:

$$\log K=\log\frac{p_{H_2O}}{p_{H_2}}=\frac{26,600}{4.573T}-3.63. \qquad (5)$$

The equilibrium constant of water gas reaction was given very accurately by Neuman and Köhler⁽¹¹⁾ as follows:

$$CO_2 + H_2 = CO + H_2O,$$

$$\log K_w = \log \frac{p_{CO}\, p_{H_2O}}{p_{CO_2}\, p_{H_2}} = -\frac{2{,}190}{T} - 0.201 \log T - 0.000{,}393T$$
$$+ 5.46 \times 10^{-8} T^2 + 2.979. \qquad (6)$$

Calculating $K_{CO\text{-}CO_2}$ and K_w from the equation (3) and (6) at several temperature, values of $K_{H_2O\text{-}H_2}$ can be calculated.

Table 7. Calculated values of $K_{CO\text{-}CO_2}$, K_w and $K_{H_2O\text{-}H_2}$ at several temperatures.

Equilibrium temp.		$K_{CO\text{-}CO_2}$	K_w	$K_{H_2O\text{-}H_2}$
°C	°K			
1,550	1,823	0.109,8	3.87	0.425
1,600	1,873	0.095,4	4.05	0.387
1,650	1,923	0.083,5	4.23	0.353

Table 7 gives these calculated values. And the temperature function of log $K_{H_2O\text{-}H_2}$ becomes as follows:

$$\log K = \log \frac{p_{H_2O}}{p_{H_2}} = \frac{6{,}390}{T} - 4.07, \qquad (7)$$

$$\Delta F^\circ = -29{,}200 + 18.6. \qquad (8)$$

VII. The equilibrium of the reaction, FeO(l)=Fe(s)+1/2O$_2$

The dissociation pressure of this reaction can be calculated from the equilibrium constant of the reaction, FeO(l)+CO=Fe(s)+CO$_2$ and dissociation constant of CO$_2$, that is, $P_{O_2}{}^{1/2} = D_{CO_2}/K_{CO\text{-}CO_2}$. The temperature function of dissociation constant of CO$_2$ was given by Wartenberg⁽¹²⁾ as follows:

$$CO_2 = 1/2\ O_2 + CO,$$

$$\log D_{CO_2} = \log \frac{p_{CO}\, p_{O_2}{}^{\frac{1}{2}}}{p_{CO_2}} = \frac{-14{,}750}{T} + 1.375 \log T - 0.607{,}5$$
$$\times 10^{-3} T^2\, 0.675 \cdot 10^{-7}\, T^2 + 1.1. \qquad (8)$$

Table 8. Calculated values of $P_{O_2}{}^{1/2}$ at several temperatures.

Equilibrium temp.		$\log D_{CO_2}$	$\log K_{CO_2\text{-}CO}$	$\log P_{O_2}{}^{1/2}$
°C	°K			
1,400	1,673	−4.11	−0.777	−3.34
1,450	1,723	−3.86	−0.910	−2.95
1,500	1,773	−3.62	−1.036	−2.58

From the equation (3) and (8), values of $K_{CO\text{-}CO_2}$, D_{CO_2} and $P_{O_2}{}^{1/2}$ can be calculated at each temperature. Table 8 gives these calculated values at several temperatures.

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(11) B. Neuman and G. Köhler, Z. Electrechem., 34 (1928), 218.

(12) H. V. Wartenberg, Z. phys. Chem, 58 (1906), 548.

Calculating the temperature function of log $P_{O_2}{}^{1/2}$ from these data the following equation is obtained:

$$\log P_{O_2}{}^{\frac{1}{2}} = -\frac{3,000}{T} + 10.39. \tag{9}$$

Summary

The author measured the equilibrium of the following reaction at the temperature range from 1,360°C to 1,490°C.

$$FeO(l) + CO = Fe(s) + CO_2.$$

And as the temperature function of log $K_{CO\text{-}CO_2}$ the following equation was obtained:

$$\log K_{CO\text{-}CO_2} = \frac{7,680}{T} - 5.37. \tag{3}$$

Then the author calculated the equilibrium constant of the reaction, $FeO(l)+H_2=Fe(s)+H_2O$, and the following equation was obtained as the temperature function of log $K_{H_2\text{-}H_2O}$:

$$\log K_{H_2\text{-}H_2O} = \frac{6,390}{T} - 4.07. \tag{7}$$

Finally the author calculated the dissociation pressure of the reaction, $FeO(l)=Fe(s)+1/2\,O_2$, and the following equation was obtained as the temperature function of log $P_{O_2}{}^{1/2}$:

$$\log P_{O_2}{}^{1/2} = -\frac{23,000}{T} + 10.39. \tag{9}$$