for the meter, and thus to maintain it and the sample of gas at the calibration temperature.

The gas to be tested may be drawn or forced at the rate of a few cubic centimeters per minute through the test chamber, which in present models has a volume of about 4 ml., or it may be introduced after evacuating the test chamber. The instrument indicates correctly the magnetic susceptibility of the gas in the test chamber within a few seconds; the main delay in reading the instrument is caused by the time required to introduce the gas.

Meters have been constructed to cover various ranges of partial pressure of oxygen, including 0 to 20 mm. of mercury, 0 to 80, 0 to 160, 110 to 190, and 0 to 800. Dr. A. O. Beckman has also devised a meter which can be switched from one partial-pressure region to another.

Calibration curves for a typical "Model P" meter at three different temperatures are shown in Figure 6. This meter has been compensated for temperature changes in the manner described above. The accuracy of a meter is usually about 1% of the range covered.

The instrument may also be used for determining the magnetic susceptibility of paramagnetic and diamagnetic gases or for any analysis dependent on magnetic susceptibility, such as the determination of nitric oxide or nitrogen dioxide in a gas not containing oxygen.

Several dozen meters were constructed at the California Institute of Technology before the summer of 1942. Dr. Arnold O. Beckman, 11 West State Street, Pasadena 2, California, who then took over the production of the meter, has manufactured several hundred. Descriptions of the various models will be published elsewhere. Some recording models of the instrument are available.

We are glad to acknowledge the assistance of David P. Shoemaker, James B. Edson, Harold Herd, Dr. Herbert Sargent, Dr. Charles D. Wagner, and Beckie Bradford in the development of this instrument at the California Institute of Technology.

Summary

A simple instrument for determining the partial pressure of oxygen in a gas is described. This instrument, the use of which as an oxygen meter depends on the fact that the magnetic susceptibility of oxygen is very much greater than that of other common gases, consists of a small glass dumbbell with attached mirror suspended on a stretched fused-silica fiber in an inhomogeneous magnetic field produced by a small permanent magnet. In the simpler models of the instrument the partial pressure of oxygen is indicated on a scale by a beam of light reflected from the mirror.

PASADENA 4, CALIFORNIA RECEIVED JANUARY 7, 1946

[CONTRIBUTION FROM THE RESEARCH LABORATORY, U. S. STEEL CORPORATION]

The System Iron–Oxygen. II. Equilibrium and Thermodynamics of Liquid Oxide and Other Phases

BY L. S. DARKEN AND R. W. GURRY

This paper, an extension of a previous paper[1] on the equilibrium between iron, oxygen and wüstite throughout its field of stable existence, deals with the results of similar measurements at the higher temperatures at which a liquid phase appears. The data, in conjunction with those in paper I, suffice not only for the construction of phase diagrams showing the relation between temperature, gas composition (oxygen pressure) and composition of the oxide phases, liquid or solid; but also for evaluation of the following thermodynamic quantities: activity and partial molal heat of iron and of oxygen throughout the several homogeneous fields, heat of formation and of fusion of iron oxide of any composition realizable at oxygen pressures up to one atmosphere.

The general method was, as before, to pass a gas mixture of constant known composition over the condensed phase, maintained at one of a series of constant temperatures, until equilibrium was attained, then to quench the iron oxide phase and determine its composition. The temperature ranged up to 1640°; the equivalent partial pressure of oxygen in the gas phase from 10^{-10} up to 1 atm.; the atom ratio of oxygen to iron in the liquid oxide from about 1.03, that in equilibrium with iron, to about 1.38, somewhat beyond Fe_3O_4. In the region studied there are several distinct, though related, equilibria, each of which must be considered separately; the system as a whole is therefore somewhat complex. For this reason, and so that the reader may more readily apprehend the precise inter-relations, it was deemed best to begin by presenting as a summary diagram, in Fig. 1, our final temperature–composition diagram for the iron–oxygen system, solid as well as liquid, at an oxygen pressure ranging up to one atmosphere and a total pressure of one atmosphere throughout. The other phase diagrams have been lettered to correspond as far as possible thereto. It is to be remarked that change in composition of the condensed phase, at least at its surface, follows quite rapidly any

---

[1] L. S. Darken and R. W. Gurry, THIS JOURNAL, 67, 1398 (1945); hereafter referred to as paper I.

change in effective oxygen pressure of the gas phase in immediate contact with it; further, and as a consequence of the rate of adjustment of the reaction, that the observed melting of an "iron oxide" may begin at any temperature from 1371 to 1597°, depending on the prevailing oxygen pressure.

For the sake of clarity, all experimentally determined points have been omitted from this phase diagram; they appear in the several special figures or in the tables. Because the scale of Fig. 1 as reproduced is, unavoidably, small, the coördinates of each point on it designated by a letter are given in the appended table; and these letters are used to identify each field or boundary discussed later. The significance of each of these points or lines, in Fig. 1, from pure iron (left) to ferric oxide (hematite, right) and the sources of the data on which they are based, are summarized below.

The solubility of oxygen in solid iron is, according to Dünwald and Wagner[2] less than 0.01% at 800–1000°; according to Sloman[3] 0.003–0.006% at "low temperature"; as calculated from the lowering of freezing point of δ-iron (line AB) on the usual assumptions, it is less than 0.01% at that temperature. Consequently, Fig. 1 was drawn on the basis that this solubility line practically coincides with the vertical axis. The solubility of oxygen in liquid iron is represented by the line BB′, according to Taylor and Chipman[4]; the percentage of oxygen at B (0.16%) agrees with that (0.15%) reported by Sloman.[3] Line CGN, the composition of liquid oxide in equilibrium with δ-iron, is determined by the results in Table III. The boundaries JQ, QH of the wüstite field are taken from Fig. 9 of paper I.[5] The third boundary, the solidus JH, was derived by reading, from appropriate graphs of the data in Table V of paper I, the composition of wüstite in equilibrium with each of the several atmospheres at each of the melting temperatures in Table IV of this paper. The liquidus curves NI, IV, VR were derived similarly from Tables I and IV, and the three boundaries VR′, YT, TV of the magnetite field likewise from Tables II and IV. Points on the line R′Y, representing compositions in equilibrium with pure oxygen, are from Table II and the data of Greig, Posnjak, Merwin and Sosman,[6] according to whom the composition of ferric oxide (line ZZ′) is essentially constant.

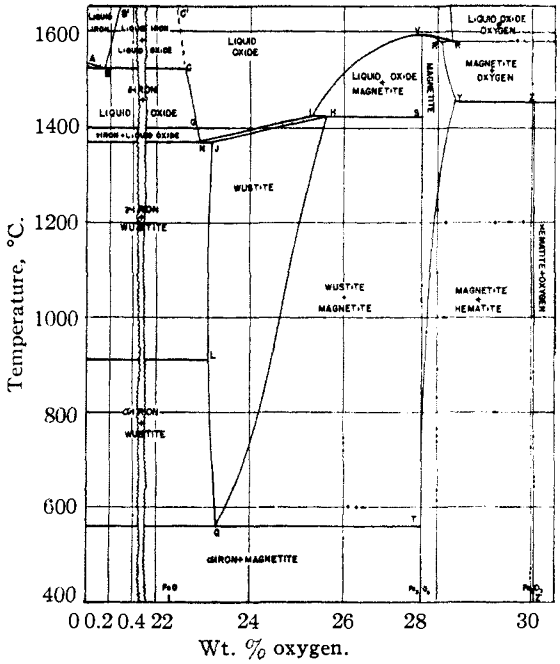


Fig. 1.—The temperature–composition phase diagram of the iron–oxygen system at a total pressure of one atmosphere. Recommended values for certain fixed points are as follows:

IRON-OXYGEN SYSTEM
AT ONE ATMOSPHERE PRESSURE

Point	°C.	% O	P_{CO_2}/P_{CO}	Point	°C.	% O	P_{CO_2}/P_{CO}	P_{O_2}- (atm.)
A	1535			Q	560	23.26	1.05	
B	1524	0.16	0.209	R	1583	28.30		1
C	1524	22.60	0.209	R'	1583	28.07		1
G	1400[a]	22.84	0.263	S	1424	27.64	16.2	
H	1424	25.60	16.2	V	1597	27.64		0.0575
I	1424	25.31	16.2	Y	1457	28.36		1
J	1371	23.16	0.282	Z	1457	30.04		1
L	911[a]	23.10	0.447	Z'		30.06		
N	1371	22.91	0.282					

[a] Value for pure iron.

In the construction of Fig. 1 and of the several diagrams upon which it is based, use was made not only of the direct measurements, but also of thermodynamic relations derived from them, as an aid in interpreting and collating the data of the more recent investigators of this system. The pertinent thermodynamic calculations of the changes in heat content and free energy and of activity are discussed in detail following the presentation of the experimental results of this investigation.

Experimental

The general procedure for determining the equilibrium was the same as was described in paper I, the only differences being a consequence of the fact that we are here dealing with a liquid instead of a solid phase; and that additional atmospheres of somewhat different composition were required. Starting materials, gas mixer, furnace and temperature controller were identical. The air atmosphere was air freed from water and carbon dioxide by passage over ascarite and activated alumina; the oxygen atmosphere was commercial oxygen (99.9%) similarly treated. The carbon dioxide atmosphere was commercial material, thoroughly dried, passed over copper at 600° and again dried.

A special device was needed to mix gas with water vapor

---

(2) Dünwald and Wagner, *Z. anorg. allgem. Chem.*, **199**, 321 (1931).

(3) H. A. Sloman, *J. Iron Steel Inst., London*, **143**, 298P (1941).

(4) Taylor and Chipman, *Trans. Am. Inst. Mining Met. Engrs.*, **154**, 228 (1943).

(5) Ref. 1, p. 1410.

(6) Greig, Posnjak, Merwin and Sosman, *Am. J. Sci.*, **30**, 239 (1935); their temperatures, on the Geophysical Laboratory scale, have been corrected to bring them to the slightly different international temperature scale.

in known ratio. This was a positive displacement rotary micro-pump, gear-driven by a synchronous motor, which was specially designed and calibrated; it delivered the gas into a thermos bottle containing water heated by a coil of platinum wire, all connections thence to the furnace being heated to obviate condensation. The rate of production of steam was measured by the watt-input, corrected for the small loss of heat and checked by condensing the output; these calibrations agreed within 1%. This same bottle supplied the steam atmosphere, the gas inlet being then closed.

The results of analyses of melts which had been equilibrated with an atmosphere lean in oxygen, then either quenched in mercury or merely pulled quickly up into the cool head of the furnace tube, were the same; but when the atmosphere was air or oxygen, the samples tended to pick up oxygen unless quenched. The results on samples quenched in mercury were erratic and are not here recorded. Consequently recourse was finally had to water as quenching liquid, despite the danger of loss of oxygen

TABLE I

COMPOSITION OF LIQUID IRON OXIDE IN EQUILIBRIUM WITH SEVERAL ATMOSPHERES AT VARIOUS TEMPERATURES

Starting material[a]	Temp., °C.	Time at temp., hours	$(Fe^{++} + Fe^{+++})/Fe^{++}$ r
A. CO_2–CO, $p_{CO_2}/p_{CO} = 0.376$			
Wüstite	1383	41	1.096
Fe_2O_3	1395	48	1.097
Wüstite	1445	75	1.091
Wüstite	1479	72	1.088
Fe_2O_3	1500	23	1.086
B. CO_2–CO, $p_{CO_2}/p_{CO} = 1.00$			
Fe_2O_3	1403	5	1.183
Fe_2O_3	1450	6	1.178
Fe_2O_3	1575	4	1.169
Wüstite	1575	6	1.169
C. CO_2–H_2, initial $p_{CO_2}/p_{H_2} = 2.23$			
Fe_2O_3	1395	$5^1/_2$	1.241
Wüstite	1395	$5^1/_2$	1.238
Fe_2O_3	1500	18	1.230
Wüstite	1500	18	1.227
Fe_2O_3	1600	$3^1/_4$	1.227
Wüstite	1600	$3^1/_4$	1.227
D. H_2O–H_2, $p_{H_2O}/p_{H_2} = 7.10$			
Fe_2O_3	1428	18	1.273
Wüstite	1428	18	1.267
Fe_2O_3	1605	4	1.250
Wüstite	1605	4	1.245
E. CO_2–CO–H_2O, initial $p_{CO_2}/p_{CO}/p_{H_2O} = 1:1:14.1$			
Fe_2O_3	1598	4	1.386
Wüstite	1598	4	1.382
Fe_2O_3	1633	4	1.392
Wüstite	1633	4	1.392
F. CO_2–H_2, initial $p_{CO_2}/p_{H_2} = 7.13$			
Fe_2O_3	1444	5	1.428
Wüstite	1444	5	1.427
Fe_2O_3	1469	5	1.426
Wüstite	1469	5	1.425
Fe_2O_3	1472	5	1.426
Fe_2O_3	1535	3	1.430
Wüstite	1535	3	1.427
Fe_2O_3	1601	4.5	1.429
Wüstite	1601	4.5	1.427
Fe_2O_3	1610	2	1.431
Wüstite	1610	2	1.427
G. CO_2–H_2, initial $p_{CO_2}/p_{H_2} = 28.3$			
Wüstite	1485	4	1.698
Wüstite	1491	3	1.710
Fe_2O_3	1496	6	1.708
Wüstite	1496	6	1.719
Fe_2O_3	1535	18	1.720
Wüstite	1535	18	1.710
Fe_2O_3	1594	2	1.732
Wüstite	1594	2	1.707
Fe_2O_3	1598	5	1.752
Wüstite	1598	5	1.758
Fe_2O_3	1603	2	1.766
Wüstite	1603	2	1.777
H. Steam, 1 atmosphere			
Fe_2O_3	1594	12	2.074
Wüstite	1594	12	2.080
Fe_2O_3	1601	18	2.045
Wüstite	1601	18	2.055
I. CO_2—1 atmosphere			
Fe_2O_3	1577	5	2.304
Fe_2O_3	1578	2	2.309
Fe_2O_3	1590	3	2.302
Wüstite	1591	5	2.291
Fe_2O_3	1592	5	2.286
Fe_2O_3	1634	4	2.256
J. CO_2–O_2, 3.91% oxygen			
Fe_2O_3	1605	7	2.824 2.850
Fe_2O_3	1606	3	2.838
K. Air, 1 atmosphere			
Fe_2O_3	1595	2	3.529
Fe_2O_3	1602	2	3.492
Fe_2O_3	1619	3	3.439
Fe_2O_3	1630	1	3.348
Fe_2O_3	1630	6	3.308
Fe_2O_3	1635	4	3.301
Wüstite	1635	4	3.281
L. Oxygen, 1 atmosphere			
Fe_2O_3	1589	6	4.237
Fe_3O_4	1589	6	4.216
Fe_2O_3	1596	1	4.067
Fe_2O_3	1603	1	4.053
Fe_2O_3	1607	4	4.023
Wüstite	1607	4	4.007
Fe_2O_3	1615	1	3.881
Fe_2O_3	1632	5	4.033
Wüstite	1632	5	3.958
Fe_2O_3	1636	1	3.998

[a] Fe_2O_3 is Riedel and de Haen's "titrimetric standard"; the wüstite was prepared by partial reduction of this material. Paired samples were in the furnace simultaneously, in separate crucibles.

with the evolved steam; these results are reasonably consistent and show no systematic departure from those on the samples quenched in mercury.

Since the platinum crucible picked up iron from the sample, particularly at the higher temperatures and lower pressures of oxygen, especial care was taken either (a) to use a crucible which had previously taken up about the appropriate amount of iron, or (b) to make the equilibration period long enough to ensure that any further removal of iron from the liquid should not affect the determination. No platinum was detected in melts when the atmosphere was low in oxygen. The largest concentration ever detected was 0.2% in a liquid equilibrated with 1 atm. of oxygen at 1630°; since in this region the precision is somewhat smaller than elsewhere, it is deemed that the presence of platinum was without measurable effect on the result, as should be the case according to the phase rule. Since the melting temperature of platinum is lowered by iron, this method could not be used at very high temperature and low oxygen pressure. For instance, at 1575° in a 50-50 CO-CO_2 atmosphere, the crucible in six hours picked up enough iron so that it melted in part and undoubtedly would soon have melted completely.

Direct Determination of Composition in the Liquid Oxide Field.—In general, simultaneous measurements were made on pairs of samples, one of which was initially ferric oxide, the other ferric oxide which had been partially reduced (or in a few cases, electrolytic iron) so that equilibrium was approached from either side; and, after preliminary measurements, each experiment was continued until equilibration was assured, when each pair of determinations agreed. The use of such pairs proved less advantageous than had been anticipated, for the reason that each sample disturbed the atmosphere appropriate to reaction with the other, and consequently a longer time was needed to ensure that both had come to equilibrium with the specified atmosphere; toward the end of the work, therefore, this procedure was abandoned and single, or duplicate, samples were used.

The results thus obtained on the composition of liquid oxide, expressed directly as the measured ratio (r) of ferrous plus ferric to ferrous iron, in equilibrium with the several atmospheres at various temperatures, are given in Table I; all preliminary measurements have been omitted. The composition range covered in the liquid field is from 22.5 to 28.5% oxygen by weight.

A direct plot of this ratio r in liquid oxide against temperature (Fig. 2) shows that all points for each gas composition lie very close to a straight line (each when produced ending on one of the liquidus curves NI, IVR which are derived later from Table IV). The precision is not quite so good as for the solid solution (Fig. 4, paper I); it is, as would be expected, best in the region of low oxygen pressure where the ratio of the components of the gas mixtures is not far from unity. When the proportion of carbon monoxide, or of hydrogen, is small, a trace of oxygen would cause a large error. In the high oxygen range the difficulty of preventing change in composition of the sample while it cools—in other words, the large temperature coefficient of the equilibrium and the rapidity of its adjustment—detracts from the precision; this is considerably exaggerated in Fig. 2 by use of r as coördinate.

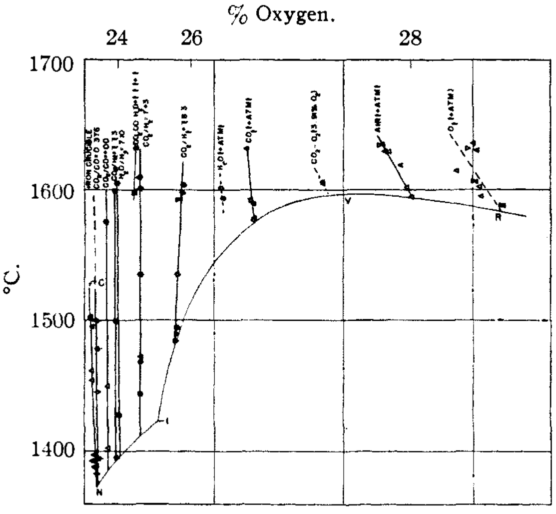


Fig. 2.—Composition of liquid iron oxide, in terms of r (ratio of ferrous + ferric to ferrous iron) in equilibrium with various atmospheres, at temperatures down to the liquidus curves NI, IVR.

From a large plot of the data in Table I in which the composition of each atmosphere was expressed in terms of the equivalent[7] (a) ratio of partial pressure of carbon dioxide to monoxide, (b) partial pressure of oxygen, the several values of r at 1400, 1500, 1600° were read off; these are plotted in Fig. 3 in which the composition of the oxide is expressed in terms of the ratio N_2/N_1, N_2 and N_1 being the atom fractions of oxygen and iron, respectively $[N_2N_1 = (3r - 1)/2r]$. In Fig. 3A, the ordinate is log p_{CO_2}/p_{CO}, yielding isotherms which, being nearly coincident, provide a more accurate basis for thermodynamic calculation and apply more directly when low oxygen pressures are being considered. Figure 3B, in which the ordinate is log p_{O_2} better illustrates the situation at higher oxygen pressures. It includes, for comparison, data of White[8] of Krings and Schackmann[9] and of the Geophysical Laboratory investigators[6]; also the several phase boundaries, lettered as in Fig. 1, as derived either from paper I, or from a later section of this paper. In this type of diagram the fields may overlap, as happens in the upper right of Fig. 3B where the field designated "magnetite + liquid oxide" is also part of the homogeneous fields of liquid oxide and of magnetite.

Direct Measurements in the Magnetite Field VR'YT.—Although in this region the equilibrium in presence of air or oxygen has been thoroughly

---

(7) Computed by use of the constants, as listed in paper I, footnote 7, p. 1401.

(8) J. White, *J. Iron Steel Inst.*, London, *Carnegie Schol. Mem.*, **27**, 1 (1938).

(9) Krings and Schackmann, *Z. Elektrochem.*, **41**, 479 (1935).

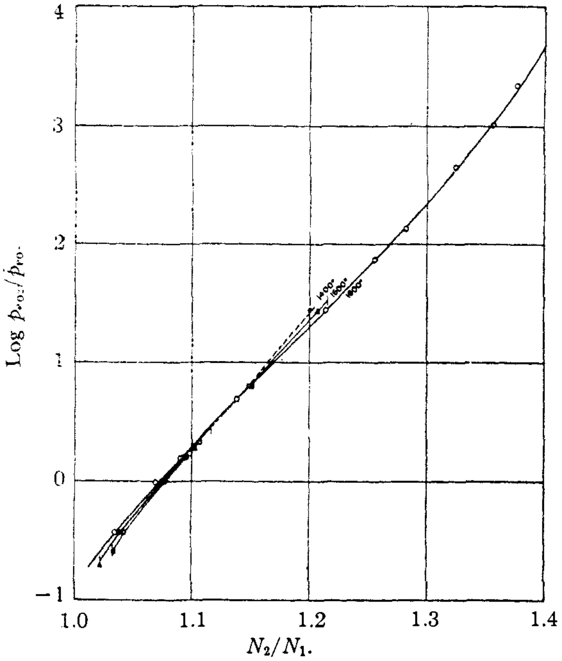


Fig. 3A.—Variation of composition of liquid oxide with ratio p_{CO_2}/p_{CO} at 1400, 1500, 1600° as read from Fig. 2. Short vertical lines represent the limiting composition of the stable liquid phase.

investigated by Greig and co-workers,[6] we thought it desirable to supplement their outstanding work in order to collate the two investigations as well as to get information at lower oxygen pressures.

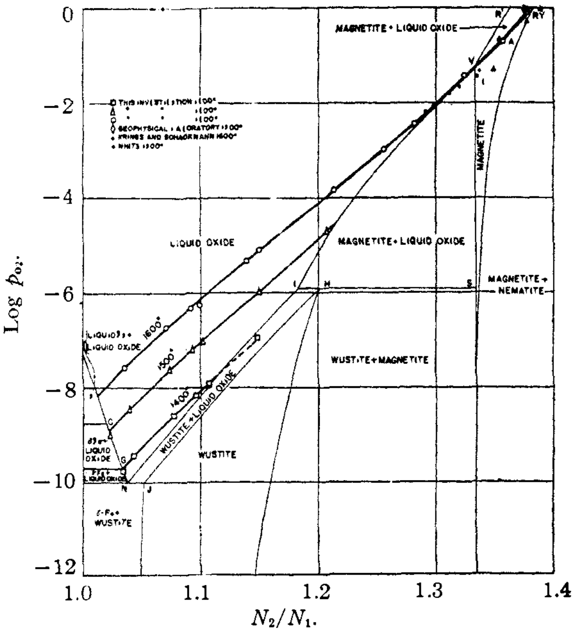


Fig. 3B.—Relation between partial pressure of oxygen and composition of liquid oxide, expressed as the atom fraction N_2/N_1, as read from Figure 2 at 1400, 1500, 1600°; with data of other recent investigations for comparison, and outlines of the several phase boundaries.

This group of measurements, carried out in precisely the same way as those on the liquid oxide, yielded the results in Table II. These are plotted in Fig. 4 in which, for ease of subsequent calculation, the abscissa is the mole fraction of Fe_3O_4 on the basis of Fe_3O_4 and Fe_2O_3 as components $[N_{Fe_3O_4} = 2/(r - 1)]$. The results of White[8] in this region are so scattered that they have been omitted. The phase boundaries are the best smooth curves through the points representing the continuation of the curve for each atmosphere to the melting temperature or the magnetite–hematite inversion temperature, as given in Table IV and indicated in Fig. 4. These are the least precise of our results, because of the relatively large error caused by possible lack of purity of the gas (carbon dioxide) at lower oxygen pressures, and at higher oxygen pressures by change of composition during quenching of the

TABLE II

COMPOSITION OF MAGNETITE IN EQUILIBRIUM WITH SEVERAL ATMOSPHERES AT VARIOUS TEMPERATURES

Starting material[a]	Temp., °C.	Time at temp., hours	$(Fe^{++} + Fe^{+++})/Fe^{++}$ r
	A. CO_2-H_2; initial p_{CO_2}/p_{H_2} = 28.3		
Fe_2O_3	1189	108	3.03
Wüstite	1189	108	3.01
Fe_2O_3	1294	18	3.00
Wüstite	1294	18	3.01
Fe_2O_3	1296	18	3.01
Wüstite	1296	18	3.01
Fe_2O_3	1390	18	3.01
Wüstite	1390	18	3.01
Fe_2O_3	1479	18	3.01
Wüstite	1479	18	2.98
	B. Steam, 1 atmosphere		
Fe_2O_3	1521	18	3.00
Wüstite	1521	18	3.01
	C. CO_2, 1 atmosphere		
Fe, electrolytic	1128	240	3.147
Wüstite	1147	72	3.205
Wüstite	1147	72	3.257
Fe, electrolytic	1148	48	3.124
Fe_2O_3	1177	60	3.124
Fe, electrolytic	1180	64	3.121
Wüstite	1198	72	3.146
Wüstite	1210	96	3.074
Fe_2O_3	1244	72	3.080
Fe, electrolytic	1256	18	3.102
Fe_2O_3	1306	24	2.999
Wüstite	1306	24	2.993
Fe_2O_3	1321	18	3.046
Wüstite	1321	18	3.019
Fe, electrolytic	1335	1	2.994
Fe_2O_3	1392	18	2.999
Wüstite	1443	72	3.012
Fe_2O_3	1542	18	2.995
Wüstite	1542	18	3.005

TABLE II (*Concluded*)

Starting material[a]	Temp., °C.	Time at temp., hours	(Fe^{++} + Fe^{+++})/Fe^{++} r
D. O$_2$-CO$_2$, p_{O_2} = 0.0391 atmosphere			
Fe$_2$O$_3$	1144	72	∞
Fe wire	1286	18	∞
Fe wire	1320	18	3.560
Fe$_2$O$_3$	1388	72	3.397
Fe$_2$O$_3$	1505	5	3.195
E. Air, 1 atmosphere			
Fe$_2$O$_3$	1502	23	3.543
Magnetite	1502	23	3.495
Fe$_2$O$_3$	1545	18	3.328
Wüstite	1545	18	3.332
Fe$_2$O$_3$	1589	18	3.299
Wüstite	1589	18	3.280
Fe$_2$O$_3$	1593	3	3.314
Wüstite	1593	3	3.305
F. Oxygen, 1 atmosphere			
Fe$_2$O$_3$	1493	45	4.108
Wüstite	1493	45	4.090
Fe$_2$O$_3$	1512	7	3.827
Wüstite	1512	7	3.870

[a] See note to Table I.

sample. Within the range covered, there is no indication of a stable magnetite with less oxygen than the formula Fe$_3$O$_4$, but a considerable range (up to O:Fe = 1.38) of solid solution of oxygen in magnetite.

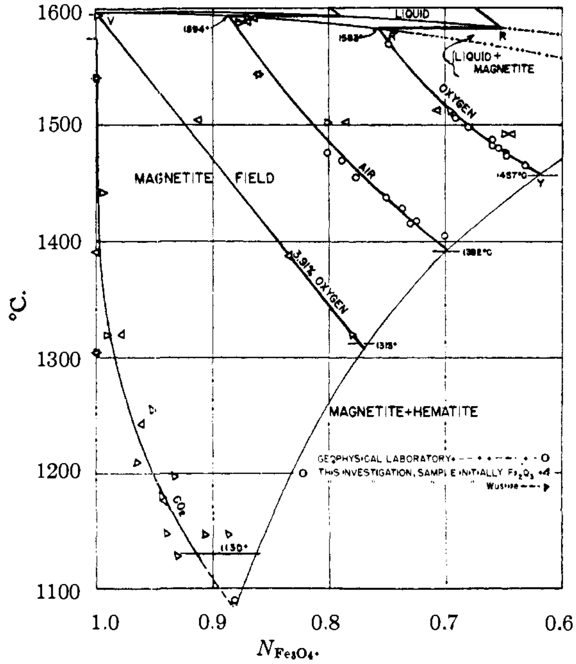


Fig. 4.—Composition of magnetite, expressed as $N_{Fe_3O_4}$ in equilibrium with various atmospheres, up to the phase boundaries; transition temperatures indicated are from Table III.

Determination of the Equilibrium Iron-Liquid Oxide: Line CN.—These measurements were made by heating an oxide, enclosed in a closed iron crucible in an atmosphere of purified nitrogen, to one of a series of temperatures from about 1370 to 1520°, then analyzing the product. The results, in Table III, are somewhat less concordant than those in Table I (which were equilibrated with a gas instead of a solid), but less erratic than those observed when wüstite was heated in an iron crucible (paper I). As an independent check, a small (1-g.) sample of electrolytic iron was suspended, at the thermal center of the furnace through which passed a constant carbon dioxide-monoxide mixture such that it would just oxidize iron at this temperature, 1455°; the liquid oxide dropping off slowly was caught in a platinum crucible below the furnace, about twenty-four hours being required to collect enough for analysis. Microscopic examination disclosed no metallic iron; the result (r = 1.067) is in satisfactory accord with the other data in Table IIIA.

TABLE III

A. COMPOSITION OF LIQUID OXIDE IN EQUILIBRIUM WITH IRON (LINE CN)

Starting material[a]	Temp., °C.	Time at temp., hours	(Fe^{++} + Fe^{+++})/Fe^{++} r
Fe$_2$O$_3$	1390	4	1.081
Fe$_3$O$_4$	1390	18	1.076
Wüstite	1392	2	1.052 1.056
Fe$_3$O$_4$	1393	6.5	1.077
Wüstite + magnetite	1397	2.2	1.069
Fe$_2$O$_3$	1454	4.5	1.057
Fe$_2$O$_3$	1461	18	1.055
Fe$_2$O$_3$	1495	1	1.056
Fe$_2$O$_3$	1501	3.5	1.051
Fe$_2$O$_3$	1502	2.5	1.045
Fe$_2$O$_3$	1502	2	1.049
Fe	1455	24	1.067

[a] See note to Table I.

B. COMPOSITION OF CO-CO$_2$ MIXTURES IN EQUILIBRIUM WITH IRON AND LIQUID OXIDE

Temp., °C.	p_{CO_2}/p_{CO}
1376	0.268
1436	.233
1493	.199

The composition of the carbon dioxide-monoxide mixture in equilibrium with iron and its liquid oxide at several temperatures was determined in precisely the same way as in the analogous case of iron and wüstite (paper I). A strip of lightly oxidized electrolytic iron was held in a known carbon dioxide-monoxide mixture, with its lower tip at the thermal center of the furnace, at a temperature such that it was oxidized only a short distance at the lower end but the remainder was reduced. The boundary between the oxidized and the deoxidized zone was not sharp but its indeterminacy was judged to correspond to about

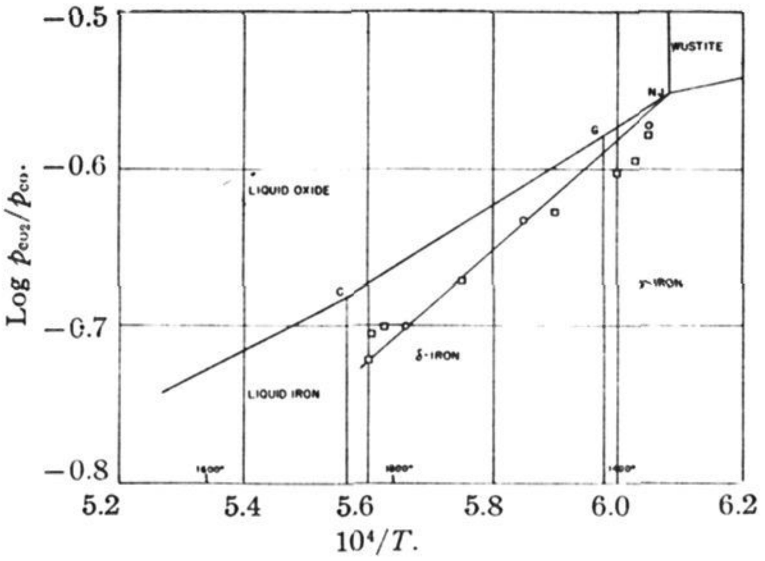
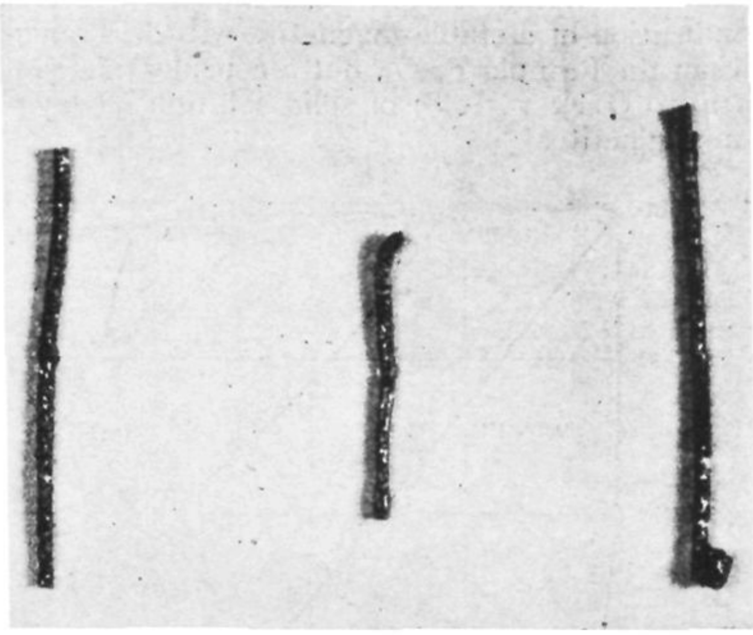


Fig. 5.—Gas composition in equilibrium with iron and its liquid oxide; direct determinations by this investigation shown as circles, by Chipman and Marshall as squares. The upper line is drawn with the slope corresponding to the more reliable heat of reaction calculated as described later in the text.

1°; its temperature, which coincided within 1° with that of the thermal center, was taken as that for equilibrium with this particular atmosphere since at lower temperature the tip was reduced. The results, in Table IIIB, when plotted in terms of log p_{CO_2}/p_{CO} against $1/T$, lie close to the straight line which also represents the data of Chipman and Marshall.[10] Yet, despite this agreement, we doubt their accuracy; in part because the slope of this line corresponds to a heat effect which differs unduly from that calculated (on a later page) from other experimental data; mainly, however, because we believe all of them to be vitiated by the experimental fact that the oxide became contaminated by silica which somehow volatilized from the porcelain tube.[11] To surmount this difficulty we tried, though without success, to procure an alumina tube, as was used by Chipman and Marshall; but in it they had a radiation shield of clay, overlooked this possible source of contamination, and did not look for silica in their product. For this reason, we preferred to draw line CN from point NJ in Fig. 5 at an angle in agreement with the computed heat effect.

Melting Temperatures of Wüstite and Magnetite (Lines NI, IVR).—The melting point (N) of wüstite in equilibrium with iron has been measured by several investigators, most recently by Chipman and Marshall,[10] who give it as 1369°. We redetermined it by enclosing ferric oxide in an (electrolytic) iron crucible, closed by pinching its top, held at a controlled temperature for half an hour in an atmosphere of purified nitrogen; after the sample was cooled it was examined. The samples which had been at 1372° had melted completely, those at or below 1370° showed no sign of melting; a sample held at 1371° had partially melted, hence this was taken as the temperature of the line NJ (Fig. 1).

The remainder of the melting curves NI, IVR—to each point of which there corresponds an atmosphere of definite oxidizing potential—was determined as follows. A short piece of electrolytic iron (strip or wire), suspended from platinum, was converted to the oxide in equilibrium with the particular atmosphere at a temperature slightly below that at which this oxide would melt. After a millimeter had been broken off and discarded in order to leave a sharp lower edge, the sample was replaced in the furnace so that this edge was at the thermal center. The temperature was raised by 1 or 2° at appropriate intervals; before each change the sample was raised into the cool glass extension of the furnace tube and inspected. The temperature at which a liquid droplet first appeared,[12] which was always sharp,[13] was taken as the melting temperature in the particular atmosphere. This temperature was measured, exactly as described in paper I, by removing the specimen, flushing the furnace tube with air, and inserting a calibrated thermocouple in the thermal center previously occupied by the lower edge of the specimen. The appearance of three separate specimens, held in the same atmosphere at 1441,



A	B	C
1441 °C.	1443 °C.	1445 °C.
8 min.	7 min.	3 min.

Fig. 6.—Photograph of specimens used for determination of the melting temperature of magnetite in one of the atmospheres.

---

[10] Chipman and Marshall, This Journal, 62, 299 (1940).

[11] Compare paper I, p. 1401.

[12] A slight rounding was not taken as an indication that the average temperature of the thermal center of the furnace exceeded the melting point, since this temperature fluctuated about 0.5° due to the action of the controller; moreover, some recrystallization occurred.

[13] The phase rule requires that the melting point be sharp under these conditions, since only one solid or liquid phase can coexist in equilibrium with an arbitrary gas composition at an arbitrary temperature. Of course, under the more usual conditions of fixed total composition of the specimen, melting takes place over a range of temperature, in accordance with the phase diagram of Fig. 1.

1443, 1445°, respectively, is illustrated in Fig. 6; the lower edge of the first is still sharp, that of the third is hidden by a drop which had been molten; and the intermediate specimen shows evidence of incipient melting. In this case, therefore, the melting temperature was taken as 1443 ± 1°. The temperatures, as finally determined in this way, with the corresponding equilibrium pressures of oxygen, are given in Table IVA, B.

TABLE IV

OBSERVED TRANSITION TEMPERATURES

Composition of gas	Log p_{O_2} (atm.)	Log p_{CO_2}/p_{CO}	Temp., °C.
A. Wüstite-liquid equilibrium			
(Iron crucible)			1371 ± 1
CO_2-CO: p_{CO_2}/p_{CO} = 0.376	−9.70	−0.423	1374 ± 1
p_{CO_2}/p_{CO} = 1.00	−8.72	0	1386 ± 1
CO_2-H_2: initial p_{CO_2}/p_{H_2} = 2.23	−8.23	+0.215	1392 ± 2
p_{CO_2}/p_{H_2} = 7.13	−6.84	0.810	1411 ± 2
p_{CO_2}/p_{H_2} = 13.62	−6.14	1.111	1421 ± 1
B. Magnetite-liquid equilibrium; fields 1VS and VRR'			
CO_2-H_2: initial p_{CO_2}/p_{H_2} = 19.35	−5.59	1.270	1443 ± 1
p_{CO_2}/p_{H_2} = 28.3	−4.88	1.440	1482 ± 2
CO_2, 1 atm.	−2.51	2.205	1575 ± 2
O_2-CO_2: 3.91% O_2	−1.40	2.675	1596 ± 1
Air, 1 atm.	−0.68	3.042	1594 ± 2
O_2, 1 atm.	0	3.428	1583 ± 2
C. Magnetite-hematite equilibrium; field TYZZ'			
O_2	0	4.000	1457 ± 2
Air	−0.68	3.990	1392 ± 2
3.91% O_2 in CO_2	−1.41	4.066	1313 ± 2
CO_2	−4.18	3.884	1130 ± 10

Equilibrium Magnetite–Hematite in Several Atmospheres: Field TYZZ'.—This transition temperature was measured in precisely the same way as that for wüstite–magnetite field (QHST) as described in paper I. The results are given in Table IVC.

The Oxygen Potential-Temperature Diagram

This pair of diagrams for equilibrium of liquid oxide with wüstite and with magnetite, and for magnetite with hematite, are based directly on Table IV; they also include the iron–liquid oxide equilibrium which is discussed later, and data on iron–wüstite and wüstite–magnetite from paper I. In Figure 7A the potential is in terms of log p_{CO_2}/p_{CO}, in 7B in terms of log p_{O_2}. The ratio p_{CO_2}/p_{CO} can be realized physically at one atmosphere total pressure only up to the equilibrium ratio which results from the decomposition of pure carbon dioxide at the temperature; but this in no wise impairs the significance of Fig. 7A. The three curves representing equilibrium between wüstite, magnetite and liquid, taken two at a time, intersect at a point IHS, the peritectic temperature, within the experimental error (equivalent to about 1% in the ratio p_{CO_2}/p_{CO}). As thus fixed, IHS is at 1424 ± 1° and p_{CO_2}/p_{CO} is then 16.22 ± 0.15. The maximum melting temperature of magnetite (to a liquid of identical composition) is at 1597 ± 2° and p_{O_2} = 0.0575 atm. The iso-activity curves of iron in its oxide, shown in Fig. 7B, will be discussed later.

The Constant Boiling Mixture of Iron and Oxygen, and the Vapor Pressure of Iron at 1600°

In addition to the measurements already described, which are the basis of all our diagrams and calculations, there is one rather special experiment which is brought in at this point even though its interpretation involves some of the thermodynamic quantities discussed later.

Since the partial pressure of oxygen in a high-oxygen melt is markedly lowered by an increment of iron, and the activity of iron in a low-oxygen melt is markedly lowered by an increment of oxygen, it is reasonable to suppose that the graph of total equilibrium pressure *versus* composition of liquid iron oxide will exhibit a minimum. If this is the case, continued evaporation of any such oxide should ultimately yield as a residue the constant boiling (azeotropic) mixture, just as is true of aqueous solutions of hydrochloric acid. Experimental determination of the composition of such a mixture permits, by combination with other data of this communication, an estimation of the partial pressure of iron in the mixture, hence of the vapor pressure of pure liquid iron. A vacuum furnace, in which a pressure of the order of 0.01 micron could readily be maintained, was used for this measurement. Inside a small heavy molybdenum winding, heated by induction, which served as the primary source of heat, was placed

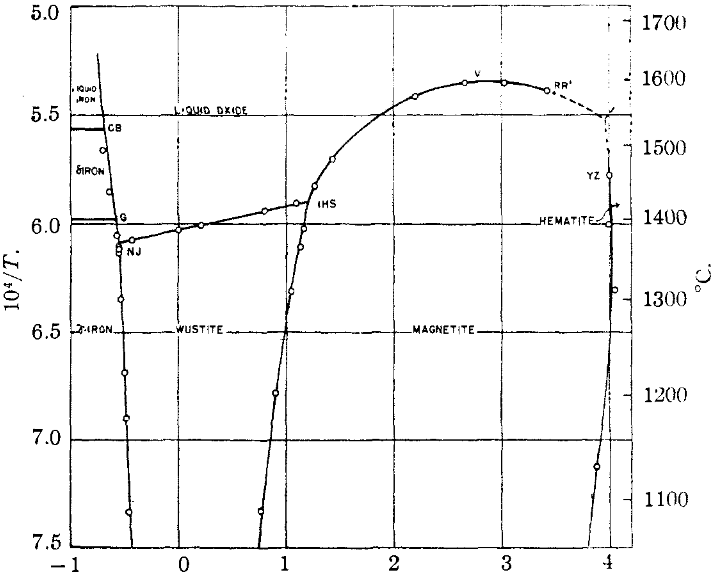


Fig. 7A.—Relation between log p_{CO_2}/p_{CO} and $1/T$ for the several three-phase equilibria.

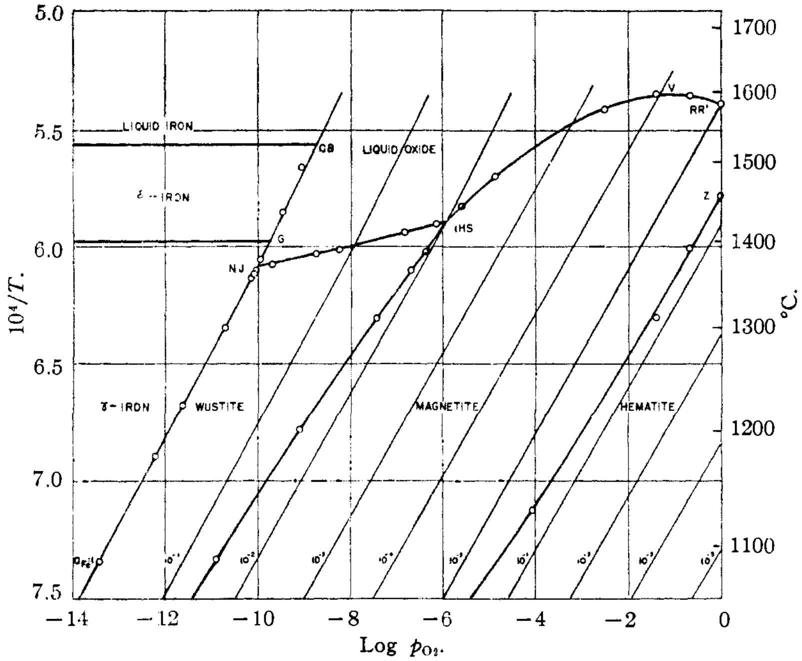


Fig. 7B.—Relation between log p_{O_2} and $1/T$ for the several three-phase equilibria; and the calculated isoactivity curves of iron in solid and liquid oxide throughout the range.

a small alumina tube which surrounded the small (2 cc.) platinum crucible containing the charge. The temperature, observed with an optical pyrometer, was held as close to 1600° as possible. In the first experiment ferric oxide lost oxygen until r was lowered to 1.6 in half an hour; in a second an oxide initially of composition nearly in equilibrium with iron lost iron until r rose to 1.2 in about the same time; thus it was verified that this system exhibits a maximum boiling point. Two subsequent experiments, started with oxides in which r = 1.6 and 1.2, respectively, placed the composition of the azeotropic mixture between the limits 1.30 and 1.32. A final experiment with oxide, r = 1.32, yielded in about two hours, a product with r = 1.304 (N_2/N_1 = 1.116), our best estimate of the composition of the azeotropic mixture.[14] In this experiment the pressure fell rapidly to 11 microns, then slowly to 5 microns, at which it remained during the final hour; consequently 5 microns is taken as the pressure in equilibrium with the azeotropic mixture at 1600°.

Since the ratio of oxygen to iron in the constant boiling mixture must be identical with that in the gas in equilibrium therewith, it follows that if the only gaseous molecular species containing oxygen or iron are O_2, O, Fe, FeO then

$$\frac{2p_{O_2} + p_O + p_{FeO}}{p_{Fe} + p_{FeO}} = N_2/N_1 = 1.116$$

At the composition of the constant boiling mixture the partial pressure of oxygen (from Table VI) is 1.66×10^{-6} atm. From spectroscopic data for the equilibrium $O_2 = 2O$, that of monatomic oxygen is 0.33×10^{-6} atm. Inserting these partial pressures in the above equation yields

$$p_{Fe} = 3.26 \times 10^{-6} - 0.104p_{FeO}$$

and the total pressure $p_{Fe} + p_{O_2} + p_O + p_{FeO}$ is $0.90\,p_{FeO} + 5.3 \times 10^{-6}$ atm. Equating this to the observed total pressure of 5 microns or 6.6×10^{-6} atm. it follows that p_{FeO} is about 1.5×10^{-6} atm. The second term in the above expression for p_{Fe} though uncertain is small (0.2×10^{-6} atm.) and the partial pressure of iron vapor in equilibrium with the constant boiling mixture at 1600° is found to be 3.1×10^{-6} atm. As the activity of iron in an oxide of this composition at 1600° is 0.054 (from Table VI) it follows that the vapor pressure of pure iron at this temperature is 5.8×10^{-5} atm. Direct measurements of the vapor pressure of iron have been made at 2220–2450°[15] and in the γ-iron region[16] (below 910°). Both these sets of measurements (and the heat capacities) are consistent with the following equation for the vapor pressure of liquid iron

$$\log p = (19400/T) - 2.4 \log T + 14.05$$

At 1600° the vapor pressure of iron as found therefrom is 7.1×10^{-5} atm.—in reasonably good agreement with the present experimental determination.

It is to be noted that even if the present determination of the total pressure be discounted and the vapor pressure [illegible] from the foregoing equation be inserted (after multiplication by the activity) along with $p_{O_2} + p_O$ in the equation expressing the equality of composition, p_{FeO} is found to be negative—a physical impossibility. Hence it is concluded that the volatility of ferrous oxide as such at 1600° is not large compared to its dissociation, and the oxide fume commonly observed in steel mills is to be attributed principally to the vaporization of iron (either from metal or by dissociation of oxide) and subsequent oxidation.

Thermodynamic Calculations

The partial molal heat of solution ($\overline{H}_2$) of oxygen in a liquid oxide is readily derived from the temperature coefficient of the oxygen pressure at constant composition. The partial molal heat ($\overline{H}_2'$) of transfer of one gram atom of oxygen from

---

(14) This sample analyzed 98.1% (FeO + Fe_2O_3), the remainder being principally oxides of molybdenum.

(15) "International Critical Tables," Vol. III, 205.

(16) Marshal, Dornte and Norton, THIS JOURNAL, **59**, 1161 (1937); Jones, Langmuir and Mackay, *Phys. Rev.*, **30**, 201 (1927).

a carbon monoxide–dioxide mixture to a liquid oxide is 4.575 times the slope of the linear plot of log p_{CO_2}/p_{CO} at round compositions, as read from Fig. 3A, against $1/T$. $\overline{H}_2'$ differs from $\overline{H}_2$ by the heat of formation of CO_2 from CO and $^1/_2$ O_2, taken as 66,660 cal. per mole CO_2 at 1500°. The results for several compositions of the oxide are given in Table V, and may be represented within the experimental error (the greatest discrepancy being about 200 cal.) by the equations

$$\overline{H}_2' = -79{,}100 + 69{,}500 \frac{N_2}{N_1}$$

$$\overline{H}_2 = -145{,}660 + 69{,}500 \frac{N_2}{N_1}$$

where, as before, N_1 and N_2 are the atom fractions of iron and oxygen, respectively, in the oxide. From Fig. 2 it is evident that a satisfactory temperature coefficient cannot be obtained when N_2/N_1 is greater than 1.2 ($r > 1.7$), since beyond this level the temperature range covered is short. Although the data of White[8] in the high oxygen range are somewhat erratic, and appear not to be in too good agreement with those of this investigation on an isothermal plot (Fig. 3B), it is of some interest to derive $\overline{H}_2$ by combining his temperature coefficients with data from our 1600° isotherm. White uses as composition variable the number of moles ferrous oxide (x) formed from one mole ferric oxide, whence, in our notation $x = 2/r = 6 - 4N_2/N_1$. From a fundamental theorem of partial derivatives and the usual expression for $\overline{H}$ in terms of partial pressures it follows that

$$\overline{H}_2 = \frac{-2.303R}{8} T^2 \left(\frac{\partial x}{\partial T}\right)_{p_{O_2}} \left(\frac{\partial \log p_{O_2}}{\partial N_2/N_1}\right)_T$$

The first of these two partial derivatives was measured at 1600° from the plots given by White, and the second from Fig. 3B. Values of $\overline{H}_2$ thus derived are shown in Fig. 8; the points fall fairly well on the extension of the straight line representing our results in the lower oxygen range. Similar treatment of the air isobar in Fig. 2 leads to a value of $\overline{H}_2 = -50{,}200$ calories (at $N_2/N_1 = 1.357$) which also is in good agreement with the same extended line.

TABLE V

PARTIAL MOLAL HEAT OF SOLUTION OF OXYGEN IN LIQUID IRON OXIDE OF SEVERAL COMPOSITIONS AT 1500°

Composition oxide N_2/N_1	From CO_2, $\overline{H}_2'$, cal.	From O_2, $\overline{H}_2$, cal.
1.04	−6860	−73,520
1.07	−4430	−71,090
1.10	−2830	−69,490
1.15	+ 640	−66,020
1.20	+4530	−62,130

The activity of iron (a_1) in liquid oxides is calculated by means of the Gibbs–Duhem equation: $\log a_1 = -\int N_2/N_1 \, d \log p_{O_2}{}^{1/2}$, from the corresponding activity (a_2) of oxygen (or from p_{CO_2}/p_{CO}). If the integration is performed from the composition of oxide in equilibrium with iron to the composition under consideration, the activity thus calculated is relative to metallic iron as unity. Although from many viewpoints this is the most desirable standard state, the accuracy of all values based upon the measurements of p_{CO_2}/p_{CO} in equilibrium with oxide and iron is seriously impaired by the suspected error in these data, and by the necessity of extrapolating above the melting point of iron. This disadvantage can be overcome by integrating from some arbitrarily chosen composition as standard, except that the activity of metallic iron would then be uncertain; this is discussed later. The activity of iron in liquid oxide relative to the liquid oxide in which $N_2/N_1 = 1.07$ is given in Table VI; this composition was selected as being near the iron side of the liquid field and in the region where the experimental error is least.

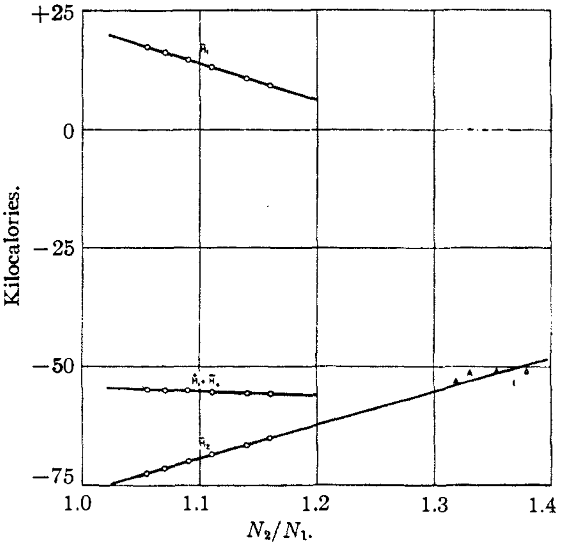


Fig. 8.—Partial molal heat of addition of one gram atom of iron ($\overline{H}$), of one gram atom of oxygen $(\overline{H})_2$, and heat of formation of one gram mole of ferrous oxide ($\overline{H}_1 + \overline{H}_2$) as functions of the composition of liquid oxide.

The activity of ferrous oxide in molten iron oxides is similarly derived from the Gibbs–Duhem equation, which in this case reduces to

$$\log a_{FeO} = - \int_{N_2/N_1 = 1.07}^{N_2/N_1} [(N_2/N_1) - 1] \, d \log p_{O_2}{}^{1/2}$$

Although a_{FeO}, relative to the composition in equilibrium with iron, is less sensitive than a_1 to experimental error in the ratio p_{CO_2}/p_{CO} in equilibrium with iron and molten oxide (since in this vicinity the integrand is small), the integration limits were again from $N_2/N_1 = 1.07$ to each composition. The values obtained are given in Table VI.

The partial molal heat of solution of metallic iron ($\overline{H}_1$) in liquid iron oxide is obtained, except

Table VI[a]

Activity of Oxygen, Iron (a_1) and Ferrous Oxide in Liquid Iron Oxide Relative to Oxide in which $N_2/N_1 =$ 1.07 as Standard State, at 1400, 1500, 1600°

N_2/N_1	Log p_{CO_2}/p_{CO}	−Log p_{O_2} (atm.)	−Log a_1	−Log a_{FeO}
Temperature 1400°				
1.034	−0.579	9.73	−0.528	−0.0255
1.04	− .470	9.51	−0.415	−0.0215
1.07	− .077	8.73	0	0
1.10	+ .257	8.06	+0.362	+0.0284
1.117	+ .450	7.67	0.576	.0494
(1.15)[b]	(+ .823)[b]	(6.93)[b]	(0.999)[b]	(.0991)[b]
(1.20)[b]	(+1.396)[b]	(5.78)[b]	(1.672)[b]	(.1994)[b]
Temperature 1500°				
1.0225	−0.663	8.92	−0.639	−0.0279
1.04	− .415	8.42	−0.383	−0.0199
1.07	− .052	7.70	0	0
1.10	+ .278	7.04	0.358	+0.0280
1.15	.820	5.95	0.968	.0957
1.20	1.36	4.87	1.60	.190
1.216	1.54	4.52	1.82	.229
Temperature 1600°				
1.012_5[c]	−0.728[c]	8.20[c]	−0.736[c]	−0.0291[c]
1.04	− .371	7.46	−0.369	−0.0191
1.07	− .021	6.76	0	0
1.10	+ .295	6.12	+0.343	+0.0268
1.15	.812	5.09	0.924	.0914
1.20	1.30	4.11	1.50	.177
1.25	1.80	3.11	2.11	.290
1.30	[2.35][d]	2.01	2.81	.439
1.333	[2.74][d]	1.23	3.33	.565
1.34	[2.825][d]	1.06	3.44	.593
1.37	[3.22][d]	0.27	3.98	.733

[a] The values in the first row for each temperature (*i. e.*, at equilibrium with metallic iron) are taken from Table VIII; the method of derivation is described later in the text. [b] Values outside the range of stability of liquid oxide. [c] Equilibrium with liquid iron. [d] Unattainable at 1 atm. pressure.

for an additive constant I, from $\overline{H}_2$ by the equation

$$\overline{H}_1 = -\int N_2/N_1\, d\,\overline{H}_2 = I - 34{,}750\,(N_2/N_1)^2$$

If values of a_1 relative to metallic iron are available, I may be evaluated by inserting in this equation values of $H_1 = 4.575\,(\mathrm{d}\log a_1/\mathrm{d}\,1/T)_{N_2/N_1}$. The average value of I thus calculated from the measurements of p_{CO_2}/p_{CO} in equilibrium with metallic iron and molten oxide (Table IIIB) is 60,420. Other methods of determining it will be discussed later.

Heat of Fusion of Wüstite.—The heat of fusion of ferrous oxide is the difference between the heat of formation of ferrous oxide in liquid oxide and that in wüstite. For example, at $N_2/N_1 = 1.07$ the value of $\overline{H}_1 + \overline{H}_2$ (from the equations given) is 50,800 cal. per mole in the liquid; the corresponding value in solid wüstite, from paper I, is 63,100 cal. The difference, 12,300 cal., corresponds to the heat of transfer of one mole of ferrous oxide from solid wüstite to liquid iron oxide both of this same composition. Since this difference is very sensitive to experimental error in the ratio p_{CO_2}/p_{CO} in equilibrium with iron and liquid oxide and its extrapolation to 1600°, the "probable error" must be regarded as large. The part of this error attributable to the absorption of silica by the sample may be estimated in the following way. From the data of Körber and Oelsen[17] saturation of liquid ferrous oxide with silicon dioxide (corresponding to about 50% silicon dioxide in the vicinity of 1600°) decreases the activity of ferrous oxide by a factor of about 3, or 0.5 log unit. In view of the unexpectedly large volatility of silica from porcelain noticed in this temperature range, it would not be surprising if the film of oxide formed were 10% saturated with silica (*i. e.*, contained 5% silicon dioxide) which would correspond to an error of about 0.05 unit in log a_{FeO} or log p_{CO_2}/p_{CO}. Over the temperature range of the equilibrium measurements (1371 to 1494°) 0.05 log unit corresponds to an error of $(4.575)\,(0.05)/0.42 \times 10^{-4} =$ 5,400 cal. in the heat of fusion; and the difference of 12,300 cal. may, from this source alone, be high by an amount of the order of 5,000 cal.

This heat of fusion will now be obtained in a different way which, being independent of the large error just discussed, is regarded as more accurate. For the reaction FeO (in wüstite) $\rightleftarrows$ FeO (in liquid iron) we may write

$$K_{FeO} = \frac{a'_{FeO(l)}}{a'_{FeO(w)}} = \frac{a_{FeO(l)}/a^0_{FeO(l)}}{a_{FeO(w)}/a^0_{FeO(w)}}$$

where $a'_{FeO(l)}$ is the activity of ferrous oxide in liquid iron relative to a standard state of some fixed composition where the activity is $a^0_{FeO(l)}$, and $a'_{FeO(w)}$ is likewise that of FeO in wüstite relative to a standard wüstite where the activity is $a^0_{FeO(w)}$; $a_{FeO(l)}$ and $a_{FeO(w)}$ are relative to any standard state. The standard state is again selected as $N_2/N_1 = 1.07$ for both solid and liquid Values of log K_{FeO} were determined at each of the melting temperatures of wüstite listed in Table IV in the following way. At each of these temperatures the corresponding compositions of solid and liquid were derived by graphical interpolation (or slight extrapolation) from tables of the ratio p_{CO_2}/p_{CO} as a function of composition and temperature. The activity at each of these compositions was then obtained by interpolation (extrapolation) from Table VI and from Table IX of paper I; these values were checked by reading direct plots (not shown) of log a_{FeO} *vs.* log p_{CO_2}/p_{CO}. The resulting values of log K_{FeO} are given in Table VII and are plotted against $1/T$ in Fig. 9. The maximum departure from the straight line drawn corresponds to a little over 1°. The heat of fusion of ferrous oxide, the slope of this line multiplied by 4.575, is 7,000 cal. per mole; strictly, this figure represents the heat absorbed

---

[17] Körber and Oelsen, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, **15**, 271 (1933).

TABLE VII

EQUILIBRIUM OF WÜSTITE WITH LIQUID OXIDE

M. p., °C.	Composition of Solid N_2/N_1	Composition of Liquid N_2/N_1	Log K_{FeO}
1371	1.052	1.038	0.0098
1374	1.060	1.045	.0106
1386	1.094	1.077	.0191
1392	1.112	1.096	.0227
1411	1.164	1.149	.0328
1421	1.191	1.175	.0383

by the transfer of one gram-atom each of iron and of oxygen from solid wüstite to liquid oxide both of the composition $N_2/N_1 = 1.07$.

The precision of this value may be estimated as follows: The total temperature range covered is 50°, so that an error of 1° of opposite sign at each extreme corresponds to 4% or 300 cal. The "probable error" of the activity of solid wüstite, as estimated previously, is about 0.0003 log unit; that of the relative activity in liquid oxide is about 0.001 log unit, which is about 4% of the range covered by log K_{FeO}, hence corresponds to 300 cal. error in the heat of fusion. Since these are the largest known errors (and they are not independent), we estimate that 7,300 cal. as the heat of fusion of ferrous oxide is probably correct within 500 cal. This error is independent of the absolute error in tabulated activities, that is, of any error in the determination of the equilibrium of oxide with metallic iron and of the extrapolation above the melting point of iron. This same quantity is derived from a different source later, and this agreement indicates that $\overline{H}_1$ as obtained by the first method is high by 12,300 − 7,300 = 5,000 cal. In other words, $\overline{H}_1$ as obtained from the relative activities of Table VI and the melting temperatures of wüstite (Table VII) is represented by the equation (obtained by subtracting 5,000 cal. from the equation derived above and rounding to the nearest 100 calories)

$$\overline{H}_1 = 55,400 - 34,750\ (N_2/N_1)^2$$

Evaluation of the Equilibrium between Iron and Liquid Oxide by Means of the Free Energy of Formation of Magnetite.—This free energy at temperatures 1100–1400° was calculated in paper I, and may be estimated at temperatures up to its melting temperature by extrapolation of the linear plot of Fig. 8 of that paper. Since in the following discussion considerable weight will be placed on these extrapolated values, we make use of other available data as a check on their reliability.

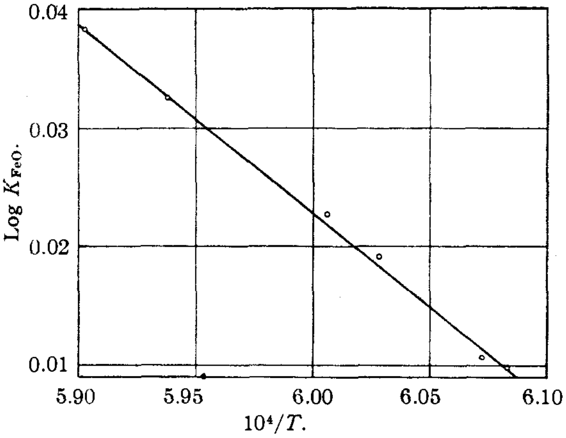


Fig. 9.—Variation with temperature of the distribution coefficient of ferrous oxide between wüstite and liquid oxide, leading to the heat of fusion of ferrous oxide.

The free energy of formation of magnetite and carbon monoxide from iron and carbon dioxide at 25° may be evaluated from calorimetric measurements[18] and from the entropies calculated from the low temperature specific heats and from spectroscopic data.[19] The equilibrium Fe–Fe_3O_4–H_2O–H_2 at 400, 500, 600° was investigated by Emmett and Schultz[20] whose data were converted from the ratio p_{H_2O}/p_{H_2} to p_{CO_2}/p_{CO} by means of the appropriate constant.[21] The several data were collated in the following way: For any reaction

$$\frac{d\ \Delta F^0/T}{d\ 1/T} = \Delta H^0$$

from which, by integrating, inserting the identity $\Delta H^0 = \Delta H^0_{298} + (\Delta H^0 - \Delta H^0_{298})$ and the definition $\Delta S^0_{298} = (\Delta H^0_{298} - \Delta F^0_{298})/298$, and rearranging, we have

$$\frac{\Delta F^0}{T} - \int (\Delta H^0 - \Delta H^0_{298})d\ 1/T = \frac{\Delta H^0_{298}}{T} - \Delta S^0_{298}$$

For the reaction 3Fe (pure, stable form) + $4CO_2(g) = Fe_3O_4$ (magnetite) + $4CO(g)$, $\Delta F^0/T$ was calculated in the usual manner from the data of Emmett and Schultz and from the measurements at 1100–1400° reported in paper I. The integral was evaluated graphically by use of data on relative heat content from sources mentioned in paper I. Unfortunately there are no data on the heat content of magnetite above 1000°; the required values were obtained by graphical extrapolation.

A plot of the left-hand side of this equation *versus* $1/T$ should be a straight line with a slope equal to ΔH^0_{298} and an intercept equal to ΔS^0_{298}. Such a plot of the data from the sources mentioned is shown in Fig. 10, from which it appears that the least certain data are ΔS^0_{298}[22] and ΔH^0_{298}. Moreover, uncertainty in the heat content of magnetite (which was extrapolated above 1000°)

---

(18) Roth and Wienert, *Arch. Eisenhuttenw.*, **7**, 455 (1933–1934).

(19) K. K. Kelley, *U. S. Bur. Mines, Bull.*, 434 (1941).

(20) Emmett and Schultz, THIS JOURNAL, **55**, 1976 (1933).

(21) From the sources referred to in paper I (page 1401). The values of the water-gas constant $\frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}}$ used in this conversion are:

400°	500°	550°	1400°	1500°	1600°
0.0835	0.200	0.284	3.32	3.72	4.09

(22) This uncertainty derives from the uncertainty in the low temperature specific heat of magnetite, S^0_{298} being 35.0 ± 0.7 as given by Kelley (ref. 19).

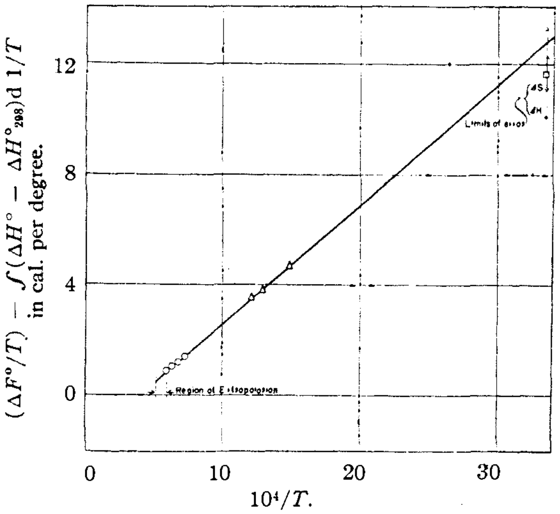


Fig. 10.—Extrapolation of lower temperature data on the formation of magnetite from iron in order to fix the activity of iron in liquid oxide relative to iron as standard.

may lead to considerable error in the ordinate in the sense that departure of the curve from strict linearity need not be interpreted as error in the free energy or entropy measurements. Extrapolation, in the range 1400–1600°, of the best line through the points from this investigation, or of any line passing through the mean of our experimental results and within range of the other points shown, yields values of $\Delta F^0/T$ which differ by not more than 0.1 unit; this corresponds to 0.02 unit in log K, 0.005 unit in log p_{CO_2}/p_{CO}, or about 1% in the ratio p_{CO_2}/p_{CO}. The line in Fig. 10 is that which fits best the mean of our results and of those of Emmett and Schultz; its equation is $\Delta F^0/T - \int_{1/298}^{1/T}(\Delta H^0 - \Delta H^0_{298})\,\mathrm{d}\,1/T = 1.73 + 4330/T$, whence $\Delta H^0_{298} = 4{,}330$ cal. for the reaction as written (corresponding to a heat formation of magnetite of 266,200 cal. at 25°, as compared to the calorimetric value 266,900 cal.[18] and 267,200 cal. obtained in paper I.

Log $K_{Fe_3O_4}$, which we define as log $\dfrac{a_{Fe}^3}{a_{Fe_3O_4}}\left(\dfrac{p_{CO_2}}{p_{CO}}\right)^4$

where the activity of iron is relative to that of the pure form stable at the temperature and that of Fe_3O_4 is relative to magnetite of composition Fe_3O_4, calculated from ΔF^0, as given by the foregoing equation, is included in Table VIII.

Combination of this definition of log $K_{Fe_3O_4}$ with the isothermal proportionality $a_{FeO} \propto a_{Fe}(p_{CO_2}/p_{CO})$ (to evaluate the activity of iron) leads to the equation

$$3 \log (p_{CO_2}/p_{CO})_{\text{l. oxide + Fe}} = \log K_{Fe_3O_4} - \log (p_{CO_2}/p_{CO})_{\text{l. oxide + }Fe_3O_4} + 3 \log \frac{a_{FeO\,(\text{equil. with }Fe_3O_4)}}{a_{FeO\,(\text{equil. with Fe})}}$$

This equation may now be used to evaluate p_{CO_2}/p_{CO} in equilibrium with metallic iron and its liquid oxide, the term on the left-hand side, by substitution of the appropriate values of log $K_{Fe_3O_4}$, of p_{CO_2}/p_{CO} in equilibrium with magnetite and liquid oxide, as obtained from Fig. 7A, and of a_{FeO} from Table VI. p_{CO_2}/p_{CO} in equilibrium with metallic iron (*i. e.*, δ-iron from 1400 to 1524° and liquid iron from 1524° up) as thus calculated is given in Table VIII and compared with direct experimental data in Fig. 5. The foregoing equation yields results which are rather insensitive to a variety of experimental errors. For example, a 1% error in the experimental determination of p_{CO_2}/p_{CO} in equilibrium with liquid oxide and magnetite leads to only 0.33% error in p_{CO_2}/p_{CO} in equilibrium with liquid oxide and metallic iron (because of the coefficient 3 in the equation); errors in measurement of p_{CO_2}/p_{CO} near the low oxygen side of the field produce only a small error in the activity of ferrous oxide (because the integrand in the Gibbs–Duhem equation is very small in this region[23]). The maximum probable error occurs at the highest temperature, 1600°; it is estimated as being between 1 and 2% in p_{CO_2}/p_{CO}.

The activity of iron (a_1) in liquid oxide of the composition $N_2/N_1 = 1.07$ relative to metallic iron may now be determined from these new values of p_{CO_2}/p_{CO}, and is given in Table VIII. A plot of these values of log a_1 (relative to a_1 for δ-iron as unity) *vs.* $1/T$ is nearly linear with a slope which corresponds to $\bar{H}_1 = 16{,}290$ cal., for the transfer of one gram-atom of iron from δ-iron to liquid oxide of the composition $N_2/N_1 = 1.07$. When this value is inserted in the equation for $\bar{H}_1$ on an earlier page the constant I is 56,080; that is, on this basis

$$\bar{H}_1 = 56{,}080 - 34{,}750(N_2/N_1)^2$$

This equation represents our best determination of $\bar{H}_1$. Values resulting from the original integration of $(N_2/N_1)\mathrm{d}\bar{H}_2$ in combination with 56,080 for I are plotted in Fig. 8; in the range of composition shown the quadratic term introduces but little curvature. At the composition $N_2/N_1 = 1.07$, $\bar{H}_2$ is (from the equation previously given) $-71{,}300$ cal, whence $\bar{H}_1 + \bar{H}_2$ is $-55{,}010$ cal. The corresponding value for solid wüstite from paper I is $-63{,}070$ cal. The difference, 8,060 cal., is the heat of transfer of one mole ferrous oxide from solid wüstite to liquid oxide, both of the composition $N_2/N_1 = 1.07$; in other words, this is the heat of fusion of wüstite,

---

(23) Actually a method of successive approximations was used; the first approximate value of a_{FeO} in equilibrium with iron (relative to the value at $N_2/N_1 = 1.07$) was obtained by integration of curves similar to those shown in Fig. 3A, but passing through points representing the direct measurements of p_{CO_2}/p_{CO} in equilibrium with iron and liquid oxide (at 1600°, the extrapolation thereof). Insertion of these values of activity in the above equation then yielded the new values for p_{CO_2}/p_{CO} in equilibrium with iron and its liquid oxide. The curves were then altered on their lower extremities (to the positions shown in Fig. 3A) to correspond therewith, and the integration was performed again. The new value thus obtained for log a_{FeO} differed from the first approximation by less than 0.0020 (about 0.5% in a_{FeO}) in the worst case.

TABLE VIII

EVALUATION OF LOG p_{CO_2}/p_{CO} IN EQUILIBRIUM WITH IRON AND LIQUID OXIDE; ESTABLISHMENT OF ACTIVITY OF IRON AT $N_2/N_1 = 1.07$

°C.	Log $K_{Fe_3O_4}$	Log p_{CO_2}/p_{CO} equilibrium of liquid oxide with δ-Fe	l-Fe	Log a_1 in liquid oxide of comp. $N_2/N_1 = 1.07$ relative to δ-Fe	l-Fe
1400	−1.158	−0.579		−0.528	
1450	−1.189	(− .622)[a]		(− .583)[a]	
1500	−1.215	− .663		− .639	
1524 (m. p. Fe)	−1.227	(− .682)[a]	(−0.682)[a]	(− .666)[a]	(−0.666)[a]
1575	−1.215	− .724[b]	− .713	− .724[b]	− .713
1600	−1.208	− .745[b]	− .728	− .753[b]	− .736

[a] Obtained by interpolation. [b] Value corresponding to metastable equilibrium or metastable standard state.

by this method. This compares reasonably well with 7,300 cal., as calculated from the melting curve of wüstites, but differs markedly from 12,300 cal., derived from the measurements of p_{CO_2}/p_{CO} in equilibrium with iron and its liquid oxide. Since the methods yielding these two results, 7300 and 8060, are essentially independent and are based on data regarded as reliable, whereas the value 12,300 is derived from data on which suspicion has already been cast, it seems reasonable to conclude that the heat of fusion of wüstite in the vicinity of this composition is approximately 7,500 cal. Moreover, the activity of iron and the heat changes derived by this later method are deemed more reliable than those from the direct measurements of p_{CO_2}/p_{CO} in equilibrium with iron and wüstite; consequently all subsequent calculations in this paper are based on Table VIII.

From the final equations for $\overline{H}_1$ and for $\overline{H}_2$

$$\overline{H}_1 + \overline{H}_2 = -89{,}580 + 69{,}500 N_2/N_1 - 34{,}750\,(N_2/N_1)^2$$

This equation gives, over the range from equilibrium with iron to $N_2/N_1 = 1.20$ and from 1400 to 1600° the heat of formation of one mole of ferrous oxide from metallic iron and gaseous oxygen. Its value for several compositions is given in Table IX; the second row is the corresponding quantity for wüstite, the fourth row the difference, which is the heat of transfer of one mole of ferrous oxide from wüstite to liquid oxide at each of these compositions (this transfer cannot be performed isothermally at equilibrium). The fifth and sixth rows are the heat of fusion of wüstite, per gram atom of iron and of oxygen, respectively, to a liquid of the same composition (not strictly, isothermal since there is a melting range). These two heats of fusion and the heat of transfer are plotted on Fig. 11; on extrapolation to the composition $N_2/N_1 = 1$ all yield the heat of fusion of the unstable (and unattained) compound ferrous oxide, which is clearly in the vicinity of

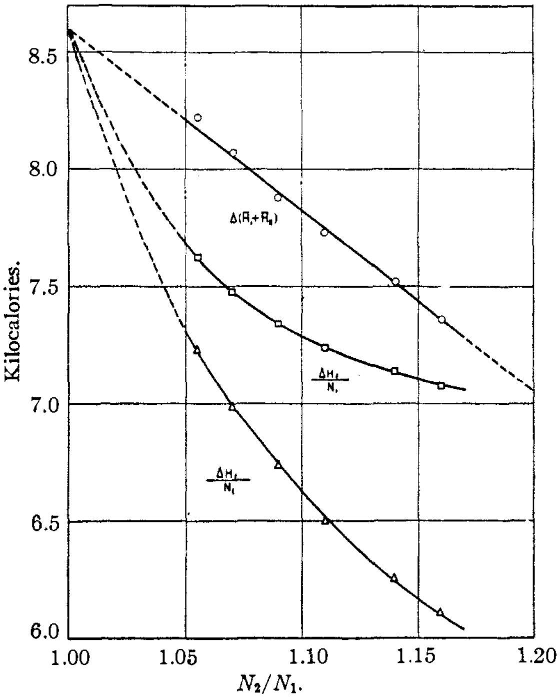


Fig. 11.—Heat of transfer of one gram mole of ferrous oxide from wüstite to liquid oxide (heat of fusion) $\Delta(\overline{H}_1 + \overline{H}_2)$; expressed also per gram atom iron $\Delta H_f/N_1$ and per gram atom oxygen $\Delta H_f/N_2$, where $\Delta H_f = N_1\Delta\overline{H}_1 + N_2\Delta\overline{H}_2$.

TABLE IX

HEAT OF FORMATION OF FERROUS OXIDE IN WÜSTITE AND LIQUID IRON OXIDE; HEAT OF FUSION OF WÜSTITE (KCAL.)

N_2/N_1	1.055	1.07	1.09	1.11	1.14	1.16
$\overline{H}_1 + \overline{H}_2$ (wüstite)	−63.15	−63.07	−62.99	−62.98	−63.03	−63.08
$\overline{H}_1 + \overline{H}_2$ (liquid)	−54.93	−55.00	−55.11	−55.25	−55.51	−55.72
$\Delta(\overline{H}_1 + \overline{H}_2)$	8.22	8.06	7.88	7.73	7.52	7.36
Heat of fusion of wüstite						
per g. atom Fe	7.63	7.48	7.34	7.24	7.14	7.08
per g. atom O	7.23	6.99	6.74	6.51	6.26	6.11
$\Delta\overline{H}_1$	18.84	16.36	13.69	12.11	10.17	8.94
$\Delta\overline{H}_2$	−10.62	−8.29	−5.81	−4.38	−2.65	−1.58

8,500 cal. The last two rows of Table IX are the partial molal heats of fusion, which show a marked variation with composition; and it is surprising that the partial molal heat of fusion of oxygen is negative over the entire range.

It is generally accepted that the crystal lattice of wüstite is of the sodium chloride type, with all sites for oxygen atoms fully occupied but a greater or smaller number of iron sites unoccupied. The energy change on fusion may be interpreted, in part, as the energy required to break some of the bonds thus giving rise to empty "lattice sites" in the liquid. Since crystalline wüstite already has empty lattice sites and their number increases with N_2/N_1, it would be reasonable to expect the heat of fusion to decrease as N_2/N_1 increases, as illustrated by Fig. 11. Further, since the empty sites in wüstite are all iron sites, it might be expected that this increase in heat of fusion might be reflected in $\Delta\bar{H}_1$ more markedly than in $\Delta\bar{H}_2$. Table IX shows that this anticipation is also realized; whereas $\Delta\bar{H}_1$ decreases by 9,900 cal., $\Delta\bar{H}_2$ increases by 9,040 cal. over the range covered. It is to be noted that if one of these quantities decreases, it is a thermodynamic necessity that the other increase.

This same line of reasoning leads to the conclusion that the entropy of fusion also should be smaller the higher N_2/N_1 is. The entropy of transfer of one gram-atom oxygen and one gram-atom iron from wüstite to liquid oxide of the same composition is readily calculable from corresponding values of ΔH and ΔF. ΔH $[= \Delta(\bar{H}_1 + \bar{H}_2)]$ is given in Table IX; $\Delta\bar{F}$ $[= \Delta(\bar{F}_1 + F_2)]$ is equal to the difference in the quantity RT ln $a_1\, p_{O_2}^{1/2}$ for wüstite and for liquid oxide, of the same composition at the same temperature (a_1 being relative to metallic iron). The quantity $(\Delta H - \Delta F)/T$, the entropy of fusion or, more strictly, of transfer of one mole of FeO from wüstite to liquid oxide of the same composition, at 1400°, is given in Table X, and does decrease with increase of N_2/N_1, as anticipated.

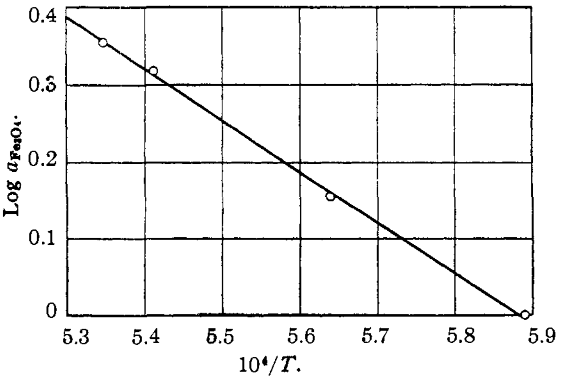


Fig. 12.—Change with temperature of activity of Fe_3O_4 in liquid oxide in equilibrium with magnetite, leading to the heat of fusion of magnetite.

Table X

Entropy of Transfer of One Mole of Ferrous Oxide from Wüstite to Liquid Oxide of Same Composition at 1400°

Composition N_2/N_1	ΔS
1.055	5.04
1.07	4.95
1.09	4.82
1.11	4.72
1.14	4.59
1.16	4.49

Heat of Fusion of Magnetite.—For the equilibrium Fe_3O_4 (magnetite) $\leftrightarrows$ Fe_3O_4 (in liquid iron oxide), we may write, since the composition of magnetite in equilibrium with molten oxide of lower oxygen content is fixed (within the experimental error)

$$K = \frac{a'_{Fe_3O_4\,(\text{liquid})}}{a_{Fe_3O_4\,(\text{mag.})}} = a_{Fe_3O_4\,(\text{liquid})}$$

The additional subscript (liquid) may be dropped, and

$$\frac{\mathrm{d}\log a_{Fe_3O_4}}{\mathrm{d}\,1/T} = -\frac{\Delta H}{2.303R}$$

where ΔH is the heat of transfer according to the above reaction, at the composition of the standard state at which $a_{Fe_3O_4}$ is unity. It would be desirable to choose this standard state to correspond to the composition Fe_3O_4, but liquid of this composition does not exist (except as a metastable supercooled liquid) in the range in which this equilibrium can be measured, *i. e.*, from the peritectic (1424°) to the melting point of Fe_3O_4 (1597°); hence, the heat of fusion at the melting point of Fe_3O_4 cannot be determined (except by extrapolation) from the data of this investigation. In order to have the greatest possible range for the plot of log $a_{Fe_3O_4}$ *vs.* $1/T$, the composition of the peritectic liquid (N_2/N_1 = 1.1825) is chosen as standard. The activity of Fe_3O_4 relative to this standard state is then equal to the quantity $a_1{}^3 p_{O_2}{}^2$ (or $a_{FeO}{}^3 p_{O_2}{}^{1/2}$) at equilibrium with magnetite divided by its value at the composition N_2/N_1 = 1.1825. The compositions of the liquid oxide in equilibrium with magnetite at 1500, 1575 and 1597° were read from the phase diagram and the corresponding activities required from Table VI; the plot of log $a_{Fe_3O_4}$, as thus obtained, against $1/T$ proves to be a line (Figure 12) whose slope corresponds to a molar heat of fusion of 30,400 ± 1,000 cal. The heat of transfer of Fe_3O_4 from the peritectic composition to any other composition in the range measured may be found from the equations given for $\bar{H}_1$ and $\bar{H}_2$; it is the difference in the quantity $(3\bar{H}_1 + 4\bar{H}_2)$ between the particular composition and the peritectic composition. This quantity when added to the heat of fusion of magnetite is the heat of solution of magnetite in iron oxide of the composition considered. Although the extrapolation is somewhat uncertain, the molar heat of fusion of Fe_3O_4 to a liquid of the same composition at 1597° is about 33,000 cal., with a probable error estimated as not more than 2,000 cal.

The Activity of Fe_3O_4 in magnetite may be represented as proportional to the product $a_1{}^3p_{O_2}{}^2$ which, with the Gibbs–Duhem equation, gives

$$\log a_{Fe_3O_4} = \int_{N_2/N_1=3}^{N_2/N_1} (4 - 3N_2/N_1)\, d \log p_{O_2}{}^{1/2}$$

In order to perform this integration the quantity $(4 - 3N_2/N_1)$ was plotted (Fig. 13) against log $p_{O_2}{}^{1/2}$ at three temperatures, selected to include as many points as possible, and to be close to the experimental points in Fig. 4; its zero points corresponding to the composition Fe_3O_4 are from Fig. 7B. The form these curves would have if magnetite behaved as an ideal solid solution of Fe_2O_3 in Fe_3O_4 is illustrated by the line designated "Raoult's Law" in Fig. 13.

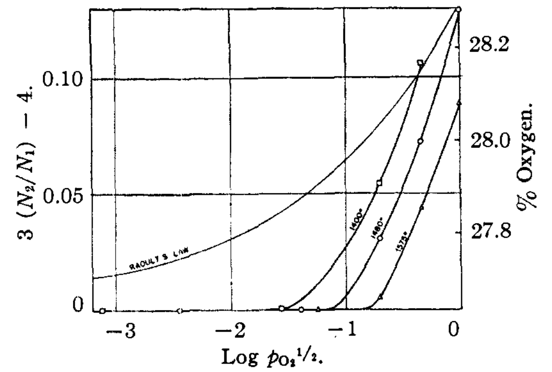


Fig. 13.—Isothermal plots of data in the magnetite field whose integration yields the activity of Fe_3O_4 in magnetite. The contour which the isotherms would have if the solid solution of ferric oxide in magnetite were ideal is the line designated "Raoult's Law."

It is rather surprising that these isotherms (at least that for 1575°) exhibit little curvature in the major portion of the magnetite field but break abruptly near the composition Fe_3O_4, and then run horizontally for a considerable distance. This means that in this vicinity the change of composition of magnetite corresponding to an order of magnitude change in partial pressure of oxygen, is immeasurably small, a type of behavior which is characteristic of traditional chemical compounds (for example, the composition of sodium chloride is independent of the partial pressure of chlorine above it). No explanation is offered for the fact that magnetite behaves in this way on the low oxygen side yet as a typical solid solution on the high-oxygen side. Integration of the curves in Fig. 13 gives the activity of Fe_3O_4 in magnetite solid solutions; the curve at 1575° (the curve for the other temperatures is not significantly different) is reproduced in Fig. 14, which again shows that the departure from Raoult's law is large.

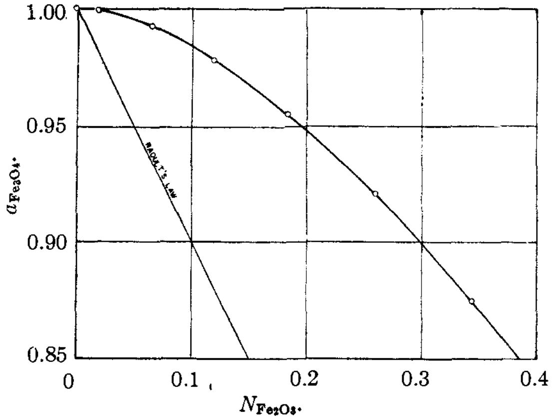


Fig. 14.—Variation of activity of Fe_3O_4 with composition of the magnetite solid solution, from integration of the 1575° isotherm Fig. 13.

The heat of solution of oxygen in magnetite of any composition may be obtained from the value of d log p_{O_2}/d $1/T$ at that composition. The only composition common to more than two curves on Figure 4 is $N_{Fe_3O_4} = 0.760$ (allowing a slight extrapolation); a plot (Fig. 15) of log p_{O_2} vs. $1/T$ at this composition is a straight line. Its slope corresponds to −67,200 cal. as the heat of addition of one mole of gaseous oxygen to magnetite of this composition, or to −33,600 cal. as the heat of transfer of one gram-atom oxygen from oxygen gas to magnetite of this composition. This is considerably smaller than the partial molal heat of oxygen in wüstite (−61,720 to −63,460 cal.).

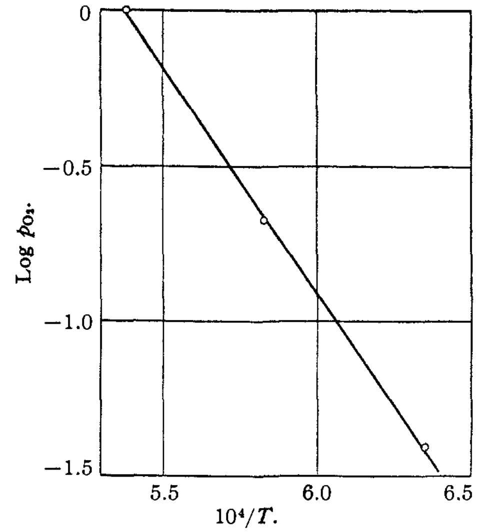


Fig. 15.—Change of log p_{O_2} with $1/T$ at the composition $N_{Fe_3O_4} = 0.760$ within the magnetite field, serving to evaluate the heat of addition of oxygen to magnetite.

The activity of ferric oxide in magnetite is proportional to $a_1{}^2p_{O_2}{}^{1/2}$; choosing as standard state at each temperature the composition in equilibrium with hematite we found (from a plot of log

$a_{Fe_3O_4}$ *vs.* $1/T$) that the heat of solution of hematite in magnetite ($N_{Fe_3O_4} = 0.760$) is +6,900 cal.

The Magnetite-Hematite Equilibrium.—For the reaction

$$2Fe_3O_4\ (\text{mag.}) + {}^1/_2O_2\ (\text{gas}) \rightleftarrows 3Fe_2O_3\ (\text{hem.})$$

the equilibrium constant may be written $K = 1/p_{O_2}{}^{1/2}\ a^2{}_{Fe_3O_4}$, since hematite is of essentially constant composition and its activity may be taken as unity. This K was calculated from p_{O_2} as given in Table IV, and $a_{Fe_3O_4}$ as read from Fig. 14 at the appropriate compositions from Fig. 4, and log K was plotted *versus* $1/T$. The three higher temperature points were colinear within the experimental error (1% of the partial pressure of oxygen, or 2°) and yielded a heat of −54,500 cal. for the reaction as written. The fourth point (corresponding to the measured transition in carbon dioxide atmosphere—the least precise of these measurements) is considerably off the line determined by the other three; the discrepancy amounts to about 50° as compared to the estimated precision error of 20° in the measurement.

From this value, −54,500 cal. combined with the heat of formation of Fe_3O_4 at 1250° (−260,900 cal.), the difference in temperature being ignored, the heat of formation of one mole of hematite from γ-Fe and gaseous oxygen is −192,100 cal. It is interesting to note that the heat of formation of wüstite per gram-atom of oxygen, as given in paper I, is −63,100 cal., that of magnetite is −65,200 cal., and that of hematite is −64,000 cal. In other words, the heat of formation of solid iron oxides per atom of oxygen is nearly independent of the oxide formed.

The Liquid Oxide Equilibria

It is of interest to consider whether the oxygen pressure isotherms in Fig. 3 may be interpreted in terms of a simple picture of the constitution of the liquid. White[8] interpreted his data, on a relatively small portion of the system, in terms of the law of mass action; in essence he assumed that the liquid oxide is composed of three molecular species, FeO, Fe_2O_3 and Fe_3O_4, and that the activity of each is equal to its mole fraction in accord with Raoult's law. He then considered the equilibria

$$Fe_2O_3 = 2FeO + {}^1/_2O_2;\ k_1 = \frac{(FeO)^2 p_{O_2}{}^{1/2}}{(Fe_2O_3)}$$

$$Fe_3O_4 = FeO + Fe_2O_3;\ k_2 = \frac{(FeO)(Fe_2O_3)}{(Fe_3O_4)}$$

the parentheses representing mole fraction; and was able to find values of k_1 and k_2 which reproduced his measurements within the experimental error. On the other hand, our 1600° isotherm, covering a much greater range, as shown in Fig. 3B, is not reproduced, even reasonably well, by any choice of k_1 and k_2, the position being fixed by k_1, the form being completely determined by k_2. Its upper one-third, with a generous allowance for experimental error, is reproduced by k_2 = 0.25, but its lower part departs by as much as a factor of ten (in p_{O_2}) from the curve thus calculated. Not only is there no value of k_2 which covers the whole isotherm, but even limited portions of the lower half cannot be represented by any positive value of k_2. In general, this mode of interpretation calls for an isotherm which differs from the experimental curve by having more marked inflection, considerably greater curvature in the lower half, and an asymptotic approach to the vertical axis ($N_2/N_1 = 1$); it seems unpromising.

Nevertheless, as it was thought that consideration of more molecular species might improve the agreement, we investigated at great length the form of the isotherm calculated similarly but on the basis of additional molecular species including Fe, $(FeO)_2$ and Fe_4O_5. A method was devised to indicate the formula of the compound (or compounds) needed to force agreement; the disturbing result was that negative mole fractions were called for unless a prohibitively complicated array of molecular species is postulated. Our final conclusion is that the system is essentially non-ideal and that no set of postulates involving the assumption that activity is equal to mole fraction is capable of yielding an adequate interpretation of the isotherms. This might be conjectured from the fact that the isotherms for the liquid oxide are somewhat similar in form to those for wüstite, and from the difficulty of ascribing any physical significance whatsoever to molecular species in this solid solution, with a sodium chloride type lattice, in which the variability in composition arises from a deficiency of iron atoms.

Another semi-empirical mode of attack is based on the fact that if the logarithm of the activity coefficient (γ_1) of one component in a binary solution is represented (at constant temperature) by a power series in the mole fraction of the other component—namely

$$\log \gamma_1 = \alpha N_2 + \beta N_2{}^2 + \cdots$$

it may be shown that $\alpha = 0$ if Raoult's law is approached at $N_2 = 1$, and that then the single term $\beta N_2{}^2$ is in some cases sufficient. It then follows, from the Gibbs–Duhem equation, that if $\log \gamma_1 = \beta N_2{}^2$, then $\log \gamma_2 = \beta N_1{}^2$. A similar relation may be deduced by the methods of statistical mechanics for regular solutions—those for which the entropy of mixing is equal to that for an ideal solution—and was applied by Kielland[24] to the data of Krings and Schackmann[9] included in Fig. 3B. If ferrous and ferric oxides are taken as components of the liquid oxide, the equilibrium constant for the reaction $Fe_2O_3(l) = 2FeO(l) + {}^1/_2O_2$ may be expressed as

$$\log K = \log (a_{FeO}{}^2 p_{O_2}{}^{1/2}/a_{Fe_2O_3}) = \log (N_{FeO}{}^2 p_{O_2}{}^{1/2}/N_{Fe_2O_3}) + \beta(2N_{Fe_2O_3}{}^2 - N_{FeO}{}^2)$$

Thus, if this approach is correct, a plot of log ($N^2{}_{FeO}p_{O_2}{}^{1/2}/N_{Fe_2O_3}$) against ($2N^2{}_{Fe_2O_3} - N^2{}_{FeO}$) for

---

(24) J. Kielland, *Z. Elektrochem.*, **41**, 834 (1935).

isothermal measurements, should be linear, as Kielland found for the limited range covered by Krings and Schackmann. However, when all our data for 1600° (Fig. 3B) were plotted in this way, the curve departed considerably from linearity, principally at the low oxygen pressure end; a straight line represented satisfactorily the high oxygen end (as found by Kielland) but this region is less than half the range covered. The reverse calculation, to predict the form of the curves in Fig. 3B from the foregoing equation, leads to an isotherm which, when forced to agree with that observed at its upper end, rises higher than observed near the center and falls again at the lower end; the maximum discrepancy amounts to a factor of about four in p_{O_2}. It must be concluded, therefore, that this is a poor way of interpreting the data. In fact, a much closer approximation is to consider the isotherms themselves (*i. e.*, the plot of log p_{O_2} *vs.* N_2/N_1) as straight lines.

As mentioned previously, there is reason to doubt if a fruitful interpretation of the behavior of liquid iron oxide in the range investigated can be based on the concept of molecular species. If this be true, it is meaningless to compare the actual behavior with that expected for an ideal solution, since the concept of an ideal solution presupposes the existence of molecular species; in special cases, such as molten alloys, the atoms of the elements may be considered as molecules, but obviously the present system behaves very differently from an ideal solution of iron and oxygen. Consequently we are forced to the opinion that adequate interpretation of the partial pressure and activity isotherms must await the development of a more satisfactory theory for this type of solution based on the methods of statistical mechanics.

It is worth noting that the relation between oxygen and iron is not reciprocal; although the plot of log p_{O_2} (or $\bar{F}_2$) *vs.* N_2/N_1 is nearly linear, that of log a_1 (or $\bar{F}_1$) *vs.* N_2/N_1 (or N_1/N_2) exhibits marked curvature. The calculated heats of solution, considered previously, indicate that $\bar{H}_2$ is also a linear function of N_2/N_1 whereas $\bar{H}_1$ is not. Thus $\bar{F}_2$ and $\bar{H}_2$ are both approximately linear functions of N_2/N_1, whence it follows that the partial molal entropy $\bar{S}_2 = (\bar{H}_2 - \bar{F}_2)/T$ is also a nearly linear function of N_2/N_1 over the range covered. Similarly $\bar{F}_1$, $\bar{H}_1$ and $\bar{S}_1$ are approximately parabolic functions of N_2/N_1. The similarity in the form of each of these three functions, although rather striking, possibly may not be of significance for the following reasons: $\bar{H}_1$ and $\bar{H}_2$ were determined over a rather limited range in this investigation, the precision is not sufficiently great to determine unambiguously the form of the relation with N_2/N_1, and $\bar{F}_2$ is linear with N_2/N_1 only as a first approximation.

Acknowledgment.—The authors acknowledge with thanks the assistance of Mark C. Lindsay, Jr., who performed some of the analyses.

Summary

By equilibration of liquid iron oxide with several controlled gas mixtures the equilibrium relations between partial pressure of oxygen, temperature and composition of oxide were determined. The range of temperature covered was from the melting curves to 1640°; of oxygen pressure from that in equilibrium with iron to one atmosphere; of oxide composition from a ratio of O:Fe of 1.03 to 1.38. The magnetite field was investigated in the same way, and the melting curves of wüstite and magnetite and the equilibrium of iron with liquid oxide and of magnetite with hematite likewise. From these data, together with thermodynamic quantities calculated from them the phase diagrams (Figs. 1, 3, 7) were constructed.

The magnetite field was found to comprise compositions with considerably more oxygen than corresponds to the formula Fe_3O_4 but none with appreciably less. This indicates that magnetite of high oxygen content behaves as a typical solid solution whereas magnetite of low oxygen content behaves as a typical compound; this conclusion is verified by its thermodynamic behavior.

The thermodynamic activity of iron and of ferrous oxide was computed and tabulated over the composition range investigated at 1400, 1500 and 1600°.

The heat of transfer at 1500° of one gram atom of oxygen from gaseous oxygen to liquid oxide of composition N_2/N_1 is (in cal. ± 200) $\bar{H}_2 = -145{,}660 + 69{,}500N_2/N_1$. The corresponding heat of transfer of one gram atom of iron from δ-Fe to liquid oxide is $\bar{H}_1 = 56{,}080 - 34{,}750 \cdot (N_2/N_1)^2$.

The heat of fusion of wüstite (the heat of transfer of one mole of ferrous oxide from wüstite to liquid oxide—both of the composition $N_2/N_1 = 1.07$) was determined from the solidus and liquidus curves to be 7,300 cal.; this same heat as determined from the partial molal heat content is 8,060 cal. The heat and also the entropy of fusion decrease with increasing oxygen content, as expected from the crystallographic nature of wüstite.

The heat of solution of magnetite (Fe_3O_4) in liquid oxide of peritectic composition is 30,400 ± 1,000 cal. From this the heat of fusion at the maximum melting point (1597°) is 33,000 ± 2,000 cal.

The heat of formation of ferric oxide from γ-Fe and O_2 (at 1400°) is −192,100 ± 1,000 cal.

No adequate solution theory is available to interpret the form of the oxygen pressure composition isotherms. To a first approximation log p_{O_2} for liquid oxides is a linear function of N_2/N_1. The departure from ideal solution behavior is wide for liquid oxides and magnetite as well as for wüstite.

The heat of addition (1450°) of one gram atom of oxygen (from O_2) to magnetite (of composition $N_{Fe_3O_4} = 0.760$, $N_{Fe_2O_3} = 0.240$) is −33,600 cal.,

much smaller than the corresponding heat for wüstite. At the same temperature for the reaction $2Fe_3O_4$ (mag.) + $^1/_2O_2(g) \rightarrow 3Fe_2O_3$ (hem.), ΔH is $-54{,}500$.

By evaporation of iron oxide in a vacuum furnace at 1600° it was found that the total vapor pressure passes through a minimum at an atomic ratio of O:Fe = 1.116 (24.23% oxygen). From this composition of the azeotropic mixture it is calculated that the vapor pressure of liquid iron at 1600° is 5.8×10^{-5} atm. and it is shown that the vapor pressure of molecular FeO is small in comparison thereto.

KEARNY, N. J. RECEIVED NOVEMBER 14, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Kinetics of the Reaction of Sodium 2-Haloethanesulfonates with Aqueous Alkali

BY E. F. LANDAU,[1] W. F. WHITMORE AND PAUL DOTY

The kinetics of the reactions of various alkyl halides with hydroxide ion[2] has been the subject of intensive and fruitful investigation, especially by the Hughes–Ingold group, for more than a decade. These researches demonstrated that in some cases the reaction proceeded to the alcohol (substitution) or to the olefin (elimination), but more frequently to the simultaneous occurrence of both types with the substitution reaction predominating. Moreover, two different mechanisms are possible for each of the above categories; one is monomolecular, the other bimolecular.

The two nucleophilic substitution mechanisms are

$$\begin{array}{ll} S_n1 & RX \longrightarrow R^+ + X^- \text{ (slow)} \\ & R^+ + OH^- \longrightarrow ROH \text{ (fast)} \\ S_n2 & OH^- + RX \longrightarrow ROH + X^- \end{array}$$

These reactions differ fundamentally only in the degree of the solvolytic ionization whose predominance is responsible for the S_n1 reaction. It has been shown that a decrease in the electronegativity of the alkyl group favors the ionization and increases the speed of the S_n1 reaction. In the S_n2 reaction the higher the electronegativity of the alkyl group the faster the reaction should be because of the increased tendency of the alkyl group to share the electrons of the hydroxide group. This situation has been illustrated by Gleave, Hughes and Ingold[3] and others[4] by showing that in the series—methyl, ethyl, isopropyl, *t*-butyl iodide—the S_n2 reaction predominated for the first two members while the S_n1 reaction is dominant for the latter two iodides.

The elimination reactions which frequently accompany these substitution reactions have the form[5]

$$OH^- + HCR_2CR_2X \longrightarrow H_2O + R_2C{=}CR_2 + X^-$$

A monomolecular reaction (E1) would be expected from an electrophilic attack by the solvent on X to form a carbonium ion. The hydroxide ion would then accept a proton in a fast reaction to give the olefin. A bimolecular reaction (E2) would conceivably result from a nucleophilic attack by the hydroxide ion on a β-hydrogen atom. The mechanism for this reaction will be discussed later. In the case of primary alkyl halides the elimination reactions studied have been of second order[6] while for halides containing secondary and tertiary halides the reactions are predominantly first order.[7,8,9,10,11]

Hughes and Shapiro[9] in their study of the mechanism of substitution at a saturated carbon atom have discovered that the two substitution reactions and the bimolecular elimination reaction have comparable velocities for the case of the isopropyl halides in a water–alcohol medium. They have evaluated the A and E parameters in the Arrhenius equation and find that these quantities are only slightly dependent upon the particular halogen present. However, when the ethyl bromide reaction is studied[12] (in anhydrous alcohol) it is found that only the bimolecular reactions occur with the substitution reaction predominating to the extent of about 99%. On the other hand, *t*-butyl halides yield mostly isobutylene via a bimolecular reaction (E2) in anhydrous alcohol.

Thus, with the course of these alkyl halide reactions apparently so dependent upon the presence or absence of a relatively electropositive group on the β-carbon, it is of interest to record a kinetic study of the reaction in water medium of sodium 2-chloro- and 2-bromo-ethanesulfonate ($CH_2XCH_2SO_3Na$) with hydroxide ions.

Experimental

It has been reported elsewhere[13] that this reaction can be represented as

---

[1] Taken in part from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Polytechnic Institute of Brooklyn, 1945. Present Address: Celanese Corp., Newark, N. J.

[2] Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, New York, N. Y., 1943.

[3] Gleave, Hughes and Ingold, *J. Chem. Soc.*, 236 (1935).

[4] Koskoski, Thomas and Fowler, THIS JOURNAL, **63**, 2451 (1941).

[5] Hanhart and Ingold, *J. Chem. Soc.*, 997 (1927).

[6] Hughes and Shapiro, *ibid.*, 1177 (1937).

[7] Hughes, Ingold and Scott, *ibid.*, 1271 (1937).

[8] Bodendorf and Bohme, *Ann.*, **516**, 1 (1935).

[9] Hughes and Shapiro, *J. Chem. Soc.*, 1192 (1937).

[10] Cooper, Hughes and Ingold, *ibid.*, 1280 (1937).

[11] Hughes and McNulty, *ibid.*, 1283 (1937).

[12] Grant and Hinshelwood, *ibid.*, 258 (1933).

[13] E. F. Landau, Thesis, Polytechnic Institute of Brooklyn, 1945.