[CONTRIBUTION FROM THE LABORATORY FOR INSULATION RESEARCH, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

The Standard Free Energy of Oxidation of Magnetite to Hematite at Temperatures above 1000°[1]

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RECEIVED APRIL 25, 1957

A correction term is derived for the van't Hoff equation used for calculating the standard free energy from the dissociation pressure data. This term also allows such calculations in cases in which solid solutions are formed. The standard free energy for the reaction $4Fe_3O_4 + O_2 = 6Fe_2O_3$ has been calculated.

The general reaction for the oxidation of magnetite to hematite is

$$\mathrm{MeO}_{x'}(1\ \mathrm{atm.}, T) + \frac{1}{2}(x'' - x')\mathrm{O}_2(1\ \mathrm{atm.}, T) + \Delta F^0 = \mathrm{MeO}_{x''}(1\ \mathrm{atm.}, T) \quad (1)$$

where x' and x'' are any possible values of x within the phase fields $'$ and $''$, respectively (Fig. 1). In Fig. 1 $\ln P'$ and $\ln P''$ are the natural logarithms of the oxygen pressures for the two two-phase equilibria (phase$'$, oxygen) and (phase$''$, oxygen), respectively, and $\ln P_\mathrm{b}$ is that for the three-phase equilibrium (phase$'$, phase$''$, oxygen). In many cases (stoichiometric) the widths $(x'_\mathrm{br} - x'_\mathrm{bl})$ and $(x''_\mathrm{br} - x''_\mathrm{bl})$ of the fields are zero, or are considered as such; then $x' = x'_\mathrm{br}$ and $x'' = x''_\mathrm{bl}$ and the standard free energy ΔF^0 can be found by the familiar van't Hoff equation

$$\Delta F^0 = \frac{1}{2}(x'' - x')RT \ln P_\mathrm{b} \quad (2)$$

But if $x' \neq x'_\mathrm{br}$ and $x'' \neq x''_\mathrm{bl}$, the standard free energy obtained by using eq. 2 would be incorrect. A correction term embodying an adaptation of the van't Hoff equation for the above case has been derived and its numerical application demonstrated.

Derivation of the Correction Term for the van't Hoff Equation.—If we denote $\Delta F^0_\mathrm{uncor}$ the standard free energy obtained from eq. 2, we can write

$$\Delta F^0 = \Delta F^0_\mathrm{uncor} + C \quad (3)$$

where C is the correction term of the present paper. We have

$$\Delta F^0 \equiv [\Delta F^0]_{x'}^{x''} = [\Delta F^0]_{x'}^{x'_\mathrm{br}} + [\Delta F^0]_{x'_\mathrm{br}}^{x''_\mathrm{bl}} + [\Delta F^0]_{x''_\mathrm{bl}}^{x''} \quad (4)$$

The standard free-energy increments refer to the reactions

$$\left.\begin{aligned}
&\mathrm{MeO}_{x'}(1\ \mathrm{atm.}, T) + \frac{1}{2}(x'' - x')\mathrm{O}_2(1\ \mathrm{atm.}, T) + [\Delta F^0]_{x'}^{x''} = \mathrm{MeO}_{x''}(1\ \mathrm{atm.}, T)\\
&\mathrm{MeO}_{x'}(1\ \mathrm{atm.}, T) + \frac{1}{2}(x'_\mathrm{br} - x')\mathrm{O}_2(1\ \mathrm{atm.}, T) + [\Delta F^0]_{x'}^{x'_\mathrm{br}} = \mathrm{MeO}_{x'_\mathrm{br}}(1\ \mathrm{atm.}, T)\\
&\mathrm{MeO}_{x'_\mathrm{br}}(1\ \mathrm{atm.}, T) + \frac{1}{2}(x''_\mathrm{bl} - x'_\mathrm{br})\mathrm{O}_2(1\ \mathrm{atm.}, T) + [\Delta F^0]_{x'_\mathrm{br}}^{x''_\mathrm{bl}} = \mathrm{MeO}_{x''_\mathrm{bl}}(1\ \mathrm{atm.}, T)\\
&\mathrm{MeO}_{x''_\mathrm{bl}}(1\ \mathrm{atm.}, T) + \frac{1}{2}(x'' - x''_\mathrm{bl})\mathrm{O}_2(1\ \mathrm{atm.}, T) + [\Delta F^0]_{x''_\mathrm{bl}}^{x''} = \mathrm{MeO}_{x''}(1\ \mathrm{atm.}, T)
\end{aligned}\right\} \quad (5)$$

If perfect gas conditions are assumed, and the volumes of the solid phases are neglected[3]

$$[\Delta F^0]_{x'}^{x'_\mathrm{br}} = \frac{1}{2}RT\int_{x'}^{x'_\mathrm{br}} \ln P'\, \mathrm{d}x \quad (6)$$

$$[\Delta F^0]_{x'_\mathrm{br}}^{x''_\mathrm{bl}} = \frac{1}{2}RT(x''_\mathrm{bl} - x'_\mathrm{br}) \ln P_\mathrm{b} \quad (7)$$

$$[\Delta F^0]_{x''_\mathrm{b}}^{x''} = \frac{1}{2}RT\int_{x''_\mathrm{bl}}^{x''} \ln P''\, \mathrm{d}x \quad (8)$$

The subsequent relationships could be derived immediately from the areas in Fig. 1 corresponding to eq. 6–8. However, in view that we must also consider the cases when a part of the isotherm or the whole isotherm is below the abscissa axis, a more analytical approach has been preferred.

Addition of eq. 6–8 gives

$$\Delta F^0 = \frac{1}{2}RT\left[(x''_\mathrm{bl} - x'_\mathrm{br}) \ln P_\mathrm{b} + \int_{x'}^{x'_\mathrm{br}} \ln P'\, \mathrm{d}x + \int_{x''_\mathrm{bl}}^{x''} \ln P''\, \mathrm{d}x\right] \quad (9)$$

If we consider (from Fig. 1) that

$$(x''_\mathrm{bl} - x'_\mathrm{br}) = (x'' - x') - (x'' - x''_\mathrm{bl}) - (x'_\mathrm{br} - x') \quad (10)$$

we can transform eq. 9 into

$$\Delta F^0 = \frac{1}{2}RT\left[(x'' - x') \ln P_\mathrm{b} + \int_{x'}^{x'_\mathrm{br}} \ln P'\, \mathrm{d}x - (x'_\mathrm{br} - x') \ln P_\mathrm{b} + \int_{x''_\mathrm{bl}}^{x''} \ln P''\, \mathrm{d}x - (x'' - x''_\mathrm{bl}) \ln P_\mathrm{b}\right] = \frac{1}{2}RT\left[(x'' - x') \ln P_\mathrm{b} + \int_{x'}^{x'_\mathrm{br}} \ln \frac{P'}{P_\mathrm{b}}\, \mathrm{d}x + \int_{x''_\mathrm{bl}}^{x''} \ln \frac{P''}{P_\mathrm{b}}\, \mathrm{d}x\right] \quad (11)$$

But since $^1/_2\, RT(x'' - x') \ln P_\mathrm{b} = \Delta F^0_\mathrm{uncor}$, we get

$$C = \frac{1}{2}RT\left(\int_{x'}^{x'_\mathrm{br}} \ln \frac{P'}{P_\mathrm{b}}\, \mathrm{d}x + \int_{x''_\mathrm{bl}}^{x''} \ln \frac{P''}{P_\mathrm{b}}\, \mathrm{d}x\right) \quad (12)$$

Since $P' < P_\mathrm{b}$, the first integral in eq. 12, which equals area l, is always negative, and since $P'' > P_\mathrm{b}$, the second integral, which equals area r, is always positive. Therefore, in order to get the sum of integrals in eq. 12, one has to planimeter the areas l and r, and, taking them both as signless quantities,

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(1) Sponsored by the U. S. Office of Naval Research, the Army Signal Corps, and the Air Force; it is based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the Massachusetts Institute of Technology.

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(3) The derivation of eq. 6 and 8 is given in W. Nernst, "Theoretische Chemie," F. Enke, Stuttgart, 1926, p. 122. Equation 7 can be found from the van't Hoff equilibrium-box considerations.

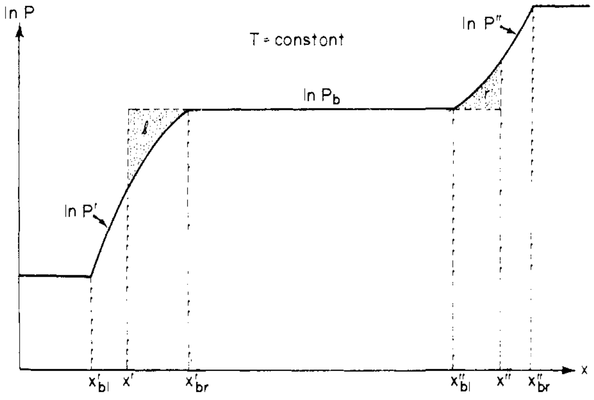

Fig. 1.—Schematic isotherm for deriving the correction term *C*.

subtract the area *l* from the area *r*

$$C = \frac{1}{2} RT\ (|\text{area } r| - |\text{area } l|) \qquad (13)$$

Calculation of the Standard Free Energy of the Oxidation of Magnetite to Hematite, Using the Correction Term *C*.—According to Greig, Posnjak, Merwin and Sosman[4] and Darken and Gurry,[5] magnetite (henceforth denoted as ′ phase) has x'_{bl} = constant = 4/3 throughout the temperature range up to the *liquidus*, but x'_{br}, from about 800°, becomes >4/3; the hematite phase (denoted as ″ phase) has $x''_{bl} = x''_{br} = 3/2$ throughout. Hence, area $r = 0$, but area $l \neq 0$, and for the calculation of the ΔF^0 of the reaction $FeO_{4/3} + {}^1/_{12}\ O_2 = FeO_{3/2}$, eq. 3 has to be used. Figure 2 is the basis for our numerical calculations.[5] The composition *vs.* temperature curve corresponding to a mixture of 99.89 vol. % CO_2 and 0.11 vol. % O_2 (squares), as well as the temperature at which hematite → magnetite in this mixture occurs (dotted line), have been determined by the author. The correctness of these values might be questioned, since perhaps the CO_2 still contained a small, undeterminable amount of residual O_2 and, what is more likely, the composition of the mixture might change in the furnace because of interaction with the walls. However, for our calculations at least one more curve was required in the gap between the 96.09 vol. % CO_2 plus 3.91 vol. % O_2 curve and the pure CO_2 curve.

Experimental Determination of the Composition *vs.* Temperature Curve of Magnetite in 99.89 vol. % CO_2 plus 0.11 vol. % O_2.—For the experimental determination of this curve the CO_2 was freed from O_2 impurity by means of copper at 500°. A special low-rate flowmeter (*ca.* 1 ml. per min.) was constructed for the O_2 admixture with the stream of CO_2 entering the furnace. In order to detect possible obstruction of the capillary, a calibration pipet was sealed directly to the flowmeter.

Our first objective was to establish the temperature of the dissociation hematite → magnetite. A Pt crucible containing 10 g. of ferric oxide[6] was suspended in the thermal center of a tubular globar furnace (2 in. i.d.). The other end of the suspension wire was attached to one stirrup of an analytical balance which was on a cooled base above the furnace. The gas mixture was introduced through the bottom of the furnace; the rate of flow was *ca.* 1 l. per min. The temperature was brought to 1100° overnight and then raised at a rate of *ca.* 10° per hour. The weight of the oxide was noted every 15 minutes. When 1179° was reached, the furnace was kept at that temperature 14 hr. to (1) ensure complete expulsion of moisture; (2) accomplish any exchange of oxygen between the furnace and gas mixture; and (3) order the structure of the hematite and increase its crystal size. After this period the weight of the oxide was found to be unchanged. The temperature level was very close to the dissociation temperature, as upon resuming the rise in temperature, progressively increasing loss of weight was observed. From the weight-loss curve (Fig. 3) 1179° was taken as the temperature of dissociation.

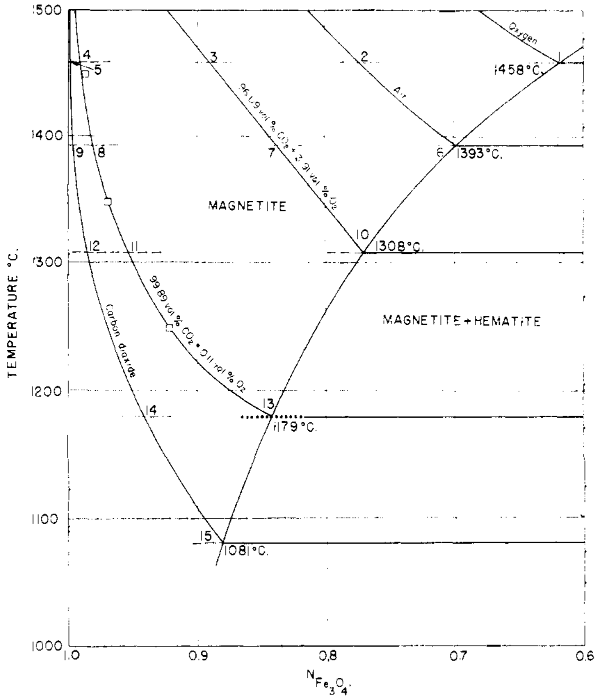

Fig. 2.—Composition of magnetite ($N_{Fe_3O_4}$ is the mole fraction of Fe_3O_4, the other component being Fe_2O_3) in equilibrium with various atmospheres. This is modified from Darken and Gurry.[5] The temperature range from 1500 to 1600° and the experimental points of the previous workers[4,5] have been omitted. The points denoted by squares and the dotted line are the author's.

Three samples of magnetite were prepared using the same gas mixture at 1249, 1348 and 1449° (each for 48 hours). The respective values of $N_{Fe_3O_4} = 2/(r - 1)$, where $r = Fe_{total}/Fe^{++}$, were 0.9217, 0.9697 and 0.9875. The ratio *r* in a sample was determined by adding dilute sulfuric acid, sealing the tube and, after solution at 100°, titrating with $KMnO_4$ for Fe^{++} and, after reduction, for Fe total. The intersection of the 1179°-temperature level (dotted line, Fig. 2) with the field-boundary curve was taken as the fourth point of the curve.

Numerical Calculation.—The numerical calculation is shown in Table I. The temperature values for the column "Temp., °C. from Fig. 2" are the temperature coördinates of the points where the gas-mixture curves intersect the field boundary From these points horizontal dashes are drawn across the magnetite field, their intersections with the gas-mixture curves marked by numbers ("No. of the point in Fig. 2") and the values ("$N_{Fe_3O_4}$ from Fig. 2") of their $N_{Fe_3O_4}$ coördinates read. Column "$\log_{10}K_p$ (from plot)" contains the logarithms of the equilibrium constant of the reaction $2CO_2 \rightleftarrows 2CO + O_2$, as read from a plot based on the

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(4) J. W. Greig, E. Posnjak, H. E. Merwin and R. B. Sosman, *Am. J. Sci.*, [5] **30**, 239 (1935).

(5) L. S. Darken and R. W. Gurry, THIS JOURNAL, **68**, 798 (1946).

(6) "Baker Analyzed": SiO_2, 0.05%; Zn, 0.01%; Cu, 0.01%; subst. not pptd. by NH_4OH, 0.01%.

TABLE I

CALCULATION OF ΔF^0 FROM DATA OF FIG. 2.

$x' = (N_{Fe_3O_4} + 3)/(N_{Fe_3O_4} + 2)$; area l = 2.303 area l_{10}; 2.303 R = 4.574; $\Delta F^0_{uncor} = 2.303\ RT\ {}^1/_{12} \log_{10} P_b$; $C = -2.303\ RT\ {}^1/_2\,|\text{area } l_{10}|$; $\Delta F^0 = \Delta F^0_{uncor} + C$.

Temp., °C. from Fig. 2	$\log_{10} Kp$ (from plot)	No. of the point in Fig. 2	Furnace atmosphere	$N_{Fe_3O_4}$ from Fig. 2	x'	$\log_{10} P_{O_2} = \log_{10} P'$ (Appendix)	|area l_{10}| from Fig. 4	ΔF^0_{uncor}	C	ΔF^0
1458	− 7.99	1	O_2	0.6189	1.3818	0 = $\log_{10} P_b$	0.04603	0	−182.2	−182.2
		2	air (20.8 vol. % O_2)	.7736	1.3605	−0.6819				
		3	i = 0.0814	.8908	1.3459	−1.40				
		4	i = 0.00228	.9911	1.3343	−2.66				
		5	CO_2	1.0000	1.3333	−2.86				
1393	− 8.64	6	air	0.6995	1.3704	−0.6819 = $\log_{10} P_b$	0.03243	− 433.0	−123.6	− 556.6
		7	i = 0.0814	.8382	1.3523	−1.41				
		8	i = 0.00228	.9811	1.3354	−2.77				
		9	CO_2	.9968	1.3337	−3.08				
1308	− 9.61	10	i = 0.0814	.7710	1.3609	−1.407 = $\log_{10} P_b$	0.02393	− 847.9	− 86.5	− 934.4
		11	i = 0.00228	.9539	1.3385	−2.87				
		12	CO_2	.9862	1.3349	−3.40				
1179	−11.24	13	i = 0.00228	.8421	1.3519	−2.930 = $\log_{10} P_b$	0.01563	−1621.8	− 51.9	−1673.7
		14	CO_2	.9419	1.3399	− 3.95				
1081	−12.72	15	CO_2	.8820	1.3470	−4.44 = $\log_{10} P_b$	0.01171	−2291.5	− 36.3	−2327.8

data of Kassel[7] and Darken and Gurry.[8] In the column "Furnace atmosphere" $i \equiv 2n^0_{O_2}/n^0_{CO_2}$ (see Appendix). Column " | area l_{10} | from Fig. 4" gives the planimetered areas between the $\log_{10}(P'/P_b)$ *vs.* $(x' - 4/3)$ curves and the coördinate axis. Coughlin, in his compilation,[9] gives equations for calculating the standard free energies for the reactions $3Fe + 2O_2 = Fe_3O_4$ and $2Fe + {}^3/_2\ O_2 = Fe_2O_3$, from which we can obtain values of ΔF^0 for comparison (Fig. 5) with our method of calculation which uses the correction term of the present paper.

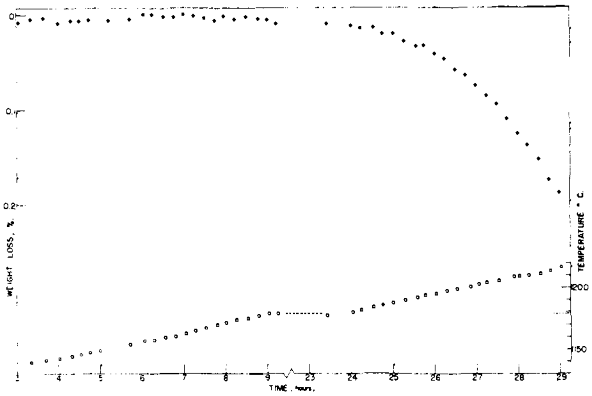

Fig. 3.—The weight-loss curve of hematite on heating in a mixture of 99.89 vol. % CO_2 and 0.11 vol. % O_2.

TABLE II

STANDARD FREE ENERGY OF THE REACTION $4Fe_3O_4 + O_2 = 6Fe_2O_3$ (12 TIMES OUR ΔF^0)

Temp., °C.	Standard free energy, cal.
1100	−25,900 ± 600
1200	−19,200 ± 600
1300	−12,600 ± 600
1400	− 5,800 ± 400

The agreement with Coughlin's values, which are largely based on thermal data, is satisfactory. The ΔF^0 values (solid line), multiplied by 12 (for the reaction $4Fe_3O_4 + O_2 = 6Fe_2O_3$) are given in Table II.

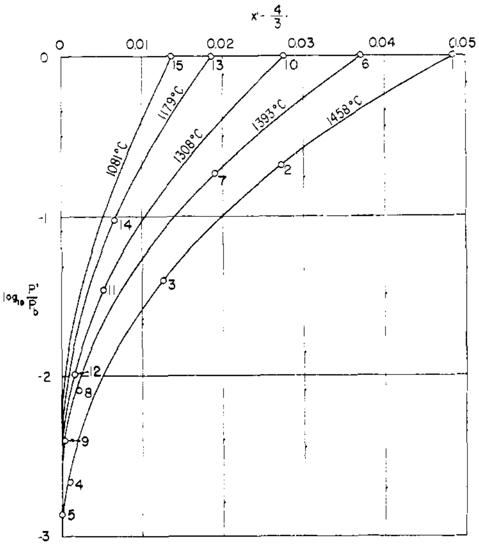

Fig. 4.—The $\log_{10} P'/P_b$ *vs.* $(x' - 4/3)$ curves at various temperatures. The point numbers correspond to those in Fig. 2.

Acknowledgments.—The author is grateful to Professors Arthur R. von Hippel, George Scatchard and James A. Beattie for their guidance and support.

Appendix

Calculation of Oxygen Pressure in Mixtures of CO_2 and O_2, and in Pure CO_2 at Various Temperatures.—If a mixture consisting of $n^0_{CO_2}$ moles CO_2 and $n^0_{O_2}$ moles O_2 is introduced into the furnace, there will be upon dissociation n_{CO_2} moles CO_2, n_{CO} moles CO and n_{O_2} moles O_2. The degree of dissociation α is $(n^0_{CO_2} - n_{CO_2})/n^0_{CO_2}$, and the equilibrium constant K_p is $P_{O_2}(P_{CO}/P_{CO_2})^2$. Since the total

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[7] L. S. Kassel, THIS JOURNAL, **56**, 1838 (1934).

[8] L. S. Darken and R. W. Gurry, *ibid.*, **67**, 1398 (1945).

[9] J. P. Coughlin, "Contributions to the Data on Theoretical Metallurgy. XII. Heats and Free Energies of Inorganic Oxides," U. S. Bureau of Mines, Bulletin 542, Washington, D. C., 1954, p. 62.

TABLE III

VALUES OF α AND LOG$_{10}$ P_{O_2} FOR TWO MIXTURES OF CO_2 AND O_2 AT VARIOUS TEMPERATURES

		99.886 vol. % CO_2 0.114 vol. % O_2 $i = 2\frac{0.114}{99.886} = 0.00228$		96.09 vol. % CO_2 3.91 vol. % O_2 $i = 2\frac{3.91}{96.09} = 0.0814$	
Temp., °C.	$\sqrt{K_p}$	α	$\log_{10} P_{O_2}$	α	$\log_{10} P_{O_2}$
1458	1.01×10^{-4}	2.145×10^{-3}	-2.657	5.089×10^{-4}	-1.405
1393	4.79×10^{-5}	1.155×10^{-3}	-2.765	2.418×10^{-4}	-1.406
1308	1.57×10^{-5}	4.269×10^{-4}	-2.869	7.935×10^{-5}	-1.407
1179	2.40×10^{-6}	7.005×10^{-5}	-2.930		

pressure is 1 atm., we can derive, without approximation

$$K_p = \frac{i + \alpha}{2 + i + \alpha}\,\frac{\alpha^2}{(1 - \alpha)^2} \qquad (1A)$$

$$P_{O_2} = \frac{i + \alpha}{2 + i + \alpha} \qquad (2A)$$

where $i = 2n^0_{O_2}/n^0_{CO_2}$. Direct solution of eq. 1A for α yields a cumbersome cubic equation. We therefore carefully approximate as follows. From eq. 1A

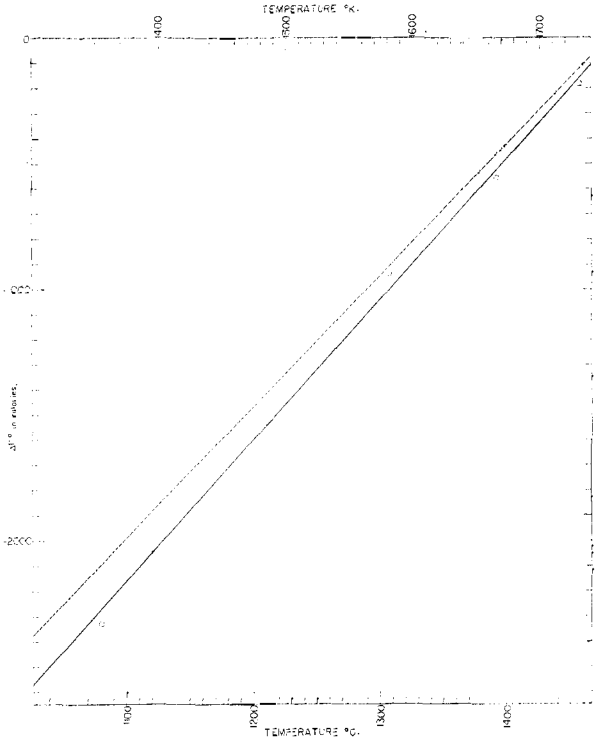

Fig. 5.—The standard free energy $\Delta F°$ of the reaction $FeO_{4/3} + {}^1/_{12}O_2 = FeO_{3/2}$ as function of temperature. Dashes, from the equation of Coughlin's compilation[9]; circles, calculated by the present correction-term method from data of others[4,5] and the author; solid line, mean of values represented by circles.

$$\alpha = \sqrt{K_p}\,(1 - \alpha)\sqrt{\frac{2 + i + \alpha}{i + \alpha}} \qquad (3A)$$

Equation 3A we iterate starting with $\alpha = 0$. The results of the iteration, together with the P_{O_2} values as calculated from eq. 2A, are shown in Table III.

In the case of pure CO_2, $i = 0$, and eq. 1A and 2A give

$$K_p = \frac{\alpha^3}{(2 + \alpha)(1 - \alpha)^2} \qquad (4A)$$

$$P_{O_2} = \frac{\alpha}{2 + \alpha} \qquad (5A)$$

From eq. 4A

$$\alpha = \sqrt[3]{K_p}\,\sqrt[3]{(2 + \alpha)(1 - \alpha)^2} \qquad (6A)$$

With the value of $\sqrt[3]{K_p} = 2.19 \times 10^{-3}$, at the highest temperature 1458° and, using eq. 6A, the values of α obtained by iteration are $\alpha_0 = 0$, $\alpha_1 = 2.759 \times 10^{-3}$, α_2 and $\alpha_3 = 2.755 \times 10^{-3}$; the value α_3 gives $\log_{10}P_{O_2} = -2.861$ (*cf.* eq. 5A). The approximation $\alpha = \sqrt[3]{2}\,\sqrt[3]{K_p}$ gives $\alpha = 2.759 \times 10^{-3}$ and $\log_{10}P_{O_2} = -2.860$. Therefore, for lower temperatures only the approximate formula

$$P_{O_2} = \frac{1}{2}\sqrt[3]{2}\,\sqrt[3]{K_p} \qquad (7A)$$

is used.

The values thus obtained are given in Table IV.

TABLE IV

VALUES OF LOG$_{10}$ P_{O_2} FOR PURE CO_2 AT VARIOUS TEMPERATURES

1458°	1393°	1308°	1179°	1081°
−2.86	−3.08	−3.40	−3.95	−4.44

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