[CONTRIBUTION FROM THE DEPARTMENT OF ENGINEERING RESEARCH, UNIVERSITY OF MICHIGAN]

Equilibrium in the Oxidation of Liquid Iron by Steam and the Free Energy of Ferrous Oxide in Liquid Steel

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Our knowledge of the behavior of non-metallic solutes in liquid metal solvents rests almost entirely upon a limited amount of data on the solubilities of certain oxides and sulfides and of the simpler gases. Considerable disagreement exists as to whether or not such systems conform to the mass law as stated in terms of concentration or mole fraction. Recent investigations of Herty and his associates,[1] Körber and Oelsen[2] and of Krings and Schlackmann[3] on the distribution of ferrous oxide between liquid iron and slag and on its reaction with manganese dissolved in the iron have shown that the simple statement of the mass law is at least approximately applicable to equilibria involving ferrous oxide dissolved in liquid iron. On the other hand, Gottschalk and Dean[4] maintain that the mass law is in no wise applicable to the reaction of ferrous oxide with dissolved carbon in liquid steel.

The fact that the solubility of the elementary diatomic gases in metals does not conform to Henry's law, but rather to that of Sieverts[5] involving square root of pressure, is readily explained on the assumption that the solute is not the molecular gas but a compound containing one atom of the gaseous element per molecule. If the activity of such a solute is proportional to its concentration, Sieverts' law necessarily follows.

In the case of oxygen in liquid iron the direct determination of gas solubility would involve great difficulties since any considerable pressure of oxygen would ultimately convert all of the iron into one of its oxides. That oxygen is present in liquid steel and that it plays a very important part in the refining process is quite well known to all steel makers. An understanding of the behavior of oxygen in liquid steel will depend upon knowledge as to which of the several oxides is present, and more especially as to whether this oxide is in true solution or is suspended in the form of solid or liquid particles.

The experiments described in this paper were undertaken in order to settle this question as to the behavior of oxygen in liquid iron and to lay the foundations for an adequate thermodynamic treatment of the reactions involving oxidation and deoxidation in liquid steel. Consider the equilibrium

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(1) Herty and co-workers, Carnegie Inst. Tech. Mining Met. Investigations, *Bulletin* **34** (1927).

(2) Körber and Oelsen, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, **14**, 181 (1932); *Stahl u. Eisen*, **52**, 133 (1932).

(3) Krings and Schlackmann, *Z. anorg. allgem. Chem.*, **202**, 99 (1931); **206**, 337 (1932).

(4) Gottschalk and Dean, *Am. Inst. Mining Met. Eng.*, Preprint (1932).

(5) Sieverts and Hagenacker, *Ber.*, **42**, 338 (1909).

$$Fe_xO_y + yH_2 = xFe(l) + yH_2O;\ K = \frac{p^y_{H_2O}\, a^x_{Fe}}{p^y_{H_2}\, a_{Fe_xO_y}} \qquad (1)$$

If the oxide is dissolved in liquid iron to form a dilute solution, it is evident that when $y = 1$, the ratio p_{H_2O}/p_{H_2} is proportional to the oxygen concentration in the metal. If $y = 2$, the ratio becomes proportional to the square root of the oxygen content, and similarly for higher values of y the ratio is proportional to higher roots of the oxygen concentration. On the other hand, if the compound is insoluble in liquid iron but is held in suspension—conceivably stabilized by a gas film—then as long as the oxide is present its activity is constant and the oxygen content of the metal is not a function of the ratio of steam to hydrogen.

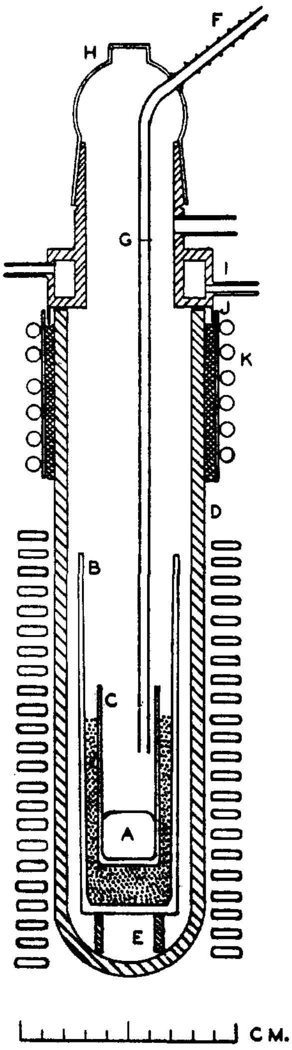

Fig. 1.—Induction furnace.

Experimental Method

A controlled mixture of steam and hydrogen was passed over the surface of the liquid iron, heated by high-frequency induction, for a longer time than necessary to establish equilibrium. The metal was then allowed to solidify and its oxygen content determined by the vacuum-fusion method.

Furnace.—Details of the furnace are shown in Fig. 1. The charge A was placed in the crucible C which was packed inside a large Alundum thimble B. This assembly was placed inside the fused silica tube D, resting upon a silica ring E. The mixture of steam and hydrogen entered the furnace through the tube F which was made of Pyrex glass and was sealed into the cap H. At the point G a refractory porcelain tube was sealed to the end of the Pyrex tube; the porcelain tube extended to within 2 to 3 cm. of the surface of the metal. Pyrex-to-porcelain seals are as easily made as any glass-to-glass seal and may be made by essentially the same technique. Seals of this kind are quite rugged and are exceedingly useful in high-temperature work. The upper portions of the assembly consisted of the Pyrex cap H, ground to fit the brass head I which was cemented to the fused silica tube by picein wax, held in the annular groove formed by the brass sleeve J. This sleeve was cemented to the quartz tube by a mixture of zinc and water glass and was surrounded by a coil of copper tubing K. To prevent condensation of water the inlet tube was heated by a resistance coil covered with asbestos. Considerable heat was generated in the sleeve J, by virtue of its proximity to the induction coil, and this heat was distributed to the brass head by passing a slow current of air through the coil K and the annular space in I. The cap H was warmed occasionally with a Bunsen flame.

Steam–Hydrogen Mixture.—Hydrogen from a commercial cylinder was passed through a flow meter, then through Ascarite to a silica tube packed with platinized asbestos and heated to about 500°. It was then passed through a saturator consisting of five bottles, the first four of which were packed with glass rings and filled with distilled water, while the fifth served only as an entrainment separator. A calibrated thermometer was placed in the fifth bottle and the whole assembly was immersed in a water thermostat which was manually controlled to ±0.2° at the highest temperature employed or ±0.1° at the lower temperatures. The mole ratio of steam to hydrogen was computed from the barometric pressure and the vapor pressure and vapor density of water.[6] The efficiency of the saturator was checked at 35 and 47° by absorbing and weighing the water vapor carried by a measured volume of hydrogen. The calculated and experimental mole ratios checked within 1%. The rate of flow of hydrogen from the tank was 450 cc. per minute in the first four runs and 250 to 300 cc. per minute in all the others.

Iron.—Electrolytic iron previously melted *in vacuo* was used in all but three of the runs. In these three runs an attempt was made to employ a commercial ingot iron but the resulting ingots were so porous, due to evolution of gases during solidification, that representative analyses could be obtained on only one of the three. The analysis of the electrolytic iron and partial analysis of some of the vacuum melted specimens are given in Table I.

TABLE I

ANALYSIS OF ELECTROLYTIC IRON (PER CENT.)

	C	Mn	Si	S	P	O	N
As received	0.027	0.008	0.001	0.007	0.002	0.013	<0.0005
Vacuum melted	.01	...	...	...	...	0.01–0.03	< .0005

Crucibles.—In the first eleven runs Alundum extraction thimbles (R. A. 84) 25 mm. inside diameter were used. These thimbles were very satisfactory for melts which were low in oxygen but were severely attacked when the oxygen content of the metal exceeded 0.06%. Magnesia crucibles were made by tamping crystalline periclase of high purity around a steel core in a graphite mold. The steel core was withdrawn and the crucible and mold heated to about 1800° in the induction furnace. The crucibles were dense and strong, though not impervious to gases. They were only slightly attacked by iron oxide up to the highest oxygen concentrations. One crucible of beryllium oxide was produced in the same manner and its behavior in service was similar to that of the magnesia crucibles. For thermal insulation between the crucible and the outer thimble, crystalline magnesia of 60–90 mesh grain was used in packing magnesia and beryllia crucibles; for the alundum crucibles crystalline alumina was employed.

Temperature Measurements.—Temperatures were measured by means of an optical pyrometer of the disappearing filament type which was sighted through a prism and through the flat, clear portion of the Pyrex cap. The instrument was calibrated up to 1340° against a standard platinum–platinum-rhodium couple placed in the uniformly heated portion of a Globar furnace and surrounded by a hollow body of magnesia having a small hole for sighting. The correction for absorption of light by the prism and cap was also determined. The emissivity of liquid iron for red light was taken as 0.37, the value given by Foote, Fairchild and Harrison.[7] During each run the melting point of iron in dry hydrogen was observed by reducing the power input to the furnace so as to cause a slow solidification of the metal. The average temperature was 1528 ± 8°. The temperature of each run was controlled by careful regulation of the power input.

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(6) Landolt–Börnstein, "Tabellen," 5 Auflage, pp. 1316, 1323.

(7) Foote, Fairchild and Harrison, Bur. Standards Tech. Paper No. 170, "Pyrometric Practice," 1921.

While considerable fluctuation occurred during the initial stage of each experiment, it was possible during the final fifteen to thirty minutes of each run to maintain constancy within a 10° range. The temperatures recorded in Table IV represent the averages during the final fifteen minutes of each run. These temperatures are probably reliable within ±10° except for the three runs above 1700°, where the uncertainty is necessarily greater.

Procedure.—The hydrogen train and saturator were thoroughly flushed out before the start of each run. The furnace was evacuated, then filled with hydrogen direct from the tank and the charge was melted in a stream of tank hydrogen. After the melting point had been observed the charge was heated to approximately the desired temperature and saturated hydrogen was admitted. The duration of the run was taken from the time saturated hydrogen was admitted until the power was cut off. In the runs that were conducted at about 1620° the specimens solidified within twenty to forty seconds and cooled to 1100° within three minutes.

With the exception of three runs in which ingot iron was used and three above 1700° the ingots were sound and practically free from blow-holes. In three runs, 21, 22 and 23, a slag formed on the surface of the liquid metal during cooling. This slag was easily observed on account of its high emissivity. It was concluded, on the basis of the following evidence, that this was ferrous oxide which was ejected from the liquid iron when the temperature had fallen to such a point that the solubility of the oxide was exceeded. The bottom of ingot 21 contained 0.20% oxygen while the extreme top portion contained 0.34%. Microscopic examination showed that the top portion contained large ferrous oxide inclusions while the lower part contained only the much smaller inclusions typical of all the other ingots examined. The large inclusions had evidently been thrown out of solution and were in process of rising to the surface when they were entrapped by the solidification of the metal. In heat 23, which cooled a little more slowly, the large inclusions were absent and the small ones were uniformly distributed. This ingot contained 0.21% oxygen. It is evident that the cooling rate was not sufficiently rapid to retain the ferrous oxide in excess of about 0.21% oxygen. This corresponds to the solubility of iron oxide in liquid iron at the melting point reported by Tritton and Hanson.[8]

Analytical Method.—Oxygen determinations were carried out by the vacuum fusion method developed by Jordan and his co-workers and described in detail by Vacher and Jordan.[9] Our apparatus, which had been in service about a year before the present experiments were begun, differed from that of Vacher and Jordan only in minor details which need not be described here. The operating pressure was below 0.001 mm. and the blank corrections were approximately one-fifth those reported by Vacher and Jordan. The accuracy of the method is approximately 0.001% of the weight of the sample for steels of low or medium oxygen content. For the samples higher in oxygen the accuracy is somewhat less since the absolute errors in determining the amount of oxygen present may be as high as 2%.

In order to minimize errors due to segregation in the ingot, longitudinal segments were cut for the analyses. The analytical results are given in Table II which contains also data on the weight of metal and type of crucible used in each run and the condition of ingot and crucible after the heat.

Discussion of Results

Two series of runs at constant steam–hydrogen ratios were conducted in order to ascertain the time required for the establishment of equilibrium.

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[8] Tritton and Hanson, *J. Iron Steel Inst.* (London), **110**, 90 (1924).

[9] Vacher and Jordan, *Bur. Standards J. Research*, **7**, 375 (1931).

TABLE II

ANALYTICAL RESULTS AND CONDITION OF INGOT AND CRUCIBLE

Number	Ingot Weight, g.	Ingot Condition	Crucible Material	Crucible Condition	Oxygen, per cent. by weight Individual analyses				Adopted
1	64	Sound	Al_2O_3	*c*	0.0114	0.0120			0.0117
2	68	Sound	Al_2O_3	*c*	.0126	.0133			.0130
3	63	Sound	Al_2O_3	*c*	.0126	.0130[f]			.0128
4	69	Sound	Al_2O_3	*c*	.0117	.0112[f]			.0115
5	68	Sound	Al_2O_3	*c*	.0278	.0258			.0268
6	74	Sound	Al_2O_3	*c*	.0256	.0250			.0253
7	68	Hollow	Al_2O_3	*c*	.0281	.0270			.0275
8	65[i]	Very porous	Al_2O_3	*d*	.093[f]				[a]
9	65[i]	Hollow	Al_2O_3	*b*	.0567	.0577			.057
10	65[i]	Hollow	Al_2O_3		.059[f]				[a]
11	63	Sound	Al_2O_3	*b*	.0555	.0556			.0555
12	45	Sound	MgO	*c*	.0602[f]	.0573			.058
13	43	Sound	MgO	*b*	.115	.116[f]			.116
14	46	Sound	MgO	*c*	.080	.076	0.084	0.082	.081
15	53	Sound	MgO	*b*	.112	.113			.113
16	53	Sound	MgO	*b*	.114	.112			.113
17	54	Sound	MgO	*c*	.117				[a]
18	54	Sound	MgO	*c*	.0594	.0580			.059
19	54	Sound	MgO	*c*	.0490	.0525	.0493	.0490	.049
20	54	Sound	MgO	*c*	.087	.083[f]	.087	.084	.085
21	59	Sound	MgO	*b*	.245	.240			.242[e]
22	78	Hollow	MgO	*b*	.222[f]	.221[f]	.218[f]		.220[e]
23	53	Sound	BeO	*b*	.211	.214[f]			.212[e]
24	76	Hollow	MgO	*b*	.123	.117	.128[f]	.121	.123
25	79	Hollow	MgO	*b*	.112[f]	.117[f]	.117[f]		.116
26	54	Hollow	MgO	*b*	.168	.156	.155	.153	.155

[a] Not used in calculating equilibrium constant. [b] Crucible slightly blackened. [c] Crucible clean. [d] Crucible severely attacked. [e] Liquid ferrous oxide separated during solidification. [f] Analysis by M. G. Fontana. [i] Ingot iron.

The data on these eight experiments are summarized in Table III. The first four results indicate a slight trend although the variations are within the limits of experimental error. In the second group it is seen that the oxygen content is virtually constant after the first fifteen minutes. The

TABLE III

CONSTANCY OF OXYGEN CONTENT WITH TIME

Run	p_{H_2O}/p_{H_2}	Time, minutes	Oxygen, %	Temp., °C.
3	0.0603	30	0.0128	1610
2	.0604	52	.0130	1605
1	.0603	60	.0117	1600
4	.0605	120	.0115	1600
17	.474	15	.117	1625
16	.473	40	.113	1635
13	.477	60	.1155	1620
15	.473	90	.113	1625

rapid attainment of equilibrium is no doubt largely due to the fact that the liquid metal is constantly and vigorously stirred by the high frequency induction—a phenomenon well known to all users of induction furnaces. The constancy of oxygen content with time was the only experimental criterion of equilibrium that was used in the present investigation.

The data on all experiments are presented in Table IV. The sixth column gives the observed value of the ratio

$$K' = p_{H_2O}/(p_{H_2} \times \%\ \text{oxygen})$$

In the seventh column are shown the values of this ratio corrected to an average temperature of 1620° by means of a preliminary plot similar to Fig. 3. It is evident that at constant temperature the ratio is nearly, if not quite, constant. The oxygen concentration is approximately proportional to the ratio p_{H_2O}/p_{H_2} and we are, therefore, justified in concluding that the solute contains one atom of oxygen per molecule. For simplicity it will be assumed that the solute is FeO.

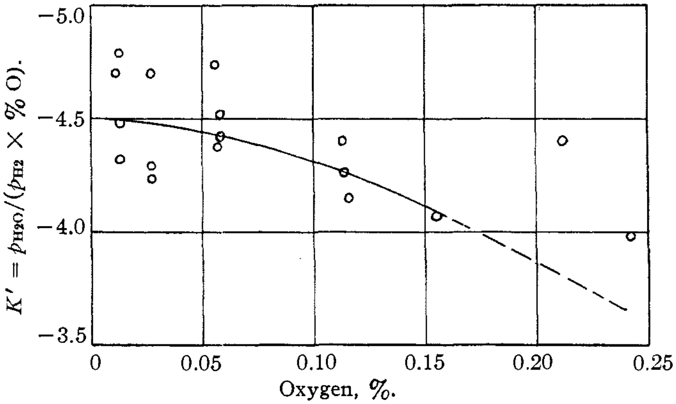

Fig. 2.—The ratio $p_{H_2O}/(p_{H_2} \times \%$ O) in liquid iron at 1620°.

In Fig. 2 the values of K' at 1620° are plotted as a function of the oxygen content of the metal. It is evident that K' is not strictly constant but decreases with increasing oxygen concentration. The line is drawn below the points representing runs 21 and 23 for the reason that liquid ferrous oxide was ejected from these ingots during cooling, and the analytical result is, therefore, certainly lower than the equilibrium concentration of oxygen. The variation in K' with concentration is no greater than would be expected to result from the departure of the system from the laws of the ideal solution. If the activity of the solute is equal to its concentration in the very dilute solution, then at higher concentrations the activity is evidently somewhat less than the concentration.

Let us define the activity of ferrous oxide by making it equal to its per cent. by weight in the very dilute solution. At higher concentrations the activity is lower than the percentage of ferrous oxide and the ratio of activity to percentage may be termed the activity coefficient and represented by the symbol γ. The value of γ at any oxygen concentration is obtained by dividing K' by the limiting value of K' at low concentrations. These data are given in Table V along with the percentage and activity of ferrous oxide at round percentages of oxygen.

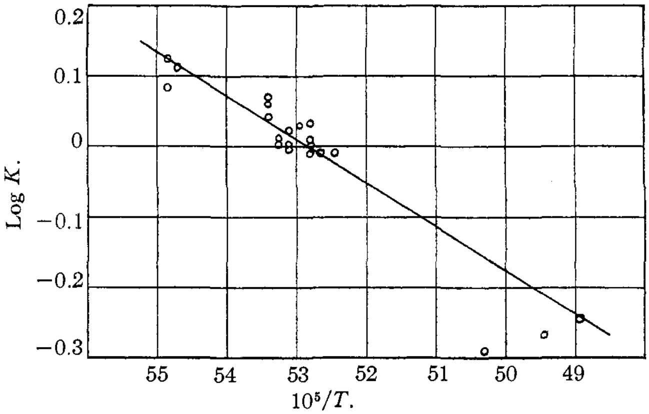

Fig. 3.—Equilibrium constant $K = p_{H_2O}/(p_{H_2} \times a_{FeO})$ as a function of reciprocal temperature.

Returning to Table IV, the eighth column contains values of the equilibrium constant, $K = p_{H_2O}/(p_{H_2} \times a_{FeO})$. The logarithm of K is plotted as a function of reciprocal temperature in Fig. 3. The line corresponds to $\log K = 6200/T - 3.28$ and the heat absorbed in the reaction is $-28{,}400$ calories. The free energy is given by the equation

$$FeO\ (\text{in Fe}) + H_2 = Fe(l) + H_2O(g);\quad \Delta F^\circ = -28.400 + 15.0\ T$$

The equation previously employed for the free energy of water[10] may be simplified for the temperature range under consideration to read

$$H_2 + {}^1/_2\,O_2 = H_2O(g);\quad \Delta F^\circ = -59{,}600 + 14.0\ T$$

By combining the two expressions one obtains the following equation for the standard free energy of formation of ferrous oxide in liquid steel.

$$Fe(l) + {}^1/_2\,O_2 = FeO\ (\text{in Fe});\quad \Delta F^\circ = -31{,}200 - 1.0\ T$$

This equation is not in agreement with the corresponding expression derived by Chipman and Murphy[11] from an extrapolation of equilibrium data at lower temperatures. Further experiments are in progress which are designed to extend the equilibrium measurements up to the saturation point and to establish the compositions of the coexistent metallic and nonmetallic phases. It is hoped that these experiments may throw some light upon the causes of the discrepancy.

(10) Chipman, *Ind. Eng. Chem.*, **24**, 1013 (1932).

(11) Chipman and Murphy, *ibid.*, **25**, 319 (1933).

TABLE IV

SUMMARY OF ALL EXPERIMENTS

Run	Time	p_{H_2O}/p_{H_2}	Temp., °C.	Oxygen, %	$K' = p_{H_2O}/(p_{H_2} \times \%O)$		$K = p_{H_2O}/(p_{H_2} \times a_{FeO})$
					Obs.	Corr. to 1620°	
1	60	0.0603	1600	0.0117	5.15	4.70	1.15
2	52	.0604	1605	.0130	4.64	4.32	1.03
3	30	.0603	1610	.0128	4.71	4.48	1.05
4	120	.0605	1600	.0115	5.25	4.79	1.17
5	60	.1216	1605	.0268	4.55	4.23	1.01
6	120	.1215	1615	.0253	4.80	4.70	1.07
7	30	.1222	1610	.0275	4.45	4.29	0.99
8	60	.478					
9	60	.262	1610	.057	4.60	4.38	1.00
10	30	.263					
11	60	.263	1620	.0555	4.74	4.74	1.08
12	60	.262	1620	.058	4.52	4.52	1.02
13	60	.477	1620	.1155	4.14	4.14	0.98
14	65	.470	1550	.081	5.80		1.33
15	90	.473	1625	.113	4.18	4.26	0.98
16	40	.473	1635	.113	4.18	4.40	.98
17	15	.474	1625	.117			
18	60	.261	1620	.059	4.42	4.42	1.00
19	75	.261	1550	.049	5.33		1.21
20	60	.478	1555	.085	5.62		1.29
21	60	.964	1620	.242	3.98	3.98	..
22	66	.483	1770	.220	2.18		0.58
23	60	.979	1610	.212	4.62	4.40	..
24	60	.260	1715	.123	2.16		.51
25	60	.263	1750	.116	2.28		.54
26	60	.691	1600	.155	4.46	4.07	1.10

TABLE V

ACTIVITY OF FERROUS OXIDE IN LIQUID IRON

Oxygen, %	FeO, %	K' at 1620°	Activity coefficient, γ	Activity a_{FeO}
0.01	0.045	4.5	1.00	0.045
.02	.090	4.5	1.00	.090
.05	.224	4.4	0.98	.220
.10	.449	4.3	.96	.429
.15	.674	4.1	.91	.613
.20	.898	3.9	.86	.770

The only data in the literature which may be directly compared with the present investigation are those of Vacher and Hamilton.[12] In their study of the equilibrium between iron oxide and carbon in liquid steel, they passed a mixture of carbon dioxide and carbon monoxide over the samples at 1620° and determined the carbon and oxygen contents of the resulting ingots. In Table VI the first column gives their oxygen concentration, the second the activity of ferrous oxide interpolated from Table V, and the

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[12] Vacher and Hamilton, *Trans. Am. Inst. Mining Met. Eng.*, **95**, 124 (1931).

third the equilibrium ratio of steam to hydrogen. The ratio of carbon dioxide to carbon monoxide which would be in equilibrium with the given sample is calculated from the constant of the water–gas reaction, which according to the writer's equation[10] is $(p_{H_2O} \times p_{CO})/(p_{CO_2} \times p_{H_2}) = 4.1$ at 1620°. This ratio is given in the fourth column while the observed ratio of Vacher and Hamilton is given in the fifth. In view of their statement that the gas compositions given were only approximate, the agreement is about as good as could be expected. Certainly the agreement is sufficiently close to indicate that their gas–metal reactions had reached equilibrium and that the constancy of their carbon–oxygen product represents a true equilibrium condition.

TABLE VI

COMPARISON WITH DATA OF VACHER AND HAMILTON

Oxygen, %	a_{FeO}	p_{H_2O}/p_{H_2}	p_{CO_2}/p_{CO} Calcd.	p_{CO_2}/p_{CO} V. and H. obs.
0.068	0.296	0.30	0.07	0.07
.106	.456	.46	.11	.09
.128	.535	.54	.13	.10
.125	.523	.52	.13	.10
.155	.632	.63	.15	.13
.133	.555	.56	.14	.08
.198	.758	.76	.18	.11

The author wishes to express his thanks to D. W. Murphy for assistance in setting up and standardizing the analytical apparatus, and to M. G. Fontana for carrying out many of the oxygen determinations.

Summary

Equilibrium in the oxidation of liquid iron by steam has been studied by determining the oxygen content of iron in equilibrium with controlled mixtures of steam and hydrogen. At constant temperature the oxygen concentration in the iron is nearly proportional to the mole ratio of steam to hydrogen. This proportionality leads to the conclusion that the solute is an oxide of iron containing one atom of oxygen per molecule. For simplicity it is called ferrous oxide and its formula is written FeO.

The activity of ferrous oxide is defined as equal to its per cent. by weight at low concentrations. Its activity at higher concentrations has been calculated from the equilibrium data.

The experimental results, which cover the range 1550 to 1770°, are expressed by the equations

$$\text{FeO (in Fe)} + H_2 = \text{Fe(l)} + H_2O\text{(g)};\; K = p_{H_2O}/(p_{H_2} \times a_{FeO})$$
$$\log K = 6200/T - 3.28;\; \Delta F^\circ = -28{,}400 + 15.0\,T$$

The change in free energy attending the formation of ferrous oxide in liquid iron from its elements is

$$\text{Fe(l)} + {}^1/_2\,O_2 = \text{FeO (in Fe)};\; \Delta F^\circ = -31{,}200 - 1.0\,T$$

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